EFFECT OF ULTRASONICS ON THE VISCOSITY OF LONG-CHAIN POLYMER SOLUTION

Part I. 250 Parts Polyoxyethylene Per Million Parts of Water

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Abstract. The effect of ultrasonic waves (2 MHz, $\sim$5W/cm²) on the viscosity of 250 p.p.m. solution of long-chain polyoxyethylene (mol.wt. $\approx$ 4,000,000) has been investigated in order to estimate the degree of depolymerization, the approximate relations obtained are:

$$t_{fo} = 0.182C + 225 \qquad (1)$$

$$10^3/C_c = 0.1567 t_e + \frac{10^3}{250} \qquad (2)$$

The study revealed that roughly 10 equivalent polyox molecules in 100 are not broken by ultrasonic waves even after prolong treatment; whilst the estimated error found from the scatter of flow times in different runs is approximately ± 3.3 in 100.

The simplicity of the viscosity measurements makes it the most widely used of all physicochemical methods for the study and characterization of polymers and their solutions. In the case of polymer molecules in the solution, the viscosity has a geometric and hydrodynamic origin. Einstein equation[1] of the intrinsic viscosity for high polymer solutions, having compactly folded spherical molecules, is independent of the weight or size of the dissolved molecules. On the other hand, the intrinsic viscosity of randomly coiled or linearly rigid macromolecules depends markedly on the molecular weight and, therefore, it is a measure of the size and shape of the polymer molecules in solution. The intrinsic viscosity is found to be temperature sensitive only at higher temperature, when the molecules can overcome their hindering intramolecular potentials and become more or less coiled.

It was observed by Alfrey *et al.*[2] that in athermal solvents the polymer molecules will assume approximately the same shape that they would have in free space. In the present investigation the solvent used was athermal, i.e. polyoxyethylene in water and, therefore, there is no curling up of polyox molecules in the experimental solutions. Staudinger[3] pointed out that the intrinsic viscosity of polymer solution is proportional to the molecular weight and the constant of the proportionality gives informations about the molecular structure.

The polymer molecules can be ruptured or broken by ultrasonic waves.[4] The forces generated between chain molecules and the moving solvent are proportional to the chain-length and the velocity of the solvent.[5] The process of breaking up or depolymerization or degradation can be enhanced by increasing the intensity of the ultrasound.[6] It was found by Larionov *et al.*[7] that the viscosity of the polymer solution decreased significantly in relation to the solution concentration and the time of waves application. The extent of depolymerization can be estimated by measuring the intrinsic viscosity of the solution.

The subject matter of the present communication is the depolymerization of 250 p.p.m. solution of long-chain polyoxyethylene[8,9] by ultrasonic treatment at 2 MHz with an average energy output of approximately $\sim$5 W/cm².

Experimental

A solution of 250 p.p.m. of long-chain polyoxyethylene (mol.wt. $\approx$ 4,000,000) was prepared in the pure conductivity water (conductivity $\approx 10^6$ ohm⁻¹ cm⁻¹). This solution was diluted to different degrees and a series of more dilute solutions were obtained. The time of viscous flow of each of the solution and that of the conductivity water were determined accurately by using Ostwald U-tube viscometer No. 1 (viscometer constant is 0.00401) at 25°C. Townson and Mercer thermostat-bath with temperature accuracy of $\pm$0.01°C was used. The data points of two separate series of solutions are given in the Table 1 and are plotted as t_{fo} (C) in Fig. 2.

Polyox solution (15 ml, 250 p.p.m. was taken in a medium-size Pyrex glass test-tube (whose bottom has been flattened to obtain large area of thin wall) and exposed to ultrasonic radiation for a given time period. The temperature of the specimen was kept at 25°C by circulating water from the thermostat-bath (maintained at slightly higher temperature) with the help of a small water pump through the jacketed metallic cylindrical water filled container fixed on the transducer inside which the sample tube was dipped. The Mullard ultrasonic generator of 2 MHz frequency 'X-cut' quartz crystal transducer with an average energy output of $\sim$5 W cm² was used as radiation source. Fig. 1 shows the block diagram of the experimental set up together with the ultrasonic generator. The air bubbles formed in the load water column due to ultrasonic cavitation may adhere on outside surface of the bottom of specimen-tube and reduced the ultrasonics energy of treatment. The formation

TABLE 1. MEASURED FLOW TIMES (sec) OF THE POLYMER SOLUTIONS PREPARED OF DIFFERENT CONCENTRATIONS (p.p.m) AT 25°C.

Concn of solution (p.p.m.)	Solution series No. 1 Time of flow (t_{fo}) (sec)	Solution series No. 2 Time of flow (t_{fo}) (sec)
00·00	225·68	225·68
25·00	—	228·97
50·00	234·59	233·81
75·00	239·18	239·01
100·00	242·83	242·17
125·00	247·60	246·31
150·00	252·15	251·20
200·00	261·28	260·67
250·00	271·58	270·30

TABLE 2. THE ULTRASONIC EXPOSURE TIME (min) FLOW TIME (sec) AND THE VALUES OF CONCENTRATION (p.p.m.) CALCULATED FROM FLOW TIME AND ULTRASONIC EXPOSURE TIME OF 250 p.p.m. POLYOX SOLUTION IRRADIATED FOR DIFFERENT TIME PERIODS AT 25°C.

Time of exposure, t_e (min)	Time of flow, t_{ft} (sec)	Concn C(p.p.m.) of ultrasonic treated solutions calculated from flow time (t_{ft}) $C—(t_{ft}—225)/0·182$.	Concn. C_c (p.p.m.) of ultrasonic treated solutions calculated from the exposure time (t_e).$10^3/C_c=0·1567$ $t_e + \dfrac{10^3}{250}$
00·00	271·58	255·9	—
5·00	259·60	190·1	208·3
15·00	251·28	144·4	157·4
30·00	245·87	114·6	114·9
60·00	240·07	82·8	74·6
120·00	233·51	46·7	43·9
180·00	230·70	31·8	31·1
240·00	229·28	23·5	24·0

of bubbles was carefully watched and released by giving short jerk to the specimen tube whenever necessary during the treatment of polymer solution.

After ultrasonic exposure the solution was taken in the U-tube viscometer for flow measurements at 25°C. The flow time was recorded to an accuracy of ±0.1 sec with a stop-watch. The above procedure was repeated by giving different ultrasonic exposure time periods to new specimen. The mean of the flow time with the time of exposure are recorded in the Table 2 and the plots of C, C_c and t_{ft} against t_e are shown in Fig. 3.

Results

The plots of the flow times against the concentrations of two separate series of polyox solutions prepared gives straight line (Fig. 2). The time of flow increases linearly with the increase of the polymer concentration in the solutions. The approximate equation of the straight line obtained is given by:

$$t_{fo} = 0.182C + 225 \qquad (1)$$

Where C and t_{fo} represent the concentration (p.p.m.) of the polyox in the solution and the time of flow (sec) of the solution respectively.

An examination of curve marked t_{ft} in Fig. 3, which is the representative plot of flow time t_{ft} (sec) against the time of ultrasonic exposure t_e (min) of a typical run of 250 p.p.m. polyox solution at 25°C; shows that the flow time of treated polymer solution decreases rapidly in the first 30 min of ultrasonic treatment and then the rate of change of flow time slows down with exposure time up to 175 min and, therefore, the change is very low. The plot of concentrations C found from the measured flow times (or calculated with the help of equation 1) of the irradiated polyox solutions against the different given exposure time periods t_e is shown in Fig. 3 (curve marked C). The straight line obtained by plotting t_{ft} against C shown by the solid circles in Fig. 2 proved that t_{fo} of equation 1 can be replaced by t_{ft}.

Next, the graphs of log C and $1/C$ against t_e are shown by the curves marked I and II respectively in Fig. 4. A good straight line with positive slope is obtained by $1/C$ plot, yielding the relation below:

$$10^3/C_c = 0.1567\, t_e \times 10^3/250 \qquad (2)$$

In Fig. 3, curve marked C_c is the plot of concentrations calculated, employing equation 2 against t_e and lastly, the solid rectangles in Fig. 2 shows the graph of t_{ft} (C_c); here C_c approximately equalled at about 230 and 246 sec flow times and between the two C_c shifted to lower and beyond to higher values.

The reproducibility of the measured flow times against the ultrasonic exposure times among the different runs of 250 p.p.m. polyox solution, using new specimen for each run, was not very good. It was found to be of ±0.6% on the average values of flow times. This may be due to the slight fluctuation of the energy output per square centimetre of the transducer during the treatment which is caused usually by day-to-day room temperature variations, the hysteresis or conditioning of the ultrasonic generator and the experimental set up itself. The transducer supplied with the ultrasonic generator is usually matched with the liquid acoustic load, but a very small amount of energy may be attenuated in the water-column used as acoustic load between the surfaces of transducer-holder and bottom of the specimen-tube and also, a portion of energy absorbed in the glass bottom of the specimen-tube during transmission. The energy attenuated was not determined but since the length of water column was kept at 3 mm, and same specimen-tube with identical physical arrangement used throughout the investigation; the amount of attenuation may be assumed to be constant. However, maximum precautions have been taken to keep the above factors in their minimum levels.

The dimension of scatter of the flow times of different runs is shown graphically by the vertical line drawn in Fig. 3 (at 243 sec flow time on t_{ft} graph), so that it can be compared with ease. However, the above scatter introduces approximately ±3.3 in 100
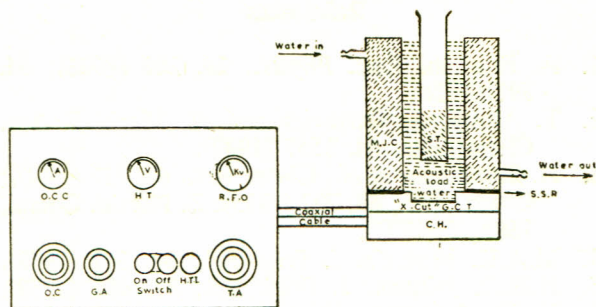
Fig. 1. Apparatus. O.C.C.,oscillator cathode current; R.F.O., R.F. output; O.C, output control; G.A., grib adjust; H.T.I., H.T. indicator; T.A., tuning adjustment; M. J.C., metallic jacketted cylinder; S.T., specimen tube; S.R.R., sealing rubber ring, 'X-cut' O.C.T., 'X-cut' quartz crystal transducer; C.H., crystal holder.
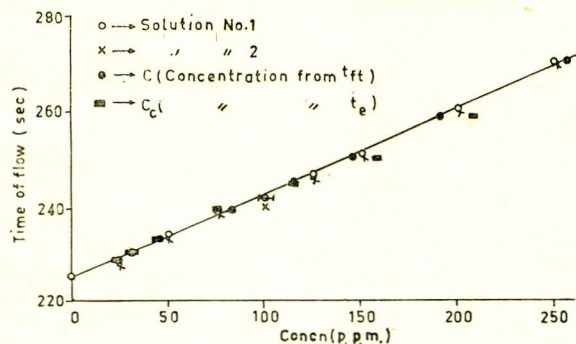

Fig. 2. The graph of time of flow t_{fo} (sec) against the (C) concentration (p.p.m.) of the untreated polymer solutions together with the plots of concentrations (C and C_c) calculated from t_{ft} and t_e of the ultrasonic irradiated 250 p.p.m. polymer solution at 25°C.

p.p.m. error in the estimation of the concentration expressed in terms of whole polymer molecule of the treated polyox solution; the width of the error estimated is shown by the horizontal line in Fig. 2 (at 100 p.p.m. concn). Circumstances prevented chemical or some other possible physical analyses from being carried out on the treated samples in order to compare quantitatively the concentration estimated by the present investigation and that of by other methods.

Discussion

In equation 1, where the flow time t_{ft} is a function of intrinsic viscosity of the polymer solution is found to be equal to the product of the slope of t_{fo} (C) line and the concentration of polyox in solution plus the flow time of the pure solvent ($t_{fs} = 225$). The second term of the equation gives the flow time of the polymer solution at infinite dilution and it is clearly the contribution of the solvent, and the first term of the equation gives the contribution of the dissolved polymer molecules and its weights distribution to the total flow time determined and, therefore, has a geometric and hydrodynamic origin. However, it is experimentally found that the flow time of the solution increased with the increase of polymer concentration (Fig. 2) which should be for the athermal solvent used in the investigations.
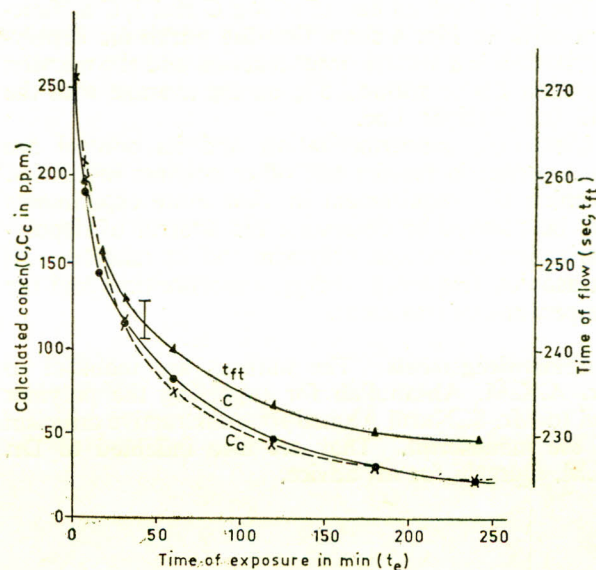

Fig. 3. The plots of concentrations (C,C_c) and flow –time, t_{ft} against ultrasonic exposure time, t_e
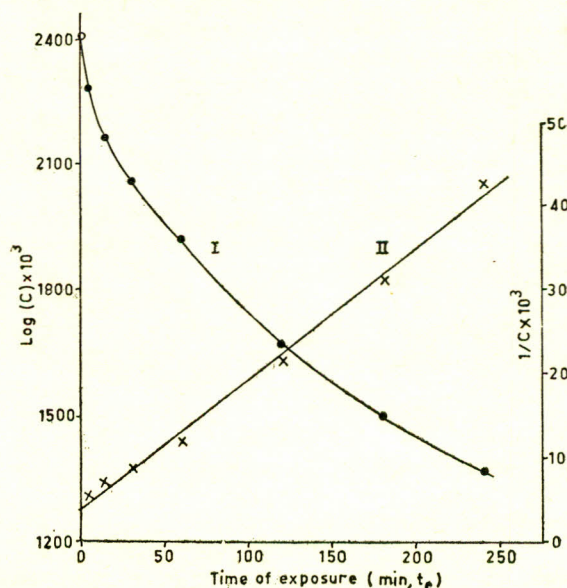

Fig. 4. The graphs of logarithm (i) and reciprocal (II) of concentration (C) against ultrasonic exposure time, t_e.

The concentration C found from the flow time measurements (i.e. using equation 1) is considered as the experimental value and that C_c according to equation 2 is the values calculated in terms of whole polymer molecule. The overall values of C_c fluctuate with the maximum amplitude of approximately ±9% of and around C (Fig. 3) in which the graphs of C, C_c and t_{ft} against t_e indicate that roughly at least equivalent of 10 polyox molecules in 100 are perhaps not depolymerized by ultrasonics and this is approximately three times the estimated error. Therefore, the flow time of the end product is that of a solution containing polymer molecules, broken polymer molecules and the solvent molecules assuming no major change in viscosity due to the distribution of molecular weights in the polymer.

The experimental curves of log C and $1/C$ as function of t_e in Fig. 4 show that the ultrasonic depolymerization is a second order reaction and the reaction equation fits to within $\pm 5\%$ on the average with the $1/C$ (t_e) straight line.

Ultrasonic depolymerization and its control are most needed in plastics and other polymer industries. Keeping this requirement in view more experiments will be planned to determine the control of depolymerization of various polymers and its relation with ultrasonics, frequency, energy, exposure time and the temperature of treatment.

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