Ultrasonic degradation of poly(methyl methacrylate)

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Ultrasonic degradation studies on a variety of molecular weights and molecular weight distributions of poly(methyl methacrylate) are reported. The extent of degradation was measured using gel permeation chromatography. Polydispersity decreased as a function of irradiation time for polymers with initial broad distributions. In contrast, polymers with an initial narrow distribution increased in polydispersity, passed through a maximum and then gradually decreased in polydispersity. Results appear to show no limiting degree of polymerization for poly(methyl methacrylate).

INTRODUCTION

Numerous studies of polymer degradation induced by ultrasonic radiation have been reported [1,2]. Such studies on poly(methyl methacrylate) have utilized measurements of solution viscosities[3] and determination of the amount of a free radical scavenger, α,α′-diphenyl-β-picrylhydrazyl, consumed[4,5] to follow the polymer degradation. Gel permeation chromatography (g.p.c.) gives considerably more information on the degradation process and was utilized in this study.

EXPERIMENTAL

Three samples of poly(methyl methacrylate) (PMMA) were obtained from Eastman Kodak (Rochester, New York, USA). These are referred to as polymers A, B and C and had number-average molecular weights $\bar{M}_n$ of 160 000, 48 600 and 19 400 respectively. Fractions were prepared from each of these polymers using precipitation of the polymer onto glass beads and column elution with a solvent/non-solvent gradient employing methyl ethyl ketone and methanol. The fractons are designated A_1, A_2, A_3, B_1, B_2, C_1 and C_2. The molecular weights of the fractions are given in the Tables reporting the degradation results.

Ultrasonic irradiation was carried out using a Brownwill Biosonic III probe operating at 60% of its full intensity, which is 28 W nominally at 20 kHz. The sample was prepared by dissolving 1.5 g of polymer in 150 ml of tetrahydrofuran (THF) which had been freshly distilled from NaOH. Thus all solutions were run at 1% w/v concentration. The solution was placed in a reaction vessel which was a 300 ml rosette cell, which has three side arms to provide good circulation. The cell was thermostatted in an ice–water bath throughout the irradiation. At 20 min intervals of irradiation a 2 ml aliquot of reaction solution was withdrawn and diluted to 0.2% w/v for the subsequent injection into gel permeation chromatograph.

The gel permeation chromatograph was an ANA–PREP Model (Water Associates, Framingham, Mass., USA). The calibration curve for PMMA was determined in a conventional method using narrow fractions of PMMA fractionated as previously described. The molecular weights for the fractions were determined from the limiting solution viscosity measurement using the following formulae[6]:

$$[\eta] = 5.2 \times 10^{-5} m^{7.6} \text{ for } 6 \times 10^4 < m < 250 \times 10^4$$

$$[\eta] = 104 \times 10^{-5} m^{0.5} \text{ for } 0.02 \times 10^4 < m < 2 \times 10^4$$

The colums consisted of four 4 ft x 3/8 in, i.d. (1.2 m x 9.5 mm) stainless steel columns packed with Bio-Glass, porous glass particles having pore sizes of 75, 374, 1250 and 2000 Å respectively. The g.p.c. was operated at ambient temperature using THF as solvent. The flow rate was 2.0 ml/min.

A Fortran IV computer programming was performed to calculate weight-average molecular weights ($\bar{M}_w$), number-average molecular weight ($\bar{M}_n$), and the ratio of $\bar{M}_w/\bar{M}_n$. $\bar{M}_w$ and $\bar{M}_n$ were computed in accordance with the following equations:

$$\bar{M}_w = \frac{\Sigma H_i M_i}{\Sigma H_i}$$

$$\bar{M}_n = \frac{\Sigma H_i}{\Sigma M_i / H_i}$$

where H_i is the relative height of a g.p.c. curve measured at each half-elution count, and M_i is the corresponding molecular weight which was found from the calibration curve. No correction on the effect of zone broadening was applied.

The calculation of the number of polymer bonds broken after a given time t of irradiation, β_t, was based on the familiar equation[5,6]:

$$\beta_t = \frac{\eta_0 (\bar{M}_{n0} - \bar{M}_n)}{\bar{M}_n}$$

where η_0 is the number of polymer molecules of initial $\bar{M}_{n0}$ which degrade to $\bar{M}_n$ after time t.

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Table 1 Results from g.p.c. analysis for polymer A and fractions

		Irradiation time (min)						
PMMA		0	20	40	60	80	100	120
A	$\bar{M}_w \times 10^{-3}$	371.2	179.9	143.3	118.7	106.5	95.3	90.2
	$\bar{M}_n \times 10^{-3}$	126.0	81.2	66.5	60.3	56.4	52.3	51.2
	$\bar{M}_w/\bar{M}_n$	2.95	2.21	2.16	1.97	1.89	1.82	1.76
	Number of bonds broken ($\times 10^{-18}$)	–	3.92	6.46	7.81	8.85	10.10	10.46
A_1	$\bar{M}_w \times 10^{-3}$	189.1	126.4	110.0	96.2	91.1	80.5	74.7
	$\bar{M}_n \times 10^{-3}$	84.7	63.6	59.6	51.1	50.0	46.5	43.7
	$\bar{M}_w/\bar{M}_n$	2.23	1.99	1.84	1.83	1.82	1.73	1.71
	Number of bonds broken ($\times 10^{-18}$)	–	3.54	4.49	7.05	7.40	8.76	10.00
A_2	$\bar{M}_w \times 10^{-3}$	333.4	190.5	139.1	113.0	97.2	88.8	80.5
	$\bar{M}_n \times 10^{-3}$	147.5	87.8	65.2	54.1	49.3	44.9	40.6
	$\bar{M}_w/\bar{M}_n$	2.26	2.17	2.13	2.09	1.97	1.98	1.98
	Number of bonds broken ($\times 10^{-18}$)	–	4.16	7.73	10.57	12.20	14.00	16.13
A_3	$\bar{M}_w \times 10^{-3}$	521.4	224.2	141	109.6	89.2	82.2	79.3
	$\bar{M}_n \times 10^{-3}$	231.0	91.0	62.6	50.8	44.0	42.9	42.9
	$\bar{M}_w/\bar{M}_n$	2.26	2.46	2.26	2.16	2.03	1.92	1.87
	Number of bonds broken ($\times 10^{-18}$)	–	6.02	10.52	13.87	16.62	17.14	17.24

Table 2 Results from g.p.c. analysis for polymer B and fractons

		Irradiation time (min)						
PMMA		0	20	40	60	80	100	120
B	$\bar{M}_w \times 10^{-3}$	148.6	114.5	99.7	90.5	82.6	76.5	74.1
	$\bar{M}_n \times 10^{-3}$	56.9	51.0	47.5	43.9	43.2	40.4	40.1
	$\bar{M}_w/\bar{M}_n$	2.61	2.24	2.10	2.06	1.91	1.90	1.84
	Number of bonds broken ($\times 10^{-18}$)	–	1.86	3.19	4.78	5.11	6.59	6.76
B_1	$\bar{M}_w \times 10^{-3}$	123.9	101.6	92.9	84.2	80.3	70.8	65.5
	$\bar{M}_n \times 10^{-3}$	68.1	54.3	50.0	45.3	43.8	40.2	38.8
	$\bar{M}_w/\bar{M}_n$	1.82	1.87	1.86	1.86	1.83	1.76	1.69
	Number of bonds broken ($\times 10^{-18}$)	–	3.37	4.80	6.68	7.36	9.21	10.02
B_2	$\bar{M}_w \times 10^{-3}$	187.3	102.7	99.2	91.9	83.4	72.0	72.9
	$\bar{M}_n \times 10^{-3}$	87.2	47.7	50.7	46.7	43.8	38.0	38.0
	$\bar{M}_w/\bar{M}_n$	2.15	2.15	1.95	1.96	1.90	1.89	1.92
	Number of bonds broken ($\times 10^{-18}$)	–	10.86	7.46	8.94	10.26	13.41	13.41

RESULTS AND DISCUSSION

Tables 1–3 list $\bar{M}_w$, $\bar{M}_n$, polydispersity ratio $\bar{M}_w/\bar{M}_n$, number of bonds broken and rate of bond breakage of the polymer as a function of irradiation time. A progressive decrease in molecular weight of the polymers A_3 can be observed in *Figure 1* as the g.p.c. peak maximum shifts gradually to a higher elution count, i.e. to a lower molecular weight. The ratio of $\bar{M}_w/\bar{M}_n$ and half-width of g.p.c. curve showed a similar pattern of decrease as irradiation proceeded. As seen in *Table 1* the broad molecular weight distribution (*MWD*) of polymer A became narrower under the influence of ultrasonic forces. The biggest change in $\bar{M}_w$,$\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ takes place in the first 20 min of the degradation. At the same time, the number of bonds broken indicated qualitatively that higher molecular weight polymer degraded rapidly while molecular weight polymer tended to slow down the rupture process.

Table 1 shows results of ultrasonic irradiation for polymers A_3, A_2 and A_1, the narrower fractions of polymer A. The molecular weight and $\bar{M}_w/\bar{M}_n$, as for polymer A, showed a decreasing rate of degradation as a function of irradiation time. However, some distinct features can be noted. Polymer A_3 degraded almost twice as rapidly and to a greater extent than polymer A. Polymer A_2 reacted somewhat faster while polymer A_1 degraded more slowly than polymer A.

Polymers A, A_3, A_2 and A_1 all showed similar *MWD* and *MW* at the termination of irradiation despite their different initial *MW* and *MWD*. After 20 min of irradiation polymer A_3 showed a broadened distribution with $\bar{M}_w/\bar{M}_n$ increasing from 2.26 to 2.46. The half-width of the g.p.c. curve increased from 3.20 to 3.72 counts. Thus well fractionated PMMA of high molecular weight first showed an increasing $\bar{M}_w/\bar{M}_n$ upon ultrasonic irradiation, which subsequently decreased on further degradation.

Table 2 lists irradiation results for polymers B, B_1 and B_2. In comparison, polymer of the B series have slower rates with less degree of degradation than polymer samples of the A series. The relatively narrow polymer B_1 broadened its distribution after 20 min of irradiation, followed by a subse-

Table 3 Results from g.p.c. analysis for polymer C and fractions

		Irradiation time (min)						
PMMA		0	20	40	60	80	100	120
C	$\bar{M}_w \times 10^{-3}$	70.8	70.1	66.8	63.6	62.7	60.1	59.0
	$\bar{M}_n \times 10^{-3}$	28.9	31.1	30.3	31.0	30.5	29.8	29.4
	$\bar{M}_w/\bar{M}_n$	2.45	2.26	2.20	2.05	2.05	2.02	2.01
C_1	$\bar{M}_w \times 10^{-3}$	56.7	56.7	52.2	52.2	51.4	49.5	47.5
	$\bar{M}_n \times 10^{-3}$	31.6	31.7	30.9	30.4	28.9	28.9	25.6
	$\bar{M}_w/\bar{M}_n$	1.79	1.79	1.69	1.73	1.77	1.71	1.86
C_2	$\bar{M}_w \times 10^{-3}$	108.8	93.6	91.0	85.0	80.7	74.7	73.1
	$\bar{M}_n \times 10^{-3}$	54.7	49.5	48.9	45.9	43.6	41.0	38.7
	$\bar{M}_w/\bar{M}_n$	1.99	1.89	1.86	1.85	1.85	1.82	1.89
	Number of bonds broken ($\times 10^{-18}$)	–	1.73	1.96	3.17	4.20	5.52	6.83

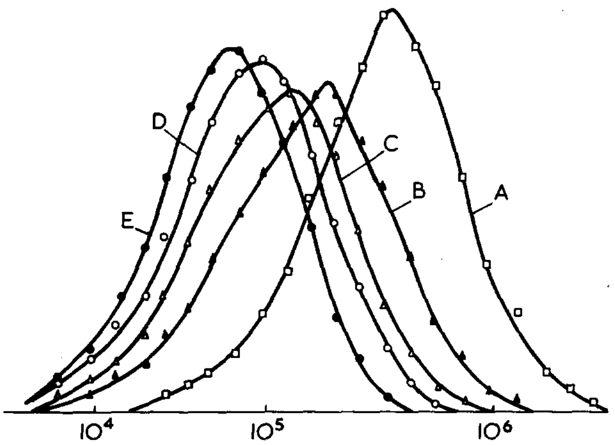

Figure 1 Differential *MWD* for polymer A_3: A, 0; B, 20, C, 40; D, 60; E, 120

quent decrease in heterogeneity. This is similar to the behaviour of sample A_3.

Table 3 lists computed results of degradation for polymers C, C_1 and C_2. The polymer degradation occurred less rapidly and to a small degree when compared with polymers A and B series under the same experimental conditions.

There is controversy in the broadening or narrowing of the distribution, but we believe it is probably not a controversy at all. Clearly, if one starts with a monodisperse fraction and breaks bonds, out of necessity the distribution will be broadened. In general, since one works with polydispersed or highly dispersed systems, the high molecular weight materials will degrade more rapidly and we will see the effect of narrowing the distribution.

It is apparent from these results that the discrepancies discussed occasionally, wherein some workers report a broadening of distribution on degradation while others report the narrowing of the distribution, probably do not really represent a disagreement at all. Thus the broader distributions consistently show a narrowing of the distribution while moderately sharp fractions can show broadening followed by narrowing of the distribution. The irradiation time employed was sufficiently long for the resulting molecular weights and their distributions to appear to be very similar regardless of the initial molecular weight. The degradation rate is decreased but there is still a finite amount of degradation continuing.

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