

Degradation of poly (methyl methacrylate) by flash irradiation

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Degradation of poly(methyl methacrylate) (PMMA) caused by irradiation of flash light from discharged xenon lamp was investigated in a vacuum and in the presence of nitrogen. Degradation products at a sequence of flashes were analysed by a gas chromatograph with hydrogen flame ionization detector after each flash. Among the degradation products of PMMA in vacuum by regular flash light, an amount of monomer was detected with the significant production of methanol and gaseous mixture. The molecular weight of the residual polymer decreased markedly by the first several flashes, showing that chain scission occurred. By filtering the u.v. component of flash light the monomer formation and molecular weight decrease were not observed. From these facts the flash degradation of PMMA in vacuum was concluded to be conducted by a photodegradation mechanism. The absorption of u.v. light by ester groups forms active radicals, which initiate chain scissions and depolymerization of main chains following methanol and monomer formation. At the flash degradation in nitrogen at atmospheric pressure PMMA degraded in the different manner. At the initial several flashes the photodegradation mechanism is also conducted in the polymer matrix and decomposed secondarily at the subsequent flashes to form a significant amount of carbon particles. Thereafter, carbon particles acted as a photo-absorber, and the thermal degradation of the polymer occurred predominantly around the heated carbon particles.

INTRODUCTION

Lundberg and Nelson¹ first observed the degradation of polymers by flash irradiation, and they² found the marked formation of carbon in the degraded samples. In the discussion on the mechanism of degradation, they concluded that the major part of degradation is caused by thermal degradation around the rapidly heated dust particles contaminating polymer samples. After the formation of carbon particles, which act as an effective absorber of the radiation energy, the polymer degrades thermally around the high-temperature carbon particles. They did not rule out the minor part of homogeneous photodegradation, but the mechanism of photodegradation of solid polymers by flash irradiation has not been investigated precisely after these studies. The techniques of analysing the degradation products were proposed by gas chromatography³ and by mass spectroscopy⁴.

After the pioneering works of Grassie and Melville⁵, kinetics of the thermal and photodegradation of poly(methyl methacrylate) (PMMA) have been investigated by many workers. PMMA depolymerizes nearly completely into monomer when it is heated up to a temperature below 500°C by the usual non-rapid heating devices. Meanwhile, when it is heated up to the higher temperatures and/or at the higher heating rates, the mechanism of degradation turns to random scission, and the proportion of monomer in the degradation products is reduced to lower values⁶, and the molecular

weight of polymer residue decreases very much. On the other hand, PMMA degrades with a random scission mechanism also by photodegradation at room temperature. Therefore, the monomer production and the molecular weight decrease are the criteria for judging the type of polymer degradation.

In the present paper are shown the results of degradation of PMMA exposed to flash irradiations emitted by a discharged xenon lamp. In some experiments, we cut off the u.v. component from the flash light using a filter for eliminating photodegradation. From the proportion of the monomer and other components produced by flash degradation and the molecular weight change of the residual polymer, we discuss the mechanism under several conditions.

It is concluded that the flash degradation in vacuum by regular non-filtered flash light of xenon lamp is caused by a photodegradation mechanism. The amount of monomer was depressed very much by filtering the u.v. component below 330 nm from the flash light. At flash degradation in nitrogen at atmospheric pressure, PMMA was degraded in a different way. The degradation is initiated by photodegradation and after several flashes the secondary degradation of primary low molecular products occluded in the polymer matrix forms the carbon particles, which absorb the radiation energy and are heated rapidly. In these situations the polymer degrades thermally by these heated solid particles, as Lundberg and Nelson observed. The amount of degradation products increases rapidly by the first several flashes

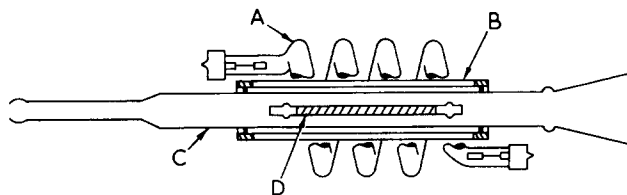


Figure 1 Sample tube assemblage: A, xenon lamp; B, filter solution; C, sample tube; D, sample film

compared with the simple photodegradation observed in vacuum, indicating the cumulative effect of primary degradation products.

EXPERIMENTAL

Materials

The PMMA sample with a molecular weight of 2.76×10^6 was synthesized by anionic polymerization using benzaldehyde radical anion as an initiator. The sample was purified by reprecipitation with methanol from a chloroform solution. A commercial product (supplied by Mitsubishi Rayon Co. Ltd.) with a molecular weight of 7.59×10^5 was used in preliminary experiments after purification by reprecipitation.

Sample films were cast on a glass plate from chloroform solution and dried in vacuum for two days. No impurities or residual solvents were detected by i.r. spectroscopy of the film. The thickness of the sample film was about $8 \mu\text{m}$.

Flash degradation apparatus and procedure

The flash degradation apparatus was described in detail in a previous report⁷. A PMMA film was irradiated by a sequence of flashes emitted at the discharge of a xenon lamp. A sensitive gas chromatograph Yanagimoto Model GCG-220 with hydrogen flame ionization detector GCF-100 was used to analyse degradation products at each flash. A di-2-ethylhexyl phthalate column, 30 wt % on Celite-545, was used at 100°C . The degradation was carried out in vacuum or in flowing nitrogen with a flow rate of 40 ml/min under atmospheric pressure.

The flash lamp was charged at 3 kV by a condenser bank of the capacitance of $308 \mu\text{F}$ and discharged by triggering with a radio frequency a.c. pulse. The energy liberated at a flash was 1375 J, when calculated from initial and residual voltages and the capacitance of the condenser bank.

The spectrum of radiation energy of the regular flash light is distributed broadly in a wavelength range of 200–600 nm with a maximum at around 400 nm. After triggering the discharge of the lamp the current pulse reaches a maximum at about 0.1 msec and extinguishes within 5 msec.

As shown in Figure 1, the sample film was wrapped around a glass tube situated in the centre of a fused silica sample tube with a cylindrical silica outer jacket containing a filter solution. The sample tube was set onto the axis of a helical xenon lamp stored in a cylindrical case with a silvered inner surface. A 0.07 mol/l aqueous solution of $\text{K}_2[\text{Hg}(\text{SCN})_4]$ was used for cutting off the u.v. component below 330 nm by a light pass of 1.44 mm in the jacket. Otherwise, pure water filled the jacket. The light intensity was decreased by 20% when filtered.

For the degradation in vacuum a cold trap using liquid nitrogen was used to collect the degradation products. After evacuating the sample tube and cold trap by an oil diffusion

pump, the system was kept in vacuum at irradiations. After each irradiation the degradation products were swept out from the trap to the gas chromatograph by flowing nitrogen as a carrier.

For the degradation in nitrogen, the carrier gas was filled in the sample tube after evacuation. Flash irradiations were repeated in flowing nitrogen at the rate of 40 ml/min. Degradation products were introduced directly into the gas chromatograph and analysed continuously. The amount of products was calibrated by the peak area of the chromatogram.

Sample temperature at irradiations

The flash irradiation was carried out at a room temperature of $10^\circ\text{--}30^\circ\text{C}$, but the sample temperature could not be monitored, though we have tried the following methods. If the flash degradation of the polymer was conducted by a thermal degradation mechanism, as suggested by Lundberg and Nelson, the sample temperature would be increased very rapidly. First, we tried to measure the sample temperature by a very thin thermocouple of gold–constantan directly attached to the sample surface, using a memory oscilloscope. We could not obtain a satisfactory result by this method, because a real thermal equilibrium was difficult to attain around the surface of the sample and the response time of the thermocouple system was too long to detect a rapid temperature increase.

If the sample temperature could be raised heterogeneously, the average temperature of a sample film would not be so high. We tried to observe directly a possible melting of the metal powder (Cu, Ag, and Pb) dispersed in the polymer sample at flash irradiations. The melting of the metal powder, however, was not observed in the present conditions.

Finally, we tried to measure the black body radiation spectrum of the heated sample. In this case, it was difficult to remove the interference by the surface reflection, and the spectroscopic method was not applicable for this purpose. In conclusion, we abandoned attempts to measure the actual temperature of the sample at irradiations in this study.

Molecular weight measurement

After irradiation of several flashes the molecular weight change of the residual polymer was measured from the intrinsic viscosity $[\eta]$ of chloroform solution at $25^\circ \pm 0.05^\circ\text{C}$. The weight-average molecular weight \bar{M}_w was obtained by the Mark–Houwink equation⁸:

$$[\eta] = 0.34 \times 10^{-4} \bar{M}_w^{0.83}$$

RESULTS AND DISCUSSION

Preliminary experiments

In some preliminary experiments, we degraded a commercial PMMA ($\bar{M} = 7.59 \times 10^5$) with flash irradiations. The sample was purified by reprecipitation and examined by i.r. spectroscopy not to involve copolymer constituents or additives.

The degradation in nitrogen was similar to that observed by Lundberg and Nelson. The carbon particles formed by the several initial flashes cause the thermal degradation of the polymer. By microscopic observation we found bubbles around carbon particles. However, flash degradation in vacuum gave a completely different phenomenon. The products were the same as in nitrogen, but the amounts of products at a flash showed constant values at repeated flashes, indicating no cumulative effect existed in this con-

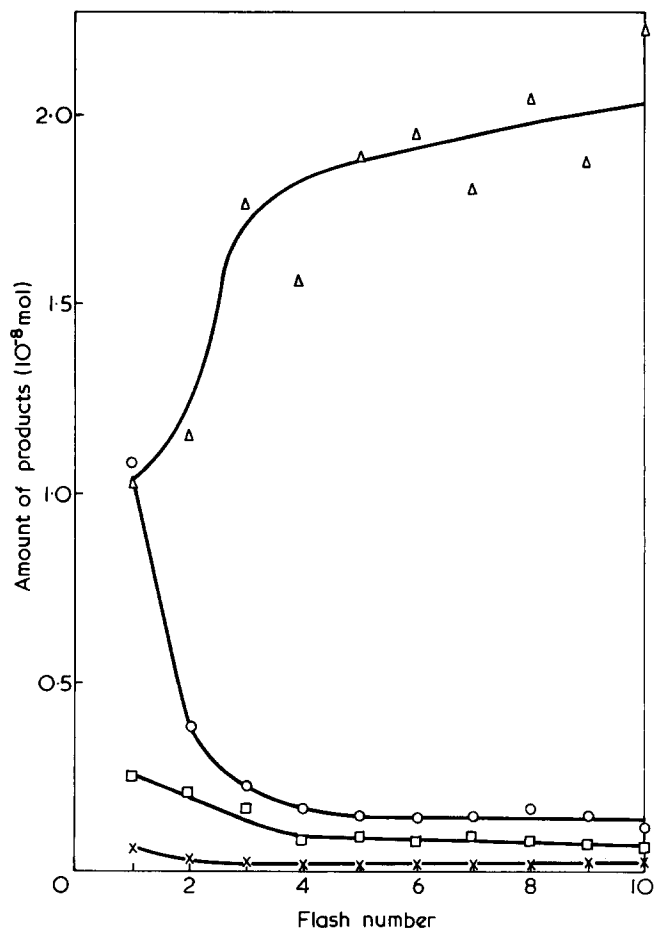


Figure 2 Amount of products by flash degradation of anionic PMMA in vacuum by the regular light: O, gaseous products; Δ, methanol; X, ester; □, monomer

dition. The molecular weight decreased successively. No carbon formation was observed. These results suggest strongly that the photodegradation mechanism is dominant for the flash degradation of PMMA in vacuum.

In the present paper, we show more elaborate experimental results to confirm the photodegradation mechanism for degradation in vacuum.

Degradation by regular light involving the u.v. component

In this case, a fused silica sample tube with a cylindrical jacket containing pure water was used. Therefore, the effect of the u.v. component of the flash light on the degradation of PMMA was contained in the result.

For the sample of synthesized anionic PMMA, four significant peaks were obtained in gas chromatograms of degradation products in this condition. The first peak was identified as a mixture of gaseous products. Using a Molecular Sieve 13 column, we identified methane, ethane, C₂-hydrocarbons, and C₃-hydrocarbons in the gaseous mixture. By using a thermal conductivity detector, hydrogen, carbon monoxide, and carbon dioxide were also found in the mixture. In this study, however, the amount of gaseous products was calculated in terms of methane.

The second peak was identified as methanol and the fourth as methyl methacrylate monomer. The third small peak has not yet been identified. By considering the chemical structure of the original polymer, it is tentatively attributed to methyl isobutyrate and called an ester peak in this paper, though the retention time of this compound was not precisely coincident with that of the third peak. The

amount of this product was calculated in terms of methyl isobutyrate.

The change of the amounts of products with the repeated number of flashes are shown in Figure 2. The amounts of gaseous products, monomer, and ester produced at each flash decrease with the flash number. On the contrary, the amount of methanol increases with the initial several flashes. After irradiation of ten flashes, the molecular weight of residual polymer decreased from the initial 27.6×10^5 to 2×10^5 .

Degradation by filtered light not involving the u.v. component

In this case, a 0.07 mol/l aqueous solution of K₂[Hg(SCN)₄] was used as a filter for cutting off the u.v. component below 330 nm from the flash light.

The gas chromatograms of degradation products of the anionic PMMA in this condition differed much from those obtained by regular light. Only two peaks identified as gaseous products and ester were observed. The monomer was not detected in this condition. As shown in Figure 3, the amounts of two products were less than those obtained in the preceding condition.

After irradiation of ten flashes, the molecular weight of residual polymer was found to be unchanged within an experimental error.

Mechanism of flash degradation in vacuum

Comparing Figure 2 with Figure 3, it is clear that the flash degradation of anionic PMMA in vacuum by the light involving the u.v. component is conducted by a photodegradation mechanism. The essential effect is due to the u.v. component below 330 nm. The u.v. absorption spectrum of PMMA shown in Figure 4 exhibits a broad absorption below 300 nm. The C—C energy corresponds to the light energy at about 340 nm. Therefore, the photodegradation mechanism is to be considered by the u.v. light below 330 nm.

The photodegradation of PMMA was studied by Allison⁹. The chromophore of PMMA is the pendant ester group. When it absorbs the u.v. light, methoxy and carbomethoxy radicals are produced. These radicals are transferred to the polymer chain following the chain scission. Methanol and methyl formate could be formed by this mechanism. In our analytical conditions, the retention time of methyl formate is coincident with that of methane. Then, the peak of methyl formate is hidden in that of the gaseous products. The monomer is produced by the depolymerization of chain fragments formed at radical transfer. The chain scission is

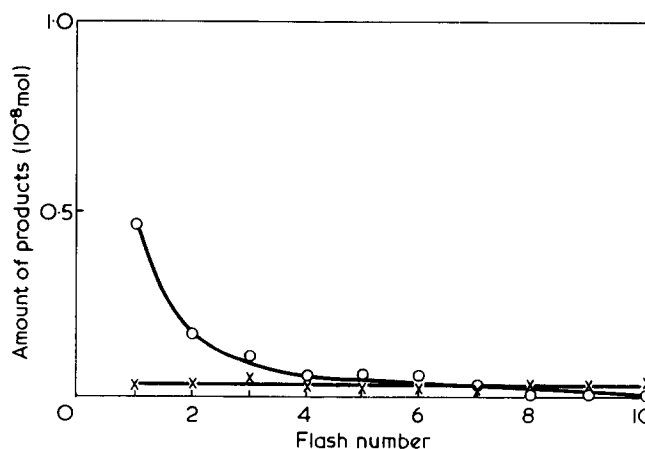


Figure 3 Amount of products by flash degradation of anionic PMMA in vacuum by the filtered light: O, gaseous products; X, ester

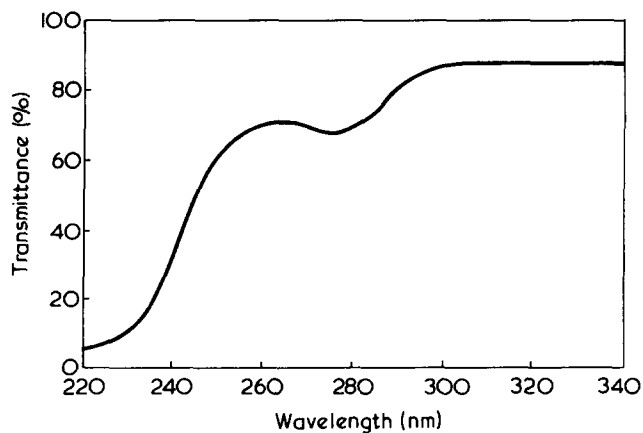


Figure 4 Absorption spectrum of PMMA

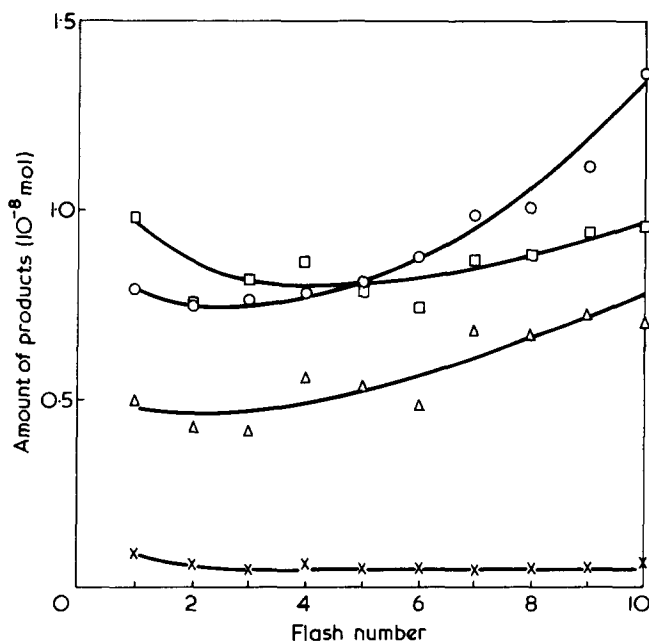


Figure 5 Amount of products by flash degradation of anionic PMMA in nitrogen by the regular light: O, gaseous products; Δ, methanol; X, ester; □, monomer

evidenced by the molecular weight decrease down to one-tenth of the initial value observed in our experiment.

When the u.v. component is cut off, the photodegradation of PMMA is very much depressed. Our experimental data showed no monomer production and no change of the molecular weight in this condition. Chain scissions are difficult to occur at flash degradation by the light not involving the u.v. component. This is strong evidence of the photodegradation mechanism of flash degradation of PMMA in vacuum.

Degradation in nitrogen by regular light

The fused silica sample tube filled with nitrogen and covered with a water jacket was used. The u.v. component of the flash light is transmitted to the sample.

Four peaks were observed in gas chromatograms of degradation products of anionic PMMA. These products were identified as the same as those obtained at flash degradation in vacuum by the regular light.

The amounts of products at a flash changed with the flash number, as shown in Figure 5. The amount of gaseous products and methanol increased slightly with the flash number. The amount of monomer showed a shallow mini-

mum at several flashes. Ester production was not changed with repeated flashes. After irradiation of ten flashes, the molecular weight of residual polymer decreased from 27.6×10^5 to about 1.0×10^5 . The molecular weight decrease is more significant in nitrogen than in vacuum.

The carbon formation was not observed in these experiments. However, if flash irradiations were continued more times, it would be possible to find carbon particles in the polymer.

Degradation in nitrogen by filtered light

A fused silica sample tube filled with nitrogen and with a filter solution in the jacket was used in this case.

Degradation of anionic PMMA in this condition gave three major products; gaseous products, ester, and monomer. It is remarkable that the monomer was detected in the products under the flowing nitrogen in contrast to the degradation in vacuum with the same filtered light. The change of product amounts with the flash number are shown in Figure 6. The amounts of ester and the monomer decreased gradually with the flash number, although gaseous products showed a minimum production after several flashes. The molecular weight of the residual polymer decreased a little up to several flashes, as shown in Figure 7.

From the production of monomer and the decrease of the molecular weight by a few flashes, it is concluded that PMMA degraded slightly in nitrogen even by the filtered light not involving the u.v. component.

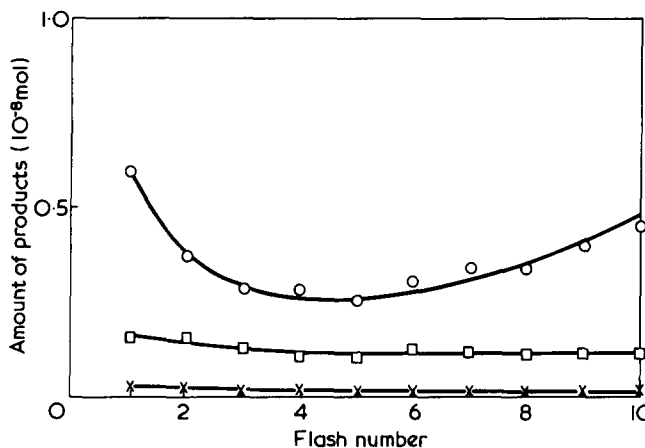


Figure 6 Amount of products by flash degradation of anionic PMMA in nitrogen by the filtered light: O, gaseous products; X, ester; □, monomer

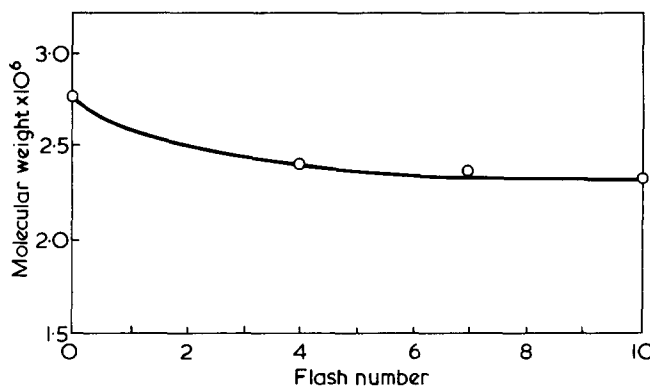


Figure 7 Molecular weight change with flash number for flash degradation of anionic PMMA in nitrogen by the filtered light

Table 1 Amount of adsorbed products in the polymer after several flash irradiations in nitrogen by the filtered light (10^8 mol)

Products	Flash number		
	4	7	10
Gaseous products including methyl formate	Trace	0.12	—
Methyl propionate	0.561	0.442	—
Unidentified ester	0.060	0.060	0.200
Methyl methacrylate	0.049	0.033	—

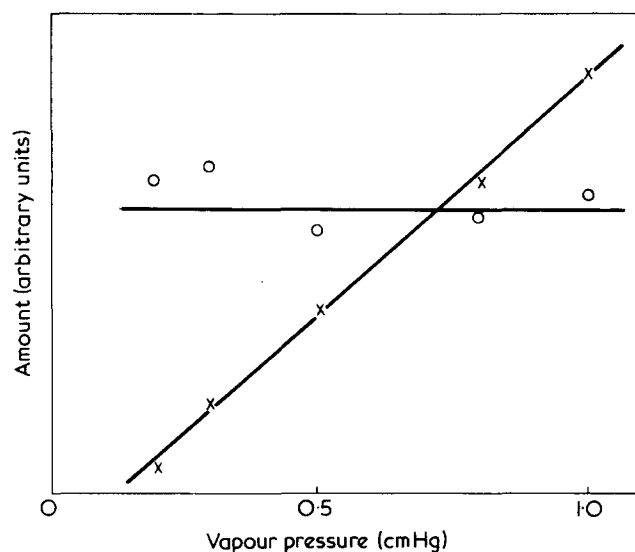


Figure 8 Amount of products by flash degradation of methyl methacrylate monomer vapour

Mechanism of flash degradation in nitrogen

Comparing Figure 2 and 3 with Figures 5 and 6, respectively, it is clear that the amount of products at flash degradation in nitrogen is much more than those in vacuum. Probably, the initial degradation would be caused by the photodegradation mechanism also in nitrogen. The ambient pressure of the atmosphere at degradations in nitrogen suggests that the primary decomposition products would be sorbed in the polymer during the initial several flashes. The effect of secondary decomposition of the sorbed products was confirmed by the following experiments.

After irradiation in nitrogen by the filtered light, the sorbed materials were chased out from the residual polymer and caught by the cold trap by evacuating the sample tube through the trap. Table 1 shows the sorbed products after various numbers of flash irradiation. Methyl formate,

methyl propionate, unidentified ester and methyl methacrylate monomer were detected. The amount of monomer decreased with the flash number. The methyl propionate peak was not detected in the gas chromatograms of degradation products in the flowing nitrogen.

The detection of several sorbed materials suggests the secondary decomposition of these materials at subsequent flashes. From the largest content of methyl propionate in the primary products, it would be a main source of secondary products as a gaseous mixture. Monomer is another possible source of gaseous products.

In Figure 8 is shown the result of flash degradation of the monomer vapour at various pressures. The amount of gaseous products by flash degradation of the monomer shows no dependence on the monomer content. Therefore, it is concluded that the formation of gaseous products is not simply due to the secondary decomposition of the monomer primarily formed by depolymerization.

In experiments in vacuum, the primary products would be swept out from the system after each flash irradiation. It was difficult to find a cumulative effect in this case.

The increase of monomer formation is very noticeable in nitrogen and the molecular weight decrease is observed even by the filtered light. Nitrogen absorbs only the light of wavelength below 134 nm, which is not involved in the flash light of the present experiment. A possible mechanism will be proposed in detail in a forthcoming paper.

The decomposition of primary products sorbed in the polymer at the flash degradation in nitrogen would cause the final result of carbon formation as observed in preliminary experiments. After this stage thermal degradation prevails in the reaction.

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