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An Apparatus for Measurement of the Flash Degradation of Polymers

By

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Summary: An apparatus for measuring degradation reactions of polymer samples by flash irradiation was constructed for the investigation of fast degradation mechanisms of polymers in vacuum or in various atmospheres.

The essential part of the apparatus is a sample tube surrounded by a helical xenon flash lamp stored in a cylindrical mirror, with an optical filter system, if necessary. A high-voltage capacitor bank charges the flash lamp, which is discharged in turn at triggering by high-frequency current. Polymer sample films were degraded by a number of flash irradiations repeated in sequence, in vacuum or in an inert gas. Degradation products were analyzed by a highly sensitive gas chromatograph with a hydrogen flame ionization director.

Typical results on flash degradation of polymethyl methacrylate in vacuum and in nitrogen are shown.

INTRODUCTION

The flash photolysis technique has been developed by Porter, Norrish, and others [*1*~*3*] for studying fast reactions particularly in a gas phase, using a flash discharge lamp and a delayed device for analyzing the short-life reaction products spectroscopically. The flash photolysis of solids has scarcely been carried out, however, because of the difficulty of applying spectroscopical method to analyze very little amount of decomposition products.

In 1957, Lundberg and Nelson [*4*~*6*] studied flash degradation of polymer solids for the first time. They concluded from the observations of the process that dust particles contaminating polymer samples absorb instantaneously a large amount of light energy at flash irradiation and particles heated at a very high temperature within a short period initiate the thermal degradation of polymer material around them. With this mechanism, however, it is difficult to consider the initiation of flash degradaton for "clean" polymers.

In the late 1950's, we commenced the investigations on thermal stability of high polymers, considering the application of these materials to aerospace technology. Principally we developed thermoanalytical techniques, such as differential thermal analysis and thermogravimetry, but we also felt the need of high speed degradation technique. Then, we set to apply the flash photolysis to polymeric materials.

Our first experimental assembly using a helical xenon flash lamp developed for ruby laser activation was constructed in 1962. After some preliminary measurements, we investigated the flash degradation of polymethyl methacrylate (PMMA) in nitrogen atmosphere [7]. PMMA is well known to be degraded with simple depolymerization kinetics at the usual slow heating to several hundred degrees centigrade and its degradation products are almost composed of the monomer molecule. The effect of fast heating by flash light was expected to give rise to a random scission mechanism observed usually at higher temperature range.

In this investigation, we observed the formation of carbon particles after several flash irradiations in nitrogen. The black carbon particles became much effective absorbers of light energy, and the degradation was so much accelerated with the number of flashes repeated in sequence. The rôle of carbon particles was very significant. However, the mechanism of initiation by dust particles, as suggested by Lundberg and Nelson, was not confirmed with these experiments.

In the next stage, we investigated the flash degradation of PMMA in vacuum [8]. On the contrary to the measurements in nitrogen, we found a very little amount of products and no formation of carbon particles after many flashes. From these results, we proposed a photo-initiation mechanism for the flash degradation in vacuum. PMMA is well known to degrade randomly by photodegradation mechanism at lower temperatures.

The absorption of light by PMMA is very low in the range of wavelength emitted by a xenon flash lamp. The mechanism of light absorption, particularly in the chemically effective ultraviolet range, was examined with a modified apparatus attached by the filtering solution layer around the sample tube. The photo-initiation mechanism has been confirmed by this experiment.

Results on the mechanism of flash degradation of PMMA will be published elsewhere. In the present paper, we describe the construction of the apparatus in detail.

The analysis of degradation products of solid polymers is a difficult task. Martin and Ramstad [9] showed a two-stage gas chromatograph unit for this purpose. Lundberg and Nelson analyzed gaseous products by a mass spectrometer, and Friedman [10] applied time-of-flight mass spectroscopy for the investigation of flash degradation of phenolic resins. In the present paper, we used a highly sensitive gas chromatograph with a hydrogen flame ionizing detector. A comparatively slow scanning rate of gas chromatography makes essentially impossible to determine the short-life intermediate products. The minute degree of reaction is proceeded, however, by a very short flash irradiation. Then, we repeated the irradiation in sequence on the same sample, and on the course of the change of degradation products, we could find a key to resolve the mechanism of the initial reaction.

In the essential part of the apparatus a helical xenon flash lamp stored in a cylindrical mirror surrounds a straight sample tube, enveloped by an optical filter system, if necessary. Flash degradations were investigated in vacuum and in inert gases.

Recently, flash photolysis technique has been applied to investigate photo-degradation of polycarbonate [11], but it has not yet become a common technique to be applied to investigate solid polymers.

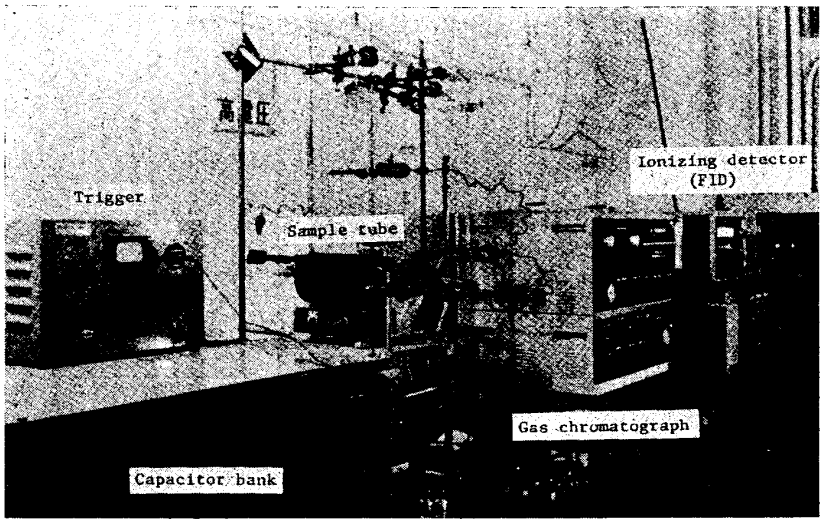

PHOTO. 1. The flash degradation apparatus.

APPARATUS

Flash degradation apparatus is composed of three parts, that is a light source, a sample tube, and an analytical equipment. The whole assembly of our apparatus is shown in Photo. 1.

Light source. A quartz flash discharge lamp of the helical shape, filled with xenon gas at about 30 mmHg, was used as a light source. This lamp was developed for activating a solid ruby laser and supplied by the Nippon Electric Co. Figure 1 shows a spectrum of the radiation energy from the discharging flash lamp, photographically measured with an Adam-Hilger quartz spectrograph. In Figure 1, the relative intensity determined with a microdensitometer is plotted against the wavelength calibrated by the line spectra of mercury. The spectrum of flash light is broadly distributed in the wavelength range of 200–600 mμ, with a maximum at 400 mμ. The shape of the radiation spectrum did not show a marked change with the charging voltage of the lamp.

In some experiments, a borosilicate glass tube was used as a sample tube. The borosilicate glass cuts off the light in the ultra-violet range below 300 mμ. Because of the large non-focused light source, we could not detect distinct lines in its spectrum. However, the photodegradation of polymers by the light absorption at a definite wavelength could not be expected.

In the course of a discharge, the voltage between electrodes of flash tube was measured by a synchronized oscilloscope, Iwasaki Model SS5156. As shown in Figure 2, the voltage at discharge reached a maximum at about 0.1 ms after triggering and decayed with a time constant of 1 ms. A flash discharge succeeds for 5~6 ms irrespective of voltage.

The high D.C. voltage was applied between electrodes of lamp by a capacitor bank manufactured by Nippon Condenser Co. The lamp was discharged by a high frequency A.C. current, supplied by an electronic trigger. The bank could be charged up to 2.0~4.0 kV by a D.C. charger. The electric capacitance of the bank

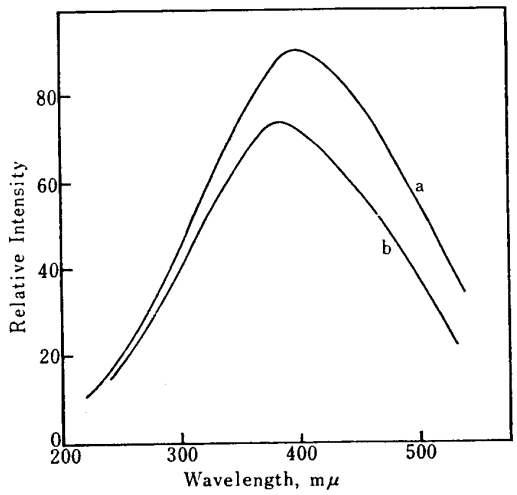

FIG. 1. Spectrum of radiation energy from the flash lamp. Charging voltage: a, 4.0 kV; b, 2.5 kV.

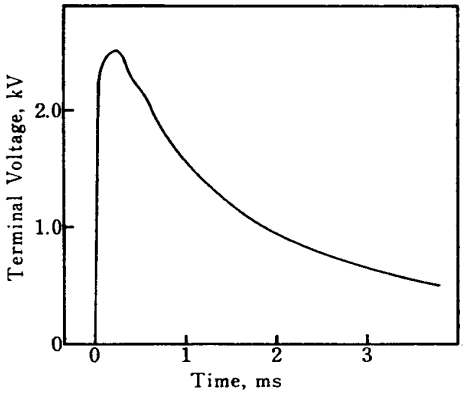

FIG. 2. The terminal voltage change during a discharge of flash lamp.

is variable between 1~500μF, but a capacitance of 308μF was used throughout our experiments. If charged at 3.0 kV, the residual voltage on the bank after a discharge through the flash tube was 0.26 kV on the average. Then, the output energy at a flash was 1375 J. calculated from the Equation (1)

$$E=\frac{1}{2}C(V_i^2-V_f^2) \qquad (1)$$

where E is output energy at a flash, C the capacitance of the condenser bank (308μF), V_i the initial voltage (3.0 kV), and V_f the residual voltage (0.26 kV).

Sample tube. The thin film of polymers was used as a sample. The sample film of the size of 5.0×1.0 cm was usually wrapped around a glass tube and situated within a sample tube, as shown in Figure 3. For avoiding the oxidizing effect, the sample should be kept in an inert atmosphere at flash irradiations. The sample tube was made of quartz or borosilicate glass and situated on the center axis of the helical flash lamp, stored in a cylindrical mirror case. A vacuum line was connected to the sample tube to evacuate the atmosphere at room temperature using an oil diffusion pump with an oil rotary pump, or to replace it with an inert gas from a gas reservoir, as shown in Figure 4. Using a four-way cock, the degradation could be carried out in vacuum or in inert gas. At the experiment in vacuum, the cold trap containing liquid nitrogen was used to capture the condensable products from the atmosphere. The products were swept out to a gas chromatograph after each flash irradiation. The nitrogen gas was usually used as an inert atmosphere, and it was also served as the carrier of degradation products to the gas chromatograph. In some cases, argon and helium were used in place of nitrogen.

For the analysis of low molecular gaseous products not condensed into cold trap, it was necessary to reduce the total inner volume of the sample tube system. For this purpose, the vacuum line system was modified in some experiments.

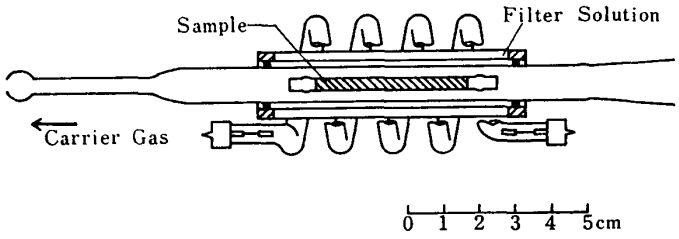

FIG. 3. Sample tube with a filter envelope.

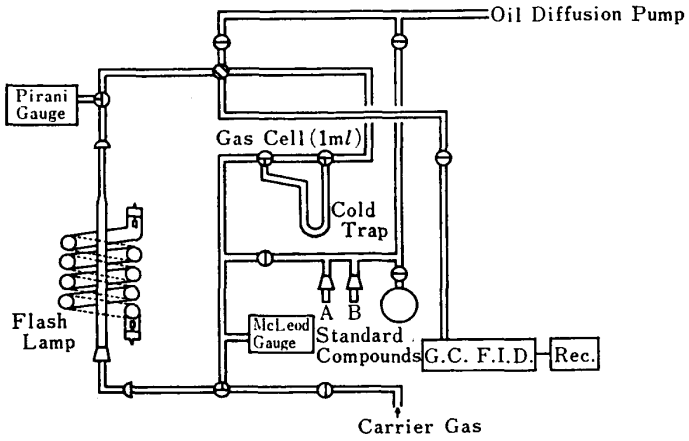

FIG. 4. Vacuum line system.

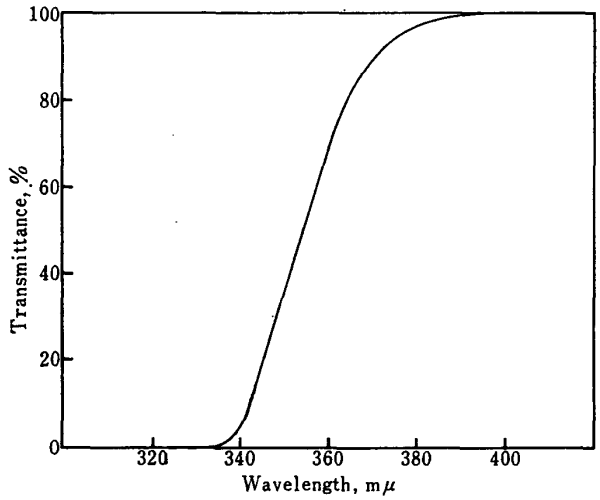

FIG. 5. Absorption spectrum of the filter solution. 0.07 M-Aqueous solution of $K_2[Hg(SCN)_4]$ Thickness: 1.44 mm.

For the calibration of the amounts of degradation products, a gas cell of the determined volume was used, as shown in Figure 4. The trap and its by-pass conduit were used together as the gas cell. Its volume was determined before setting up into the system. Using the gas cell and a manometer, we could obtain calibration curves

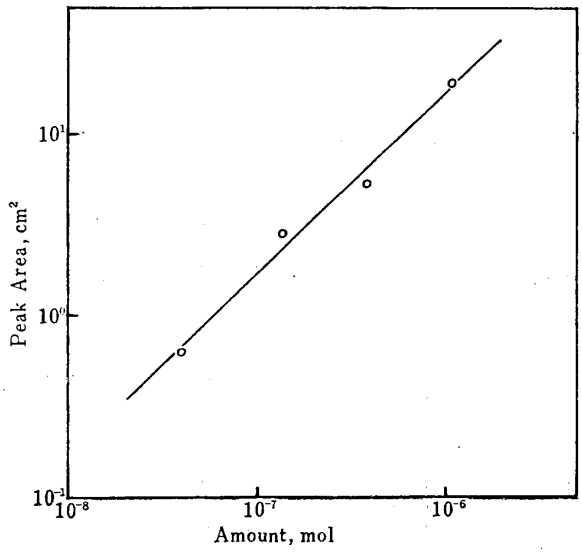

FIG. 6. Calibration curve for benzene
DOP column, N_2 40 ml/min, Chart spead 0.5 cm/min, Attenuator 1/8, sensitivity 1/10

for several standard compounds. The amounts of gases were calculated on the assumption of the validity of ideal gas law.

For the investigation of the effect of photo-degradation, the sample tube of quartz was used with a cylindrical envelope containing a filter solution, as shown in Figure 3. After several preliminary tests, a 0.07 M aqueous solution of $K_2[Hg(SCN)_4]$ was used for removing ultraviolet component from the irradiating rays. The absorption spectrum of the solution is shown in Figure 5.

Analytical equipment. The gas chromatograph, Yanagimoto Model GCG220 with a hydrogen flame ionization detector GCF100, was used for analyzing degradation products. The columns usually used for analysis was D.O.P. (dioctyl phthalate), 2 m, 30 wt% on Celite 545 at 100°C. Several other columns, DMS (dimethyl sulfolane), Molecular Sieve 13 A, and Apiezon L were used, when necessary.

The amounts of the products were calibrated by the peak area appeared on the gas chromatograms given by known amounts of the standard compounds. Using D.O.P. column, the gaseous products gave a single peak, which we calibrated with methane. For a typical example, Figure 6 shows the calibration curve of peak area against the amount for benzene.

EXPERIMENTAL

Materials. The commercial product of PMMA (the viscosity average molecular weight $M_v = 7.6 \times 10^5$) supplied by the Mitsubishi Rayon Co. and anion-polymerized PMMA ($M_v = 2.75 \times 10^6$) were used as the sample. The polymer film was cast from the solution in butanone or chloroform on a mercury surface. The cast film was dried in a vacuum desiccator for two nights. The complete removal of the solvent was comfirmed by I.R. absorption of the film.

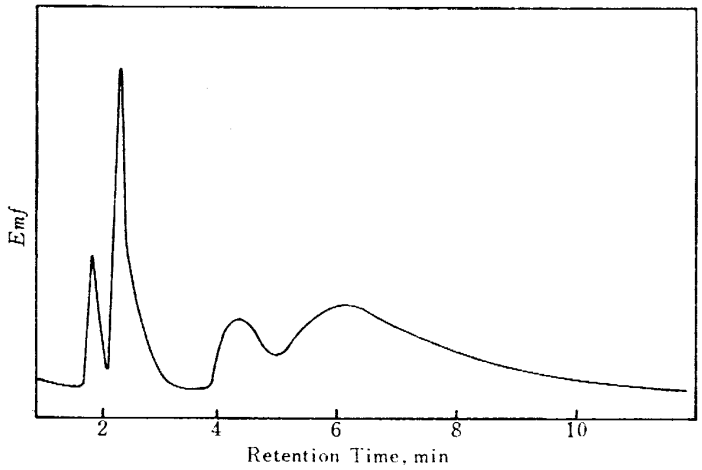

FIG. 7. Gas chromatogram for flash degradation products of PMMA in vacuum. DOP, 100°C, N_2, 40 ml/min.

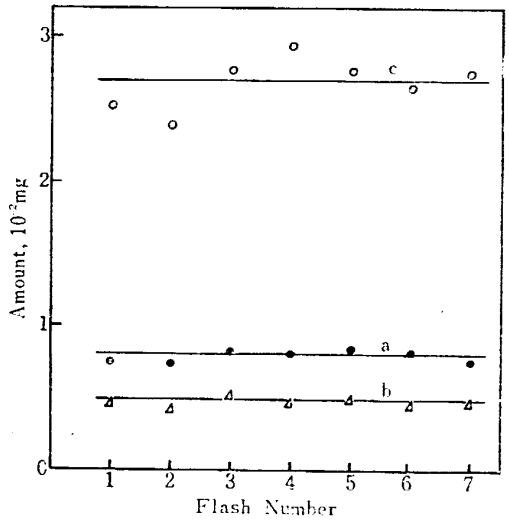

FIG. 8. Products change at repeated flash degradations of PMMA in vacuum.
a: Gaseous; b: Methyl isobutylate; c: Methyl methacrylate

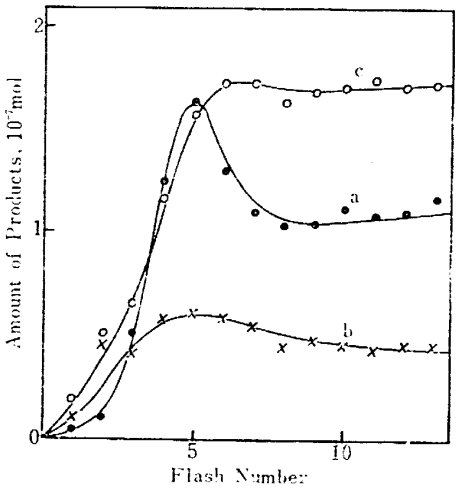

FIG. 9. Products change at repeated flash degradations of PMMA in nitrogen.
a: Gaseous; b: Methanol; c: Methyl methacrylate

Results. Figure 7 shows a typical gas chromatogram of the flash degradation products for PMMA in vacuum. The chromatograph column is composed of dioctyl phthalate (DOP) at 100°C. The carrier gas is nitrogen at a flowing rate of 40 ml/min. In Figure 7, four distinct peaks are found on the chromatogram. The first peak with the shortest retention time corresponds to a mixture of low molecular weight gaseous products. The second one was assigned to methanol, and the last one to the monomeric methyl methacrylate. The third peak is difficult to be assigned to the known compounds. It may probably a kind of ester, i.e. methyl isobutyrate.

In Figures 8 and 9, the progressive changes of the amounts of degradation products at irradiations repeated in sequence on the same sample, in vacuum and

in nitrogen, respectively. In these figures, the relative amounts of products show a characteristic change with the number of flashes.

The amounts of products are much larger for degradation in nitrogen than for that in vacuum. The significant formation of carbon was found for degradation in nitrogen, but not for that in vacuum. The detailed discussion of the mechanism of flash degradations in different atmospheres will be given elsewhere.

Discussion

As Lundberg and Nelson suggested in their papers, if flash degradation of polymer would be carried out by a thermal degradation mechanism the time for temperature elevation should be very short. Friedman [*10*] concluded that the surface temperature of his phenolic resin experiments would be estimated 1300~2100°K. Martin and Ramstad [*9*] estimated the temperature could exceed 600°C. Then the measurement of the temperature change of the sample was urgently needed.

First, we tried to measure the sample temperature by a very thin thermocouple of Au-Constantan directly attached to the sample surface, using a memory oscilloscope. We could not obtained a satisfactory result, however, because the real thermal equilibrium is difficult to be attained around the sample surface and the response time of the thermocouple system is too long to determine at such a rapid temperature rise.

If the temperature might be raised up heterogeneously as Lundberg and Nelson's supposition, the average temperature of a sample film would be not so high. Then we tried next to observe directly a possible melting of the metal powder (Cu, Ag, or Pb) dispersed in the polymer sample at flash irradiations. The melting of metal powder, however, was not observed.

Lastly, we tried to measure the black-body radiation spectrum of the heated sample. But it was also difficult to remove the effect of the reflection from the surface; therefore, the spectroscopic measurement of the temperature was not applicable for this purpose. At the present, the real temperature of the sample has not yet been measured in this study.

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