The Effect of γ–Irradiation on Poly(methyl Methacrylate) Using an Ultrasonic Technique

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Synopsis

Ultrasonic absorption measurements were made at 3.14 MHz on poly(methyl methacrylate) as a function of temperature and after various doses of γ-irradiation. The measurements showed a relaxation phenomenon. The activation energy of the various doses was determined and the smallest doses that affected the specimen was found to be 4 Mrad.

INTRODUCTION

When any polymer is exposed to high-energy radiation, free radicals are formed in the polymer as intermediates. These radicals either react to form secondary products, or become entrapped as long-lived radicals that can only enter into delayed reaction. The occurrence of these processes depends on the physical state of the polymer during and following irradiation.

The most obvious effect of radiation is a reduction in average molecular weight, described as degradation.[1,2] In degradation, the chain is scissioned randomly along its length. The number of such scissions is proportional to the dose and is independent of molecular weight.[3] It depends to only a small extent on temperature. The effect of main-chain scission can also be followed by measuring the decrease of mechanical strength.

It has been suggested that a more fundamental factor is the free energy of propagation.[4] When this is low, steric and electronic factors favor degradation. Usually, both degradation and crosslinking occur, and the ratio is affected by temperature, crystallinity, stereoregularity and the environment.

If main-chain bonds in polymer molecules were broken during irradiation, either directly or as a result of subsequent reaction, the possibility of recombination would be expected to be high, especially in the solid state.

EXPERIMENTAL

Material

The polymer poly(methyl methacrylate) (PMMA) was obtained from Nylonic Industries Ltd. (U.K.).

Sample Preparation for Ultrasonic Measurements

A pulse-reflection technique was used for measuring the attenuation of ultrasonic longitudinal waves. To avoid deviation from pure plane wave propa-

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TABLE I

Time (h)	Min	M_v 10^5 g/mol
Before irradiation		2.17
After irradiation (wtih 4 Mrad)		
20	20	0.86
70	10	1.20
188	10	1.87
480	10	1.87

gation, the sample was prepared with good parallel faces oriented normal to the direction of propagation. It was machine-cut in the form of a circular disc of diameter 1.4 cm and of thickness 0.8 cm.

A conventional ultrasonic flaw detector USM2 (Kraut Kramer, West Germany) was used in these measurements. The apparatus is capable of producing high frequency pulses in the frequency range 0.5–12.0 MHz, and operates with the same transducer, which is used as both transmitter and receiver at the same time. Since the probes delivered with the ultrasonic flaw Detector could not be used above 40°C, measurements were made with x-cut quartz crystals, which were bonded to the sample on one of their parallel faces. A signal from a pulsed transmitter operating at the fundamental frequency of the transducer or at one of its odd harmonics was applied across the faces of the transducer.

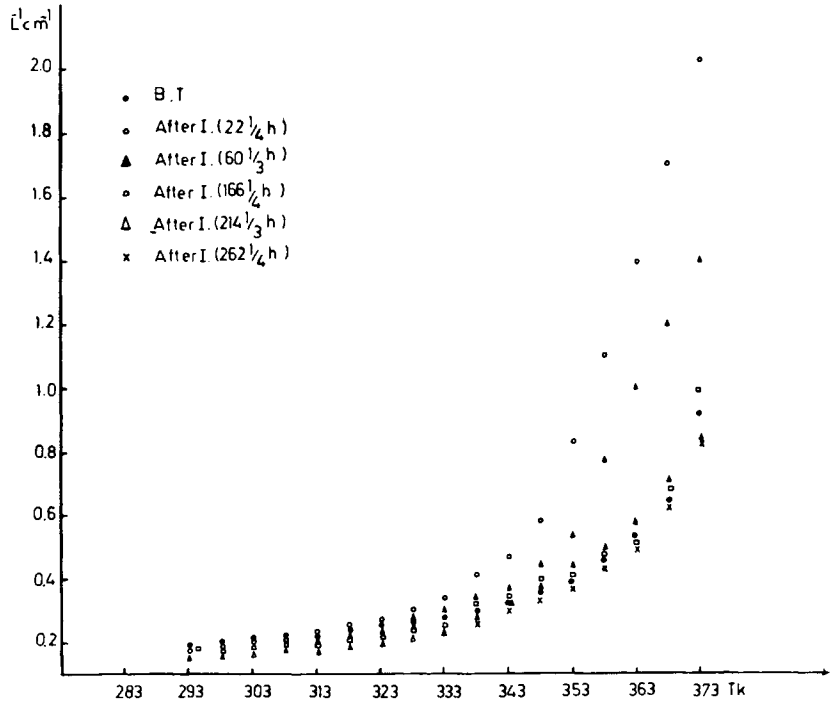

Fig. 1. Relationship between attenuation, l^{-1}, and temperature for a 4 Mrad dose.

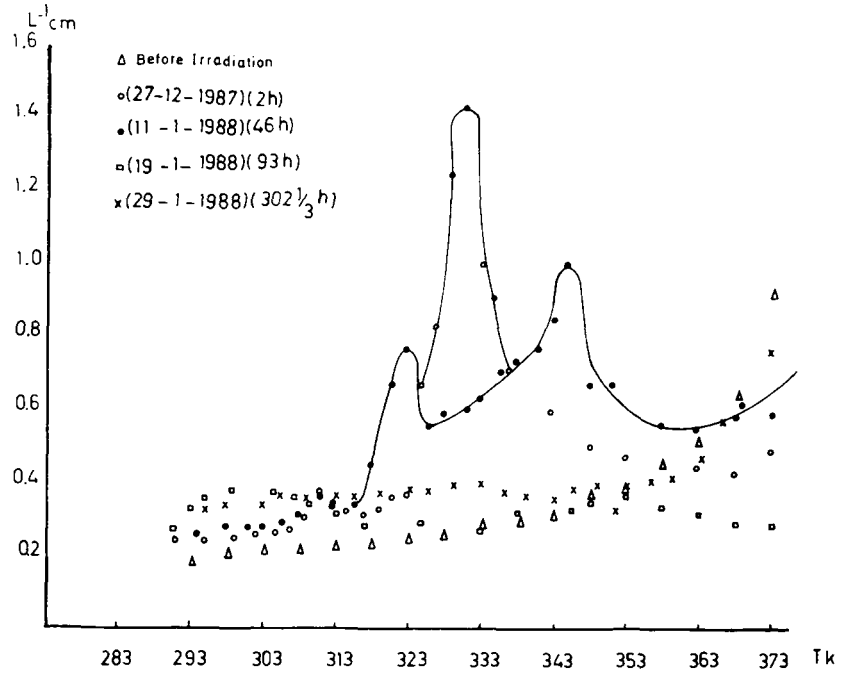

Fig. 2. Relationship between attenuation, l^{-1}, and temperature for a 5 Mrad dose.

Variation of temperatures was achieved by using an electric furnace capable of operating to 300°C, with accuracy ± 0.2°C.

The echo height (l) was measured on the face of a cathode-ray oscilloscope by means of a calibrated scale with a sensitivity of ±0.2 mm. In this way, the change of attenuation (α) with temperature was determined with ± 1.0% precision.

The specimens were exposed to various doses of γ-irradiation (4, 5, and 6 Mrad) at an ambient temperature of 30°C. We tried to study the smallest dose that allowed the formation of free-radical species.

In our experiments, the attenuation α can be determined from

$$\alpha = \text{const}(\ln l)^{-1}$$

for the purpose of comparison as stated previously[5] and for simplicity, $(\ln l)^{-1}$ can be replaced by l^{-1}, the reciprocal of the height of the echo, to represent the change of α with temperature at measuring frequency for different conditions, i.e.,

$$\alpha \propto l^{-1}$$

From the relative attenuation l^{-1} versus temperature curve, one could determine T_m, the temperature at which the peak occurs for each measuring frequency (f). The activation energy W of the relaxation can be calculated by using

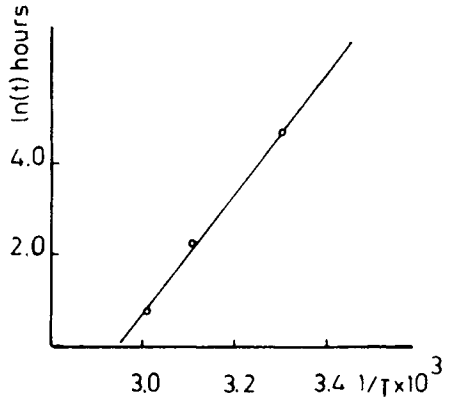

Fig. 3. Relationship between ($\ln t$) (h) and $1/[T_m\,(\mathrm{K})] \times 10^3$ for the peaks observed after 5 Mrad irradiation.

$$f = \text{const} \exp(-W/KT_m)$$

where K is Boltzmann's constant. A plot of $\ln f$ against $1/T_m$ will give a straight line from the slope of which the activation energy of the relaxation process is calculated.

Measurements

The relative attenuation l^{-1} of the ultrasonic pulse was measured for perspex samples in the temperature range from 20 to about 100°C at the single frequency of 3.14 MHz. It has previously been stated[6] that heat treatment does not affect the ultrasonic attenuation through the material. Measurements were made before irradiation and after exposing the sample to γ-irradiation (doses 4, 5, and, 6 Mrad), and the activation energy of the relaxation process was calculated for each condition of treatment.

Molecular Weight Measurement

The viscosity average molecular weight $\bar{M}$, of PMMA was determined from viscosity measurements of the polymer after being dissolved in suitable solvent, acetone. Before irradiation $\bar{M}$ is given by 2.17×10^5 g/mole. Immediately after irradiation, its value drops remarkably. However, $\bar{M}$ increases by time, but even after 150 h, its value is smaller than that obtained before irradiation (Table I).

The sharp drop in $\bar{M}_v$ after γ-irradiation implies a considerable decrease in the molecular weight of the molecule due to degradation, and accordingly due to the formation of free radicals.

The increase in the value of $\bar{M}_v$ after that with time fits very well with the ultrasonic measurements where the peak decays with time till the curve for l^{-1} versus T retains its original shape.

RESULTS AND DISCUSSION

Figure 1 shows the l^{-1} cm versus T (K) relationship obtained for PMMA after irradiation with a 4 Mrad dose and after various times. The results were

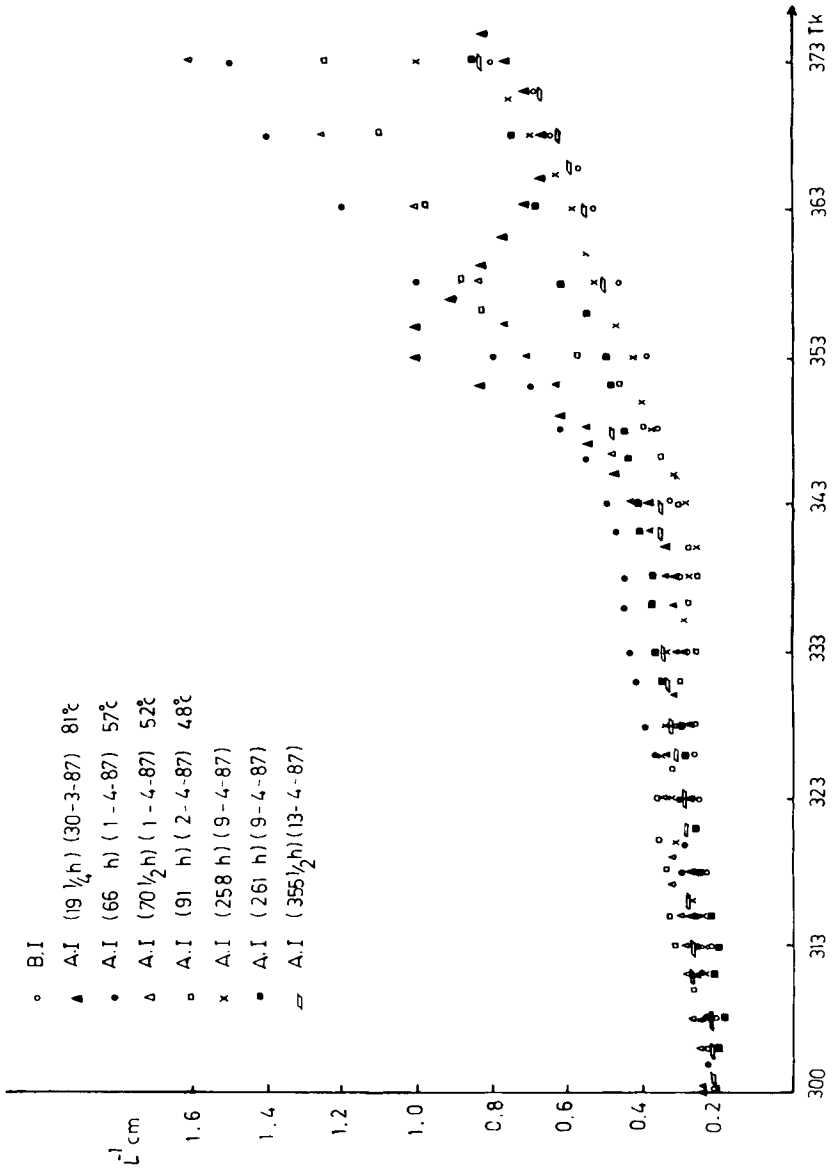

Fig. 4. Relationship between attenuation, l^{-1}, and temperature for 6 Mrad dose.

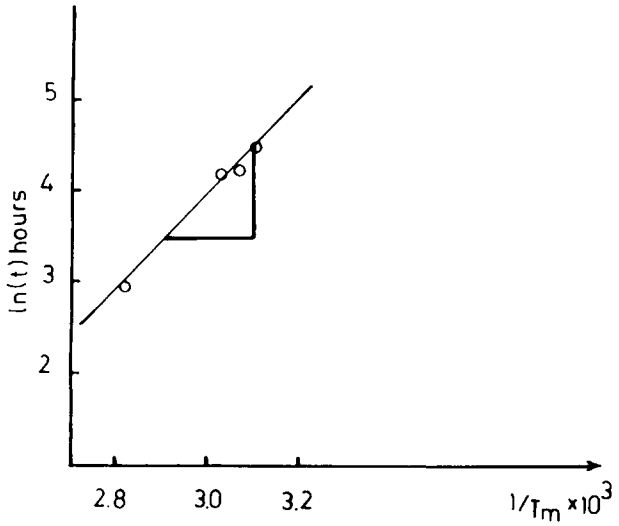

Fig. 5. Relationship between (ln t) (h) and $1/[T_m\,(\mathrm{K})] \times 10^3$ for the peaks observed after 6 Mrad irradiation.

normalized to the same starting point to facilitate comparison. From the curves we can see that before and after irradiation (with 4 Mrad), the absorption increases with the increase of temperature until the echo disappears completely, and measurement of the absorption becomes impossible. This result is in excellent agreement with earlier results.[6,7] Immediately after irradiation, the curve rises more rapidly. It has been pointed out previously[8] that the lower the molecular weight of the polymer, the higher will be the α *versus* T relationship. Thus it may be that the molecular weight of our specimen is lowered by irradiation, but by the time the curve regained its original shape which was reproducible on nine consecutive days after 262 h, the specimen had retained its original molecular weight as shown before in the molecular weight measurement.

Figure 2 shows the results obtained for the specimen before and after irradiation with a 5 Mrad dose. Immediately after irradiation a peak is observed. The peak height decreases with time after irradiation, and the temperature at which the maximum occurs is decreased. After 302 h the peak completely disappears and the curve moves back to its position before irradiation. The relationship in Figure 3 led to a value of energy of activation of 245.24 kJ/mol.

Figure 4 shows the results obtained for the specimen before and after irradiation with 6 Mrad dose. Immediately after irradiation, a peak is observed in the absorption temperature curve with a maximum height at T_m = 354 K. Increasing the time after irradiation results in decreasing the height of the peak and lowering the temperature if its maximum. After 355 h, the peak completely disappeared and the curve regained its original shape. As previously stated,[9] the activation energy of rotation of the methyl group in PMMA at the lowest temperature is 1.7–14.6 KJ/mol, and this can be considered as relaxation; the activation energy of 100.6 KJ/mol in the present case (Fig. 5) can be considered to be the energy of rotation of the main chain of the polymer.

It was found that in PMMA, fairly small doses produce little effect on a block specimen. As PMMA is characterized by the presence of two large side

groups, their presence results in steric hindrance. If a chain is broken, the two ends cannot readily rejoin, as can occur if the substituents are only H atoms as in PE. For this reason we believe that γ–irradiation results in the creation of free radicals which in time recombine or react with the main chain of the polymer and that ultrasonic measurements are sensitive to the decay of free radicals formed after γ–irradiation, the smallest dose that affects PMMA being equal to 4 Mrad.

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