YU ISSN 0015—3206
FZKAAA 15 (3) 239 (1983)

ABSORPTION OF LONGITUDINAL ULTRASONIC WAVES IN POLYMER SOLUTION (POLYMETHYL METHACRYLATE)

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Received 18 October 1982
Revised manuscript received 9 January 1983
UDC 538.951
Original scientific paper

Measurements of the change of absorption coefficient of longitudinal ultrasonic waves were carried out over the temperature range from 10°C to 50 °C in a 2% solution of polymethyl methacrylate in benzene irradiated with intense ultrasonic waves. The ultrasonic absorption measurements were performed by the pulse technique at frequencies of 2.5, 4, and 6 MHz. A marked change in absorption coefficient was observed as the temperature, and intensity of ultrasonic waves increased. A qualitative discussion is given on the assumption that the structural changes induced by intense ultrasonic waves, as well as by the temperature are related to changes in the number of degraded groups in the polymeric network.

1. Introduction

It has been known for some time that long chain molecules (polymer solutions) are broken down when irradiated with intense ultrasonic waves[1-4]. A theory has been proposed to explain the mechanism of ultrasonic degradation of polymers by Mostafa[5] who suggested a mechanism in which the macromolecules are highly extended in the solution and the model of a stretched string loaded at regular intervals is used to explain their behaviour under ultrasonic forces.

Gooberman[6] assumed that the degradation is mechanical rather than chemical and is due to the stresses set up within the macromolecules by the shock wave emanating from the collapse of a cavitating bubble. It has been proposed also that the macromolecules themselves may act as cavitation nuclei.

The investigation of the ultrasonic absorption in polymer solutions provides valuable informations about the character of the intermolecular mobility in the polymer. Also, the absorption coefficient for ultrasonic waves is a sensitive characteristic of the structural changes occuring in the polymeric solutions.

A theory[7] was formulated to account for the absorption of longitudinal ultrasonic waves in concentrated polymer solutions (~ 3 to 15%) based on the macromolecule model. In addition to the absorption that occurs in the solvent, there is an extra absorption of ultrasonic energy in the solution due to the incomplete entanglement of the polymer network by the local viscosity of the polymer network solvent system. The frequency dependence of $\Delta\,(a/f^2)$ has been given as,

$$\Delta\,(a/f^2) = \frac{4\pi^2 K T}{C^3 \varrho V} \cdot \sum_q \frac{T_q}{1 + \omega^2 T_q^2}$$

where f is the ultrasonic frequency, K is Boltzman constant, T is the absolute temperature, ϱ is the density of the medium, C is the velocity of the ultrasonic wave in the medium, V is the volume of the total network-solvent system, $\omega = 2\pi f$ is the cy clic frequency, and T_q is the relaxation time of the q-th normal mode of the system.

Measurements have shown that the ultrasonic absorption coefficient in an ultrasonically treated solution is higher than in a solution not treated ultrasonically, and always higher than that of the solvent. The difference in the absorption of ultrasonic wave in polymer solutions from that in pure solvent has been reported by Gooberman[8] and Mikhailov[9].

The work reported by Mikhailov[10] on the ultrasonically induced structural changes in polymer solutions showed that the change in absorption coefficient is ascribed solely to the change in the structure of the solutions in response to the temperature.

The object of this work is to show that ultrasonic absorption can be used to detect changes in molecular structure in polymer solution induced by intense ultrasonic irradiation.

2. *Experimental*

Sonic dismembrator-300 manufactured by Artek (USA) was the ultrasonic irradiation source. The frequency of the ultrasonic waves was 20 kHz. Five gms. of polymethyl methacrylate were dissolved in 250 ml pure benzene to give 2% polymer solution. The sample holder consists of a double wall glass container 6 cm in length and 3 cm in diameter to accomodate 50 ml of polymer solution. Four polymer solutions were subjected to ultrasonic waves where the acoustic power was kept at 8.5, 12.5, 17.5, and 25.5 W/cm^2 to study the effect of increasing acoustic intensity on the ultrasonic absorption. The time of irradiation was kept constant for 3 min. to ensure the time in each case. The irradiation was carried in air at constant temperature (25 °C).

The absorption measurements were carried out using ultrasonic material tester type 9024, produced by Funkwerk Erfurt (East Germany). Measurements were made at the frequencies 2.5, 4.0, and 6.0 MHz. Another set of measurements at 4.0 MHz was taken for benzene non radiated, and irradiated polymer solution with 25.5 W/cm^2 ultrasonic waves while increasing temperature every 4°C starting from 10°C up to 50°C.

3. *Results and discussion*

Fig. 1 shows the ultrasonic absorption expressed as (α/f^2) at 25 °C and the acoustic power at 2.5, 4.0, and 6.0 MHz. The results indicate a linear dependence of ultrasonic absorption on excess power, and the rate of increase of absorption with respect to power is equal to $0.15 \pm 0.40 \times 10^{-15}$ s^2/W · cm. Thus an

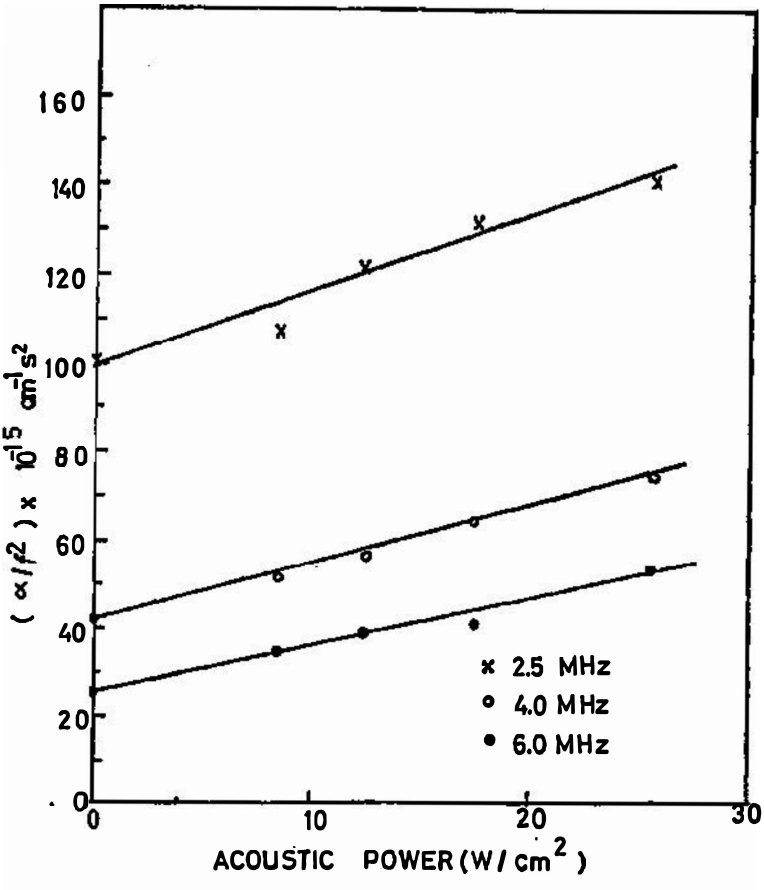

Fig. 1.

equation for the increase in absorption with power can be suggested and written in the form;

$$a/f^2 = 0.15 \times 10^{-15} P + K$$

where P is the acoustic power, and K is a constant its value depends on the frequency at which the ultrasonic absorption is measured. Such result is in agreement with that reported earlier by Towle[11] who found an increase in ultrasonic absorption of *PMMA* solution with the increase of ultrasonic intensity. On the other hand, Woodcook[12] reported an increase in ultrasonic absorption of gamma irradiated molecular solutions with increasing radiation dose. This is mainly due to fact that an increase in acoustic power will result in increasing the degradation, i. e. the breakage of chemical bonds in the polymer. The figure shows also that the increase in ultrasonic absorption is more pronounced the lower the ultrasonic frequency at which absorption was measured.

Fig. 2 represents the computed values of $\Delta\,(a/f^2)$ which represent the difference between $(a_1/f^2) - (a_2/f^2)$ where a_1 and a_2 are the ultrasonic absorption

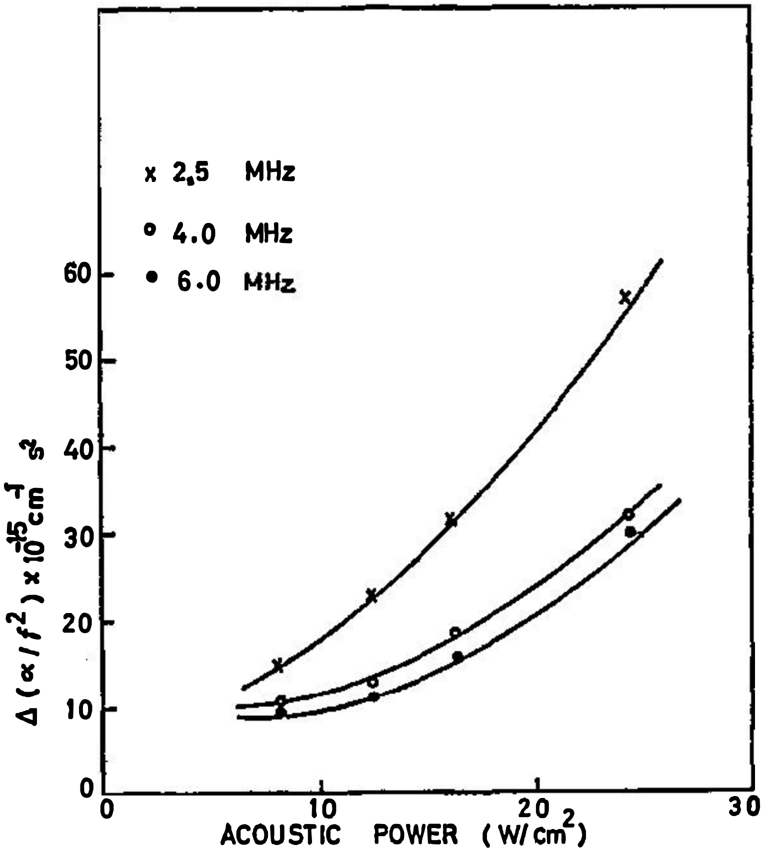

Fig. 2.

coefficients for the irradiated and non radiated polymer solution. The value of $\Delta\,(\alpha/f^2)$ is assumed to represent the change in absorption due to the structural change in *PMMA* solution resuting from subjecting it to the intense ultrasonic waves. The figure shows also a sharp increase in the value of $\Delta\,(\alpha/f^2)$ as the intensity increases above 17.5 $\mathrm{W/cm^2}$. Again, this increase in the value of $\Delta\,(\alpha/f^2)$ is more pronounced at lower frequency.

Fig. 3 displays a plot of (α/f^2) against frequency for benzene, non radiated, and irradiated polymer solution with 8.5, 12.5, 17.5, and 25.5 $\mathrm{W/cm^2}$ ultrasonic waves at 25 °C. The value of α/f^2 for benzene remains constant while it varies inversely with frequency in both irradiated and non radiated polymer solution. The measured absorption of benzene is found to be $2300 \times 10^{-17}\ \mathrm{s^2/cm}$ which is higher than the generally known value. However, for the present purpose, this discrepancy is unimportant since all measurements were taken under the same conditions with the same apparatus.

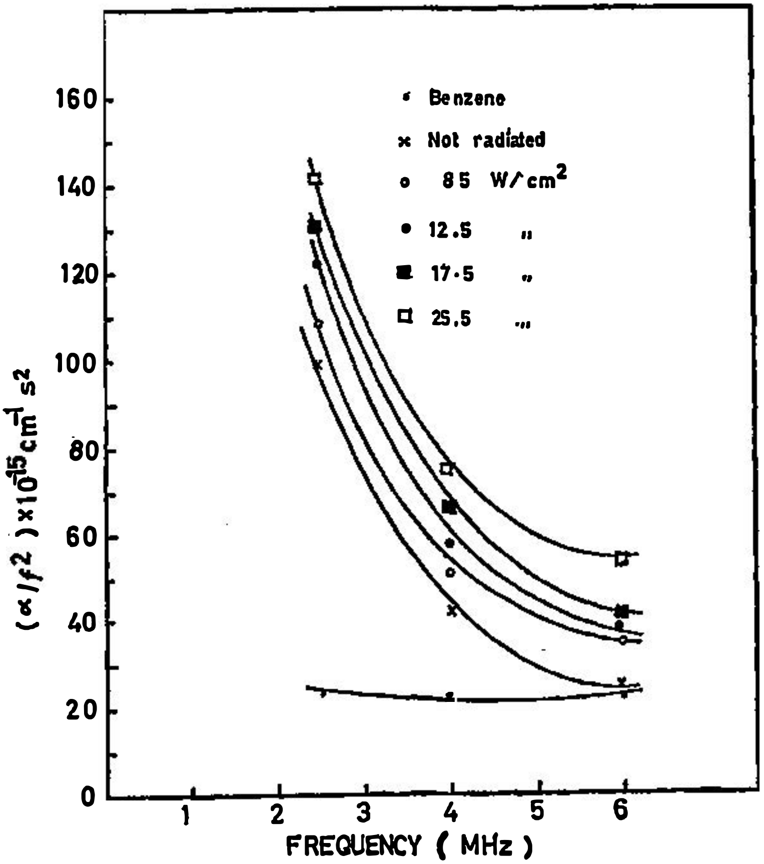

Fig. 3.

Fig. 4 shows the relation between the ultrasonic absorption at 4 MHz for benzene, non radiated, and irradiated *PMMA* solution with 25.5 W/cm^2 ultrasonic waves and the temperature. As seen, the absorption increases while we should expect a decrease in the value of α/f^2 with increasing temperature in case of non radiated and irradiated solutions since a decrease in viscosity of the polymer solution will take place with increasing temperature. Furthermore, viscosity of the irradiated solution with intense ultrasonic waves must decrease as a result of the breakage of the chemical bonds in the polymer chain. However, this increased value of α/f^2 can be attributed to the fact that as the temperature increase a change in the structure of the polymer network occures as it occures when the solution is irradiated with intense ultrasonic waves and therefore an increase in absorption will result. Gotlib[7)] reported that the additional absorption is related to an irreversible process occuring in the system of polymer chains dissolved in the solvent.

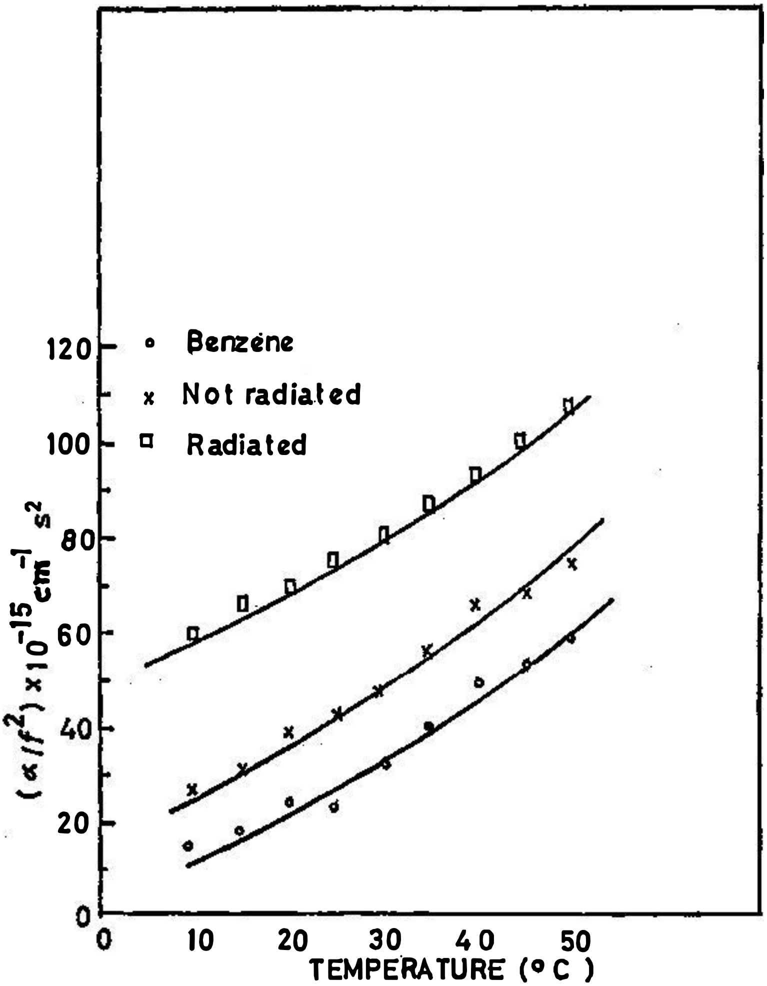

Fig. 4.

It may seem reasonable to assume that the absorption of the irradiated polymer solution is made up of; (*a*) the absorption (α_1) due to the presence of the *PMMA* in benzene, i. e. the viscous losses in the solvent as the solvent and the polymer network move with respect to each other, (*b*) the absorption (α_2) due to the structural changes in the polymer solution resulted from the increase in temperature, and (*c*) the absorption (α_3) due to structural changes occured in the polymer solution as a result of irradiation with ultrasonic waves.

With these assumptions we can express the absorption in *PMMA* solution contributed by shear viscosity and structural changes as:

$$(\alpha/f^2)_{total} = (\alpha_1/f^2)_{shear} + [(\alpha_2/f^2) + (\alpha_3/f^2)]_{struc}.$$

In this expression, the contribution to the total absorption from thermal conduction was neglected.

From the above results, ultrasonic absorption can be used to detect changes in molecular structure in polymer solutions induced by intense ultrasonic irradiation.

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APSORPCIJA LONGITUDINALNIH ULTRAZVUČNIH VALOVA U POLIMERNIM OTOPINAMA

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UDK 538.951

Originalni znanstveni rad

Mjeren je koeficijent apsorpcije longitudinalnih ultrazvučnih valova u 2% otopini polimetil-metakrilata u benzenu, na temperaturama od 10°C do 50 °C. Uzorci su prije mjerenja izloženi djelovanju akustičnih valova različitog intenziteta. Opažene su znatne promjene koeficijenta apsorpcije u ovisnosti o snazi akustičnih valova i temperaturi. Rezultati su diskutirani kvalitativno, uz pretpostavku strukturnih promjena u polimernoj mreži, uzrokovanih porastom temperature i izlaganju akustičnim valovima.