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Ultrasonic Solution Degradations of Poly(Alkyl Methacrylates)

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ABSTRACT

Ultrasonic (70 W, 20 kHz) solution (2%) degradations of poly(alkyl methacrylates) have been carried out in toluene at 27°C and in tetrahydrofuran (THF) at -20°C. $\overline{M}_w$ and $\overline{M}_n$ of all polymers (before and after sonification) were computed from GPC. Irrespective of the alkyl substituent, $\overline{M}_w$ decreased rapidly at first and then slowly approached limiting values. All $\overline{M}_w/\overline{M}_n$ ratios were in the vicinity of 1.5 at the limiting chain lengths. For identical $\overline{M}_n$, the rate constants k were $(4.2 \pm 2.0) \times 10^{-6}$ min^{-1} in toluene at 27°C and $(5.4 \pm 2.0) \times 10^{-6}$ min^{-1} in THF at -20°C. For poly(isopropyl methacrylate) and poly(octadecyl methacrylate) with higher, but identical, $\overline{M}_{n,0}$, k values were higher ($(9.0 \pm 1.0) \times 10^{-6}$ min^{-1} at 27°C and $(18.0 \pm 1.5) \times 10^{-6}$ min^{-1} at -20°C). This suggests that $\overline{M}_{n,0}$ and not the bulk size of the alkyl substituents is the factor that determines the rate of degradation. Lowering of the temperature accelerates degradation due primarily to lower chain mobility of poly(alkyl methacrylates) and enhanced cavitation. The average number of chain scissions $([(\overline{M}_n)_0/(\overline{M}_n)_t] - 1)$ calculated from component degradation data are much higher than those obtained with overall $\overline{M}_{n,t}$ values.

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INTRODUCTION

Ultrasonic solution degradations of poly(methyl methacrylate) have been reported in the literature [1-10]. When polymer solutions are subjected to ultrasonic irradiation, shearing of polymer molecules yields homolytic cleavage [11-15] due to cavitation [16-22]. Other parameters which may also affect ultrasonic solution degradation of polymers are pressure [23, 24], temperature [18-25], frequency [26], intensity of ultrasound [18, 27-35], reactor design [10], and molecular weight of the starting materials [25-33]. In an earlier report on the ultrasonic solution degradation of polystyrene in the presence of various poly(alkyl methacrylates) (PRMA) [36], it was shown that, when the substituents in PRMA were methyl, ethyl, isopropyl, n-butyl, isobutyl, or phenyl, scrambled copolymers with segments from PS and PRMA were obtained. However, when the substituents in PRMA were cyclohexyl, benzyl, hexyl, isodecyl, lauryl, hexadecyl, octadecyl, or isobornyl, no sequence copolymers were formed. The decrease in the intrinsic viscosity and shifts of their GPC chromatograms toward the low molecular weight end suggested that, on sonification, PRMA samples with bulkier substituents do degrade and yield radicals which, however, do not recombine with those from polystyrene. Furthermore, degradation of polystyrene was found to be dependent on the chain stiffness of the poly(alkyl methacrylates). With a view to extending these studies, ultrasonic solution degradation studies of poly(alkyl methacrylates) at 27°C in toluene and at -20°C in THF are presented in this report.

EXPERIMENTAL

Materials

Samples of poly(methyl methacrylate), poly(ethyl methacrylate), poly(isopropyl methacrylate), poly(lauryl methacrylate), poly(hexadecyl methacrylate), poly(octadecyl methacrylate) (Scientific Polymer Products), as well as poly(n-butyl methacrylate), poly(isobutyl methacrylate), poly(hexyl methacrylate), poly(isodecyl methacrylate), and poly(cyclohexyl methacrylate) (Aldrich Chemical Co.) were used as received.

Degradation Procedure

Ultrasonic degradations of polymer solutions in toluene (at 27°C) and in THF (at -20°C) were carried out in a batch reactor (10 cm long, 2.5 cm diameter, 50 mL capacity) equipped with a water jacket to maintain the temperature within 2°C, measured with a Ni-Cr alloy probe and a Comark digital thermometer [25, 26]. The sealed steel reactor was screwed onto a threaded nodal point on a 1.25-cm diameter disruptor horn (Heat systems, Model 375 A with a nominal frequency of 20 kHz). The ultrasonic intensity of 70 W was adjusted using the calibration curve of the meter reading, the power control setting, and the power output in watts. After sonicating the polymer solutions for a desired period of time, these were transferred to capped bottles for GPC analyses.

Gel Permeation Chromatographic Analyses

Molecular weight distributions of polymers were carried out with a Waters Associates GPC (equipped with a high-pressure solvent delivery system. Model 6000 A), an ultraviolet absorbance detector (Model 440), and a differential refractometer (Model R401) operated at 25°C. The separating system consisted of six μ-Styragel columns connected in series, each packed with crosslinked polystyrene gel having (by the Waters method) pore sizes of 100, 500, 1×10^3, 1×10^4, 1×10^5 and 1×10^6 Å, respectively. The flow of the solvent tetrahydrofuran was maintained at 1 mL/min while the concentration of the polymer solution was limited to 0.2% in order to render "concentration effects" negligible on the peak position in the chromatograms. Calibration of the instrument was performed with standard samples of poly(methyl methacrylate) [36], poly(ethyl methacrylate), poly(n-butyl methacrylate), poly(isobutyl methacrylate) and poly(octadecyl methacrylate). Nonsonicated and sonicated samples of poly(methyl methacrylate), poly(ethyl methacrylate), poly(n-butyl methacrylate), poly(isobutyl methacrylate), poly(hexyl methacrylate) and poly(cyclohexyl methacrylate) were also analyzed for their weight-average, $\overline{M}_w$, and number-average $\overline{M}_n$, molecular weights by GPC in methyl ethyl ketone as the Mark-Houwink constants in this solvent are reported in the literature [37]. Molecular weights of poly(isopropyl methacrylate) and poly(isodecyl methacrylate) were computed with the calibration curve prepared for poly(isobutyl methacrylate), whereas those of poly(hexadecyl methacrylate) and poly(lauryl methacrylate) were computed from the curve of poly(octadecyl methacrylate), as shown in Fig. 1.

Molecular weights of all polymers were computed from the uncorrected GPC chromatograms using the summation method [38]. Due to the polydisperse nature of poly(alkyl methacrylates), the GPC calibration curves of molecular weight M versus elution volume V_e were prepared indirectly by using the basic definitions of $\overline{M}_w$ and $\overline{M}_n$:

$$\overline{M}_w = \sum w_i M_i / \sum w_i, \tag{1}$$

$$\overline{M}_n = \sum w_i / \sum [w_i/M_i], \qquad (2)$$

where w is the weight of species i of molecular weight M_i and can be obtained from the GPC chromatograms. Assuming that the variation of M versus V_e is linear, one can optimize a calibration curve which, when used in combination with Eqs. (1) and (2), yields $\overline{M}_w$ and $\overline{M}_n$ similar to those of the standard sample.

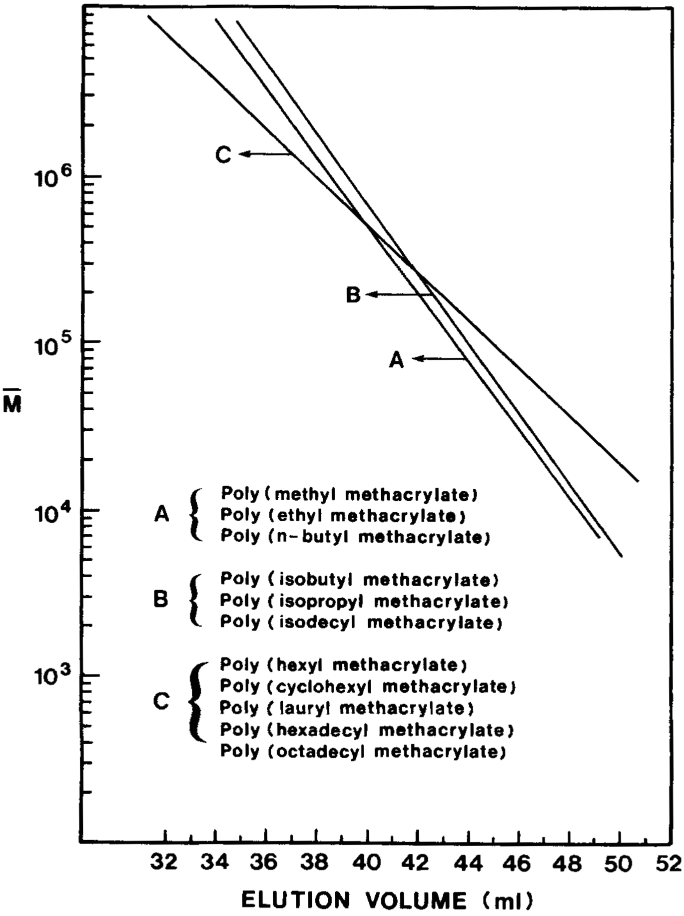

FIG. 1. Plots of log M versus elution volume, V_e, for various poly(alkyl methacrylates).

RESULTS AND DISCUSSION

Tables 1, 2, and 3 present overall values of $\overline{M}_w$, $\overline{M}_n$, and $\overline{M}_w/\overline{M}_n$ for various poly(alkyl methacrylates) before and after sonification in toluene at 27°C and in THF at -20°C. Irrespective of the nature of the alkyl substituent, $\overline{M}_w$ and $\overline{M}_n$ decreased rapidly at first (consistent with a random type of degradation) and then slowly approached limiting values. Polydispersity ratios $\overline{M}_w/\overline{M}_n$ of all poly(alkyl methacrylates) decreased with time and were in the vicinity of 1.5 at their limiting molecular weights. Based on the data in Tables 1 and 2, a typical plot of weight-average degree of polymerization $\overline{DP}_w$ as a function of irradiation time is traced and shown in Fig. 2.

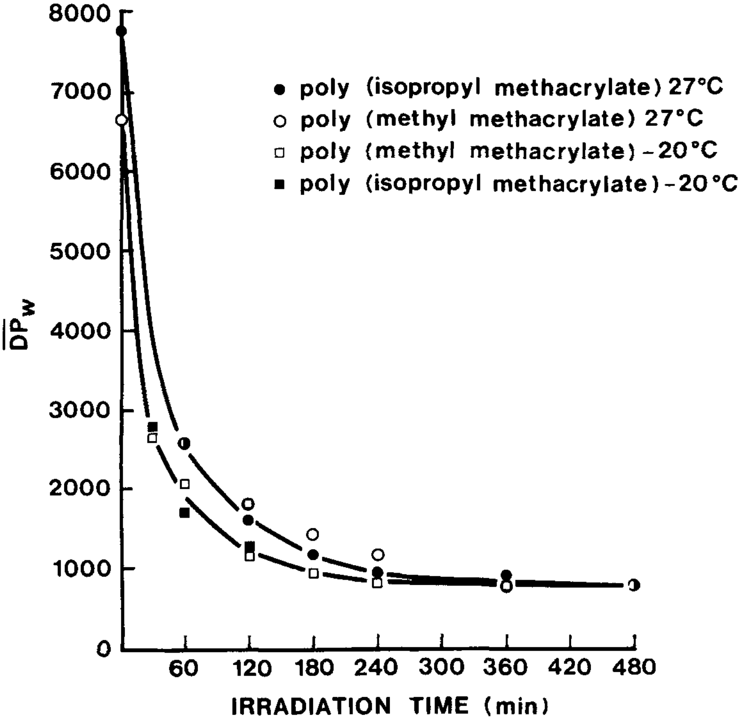

FIG. 2. Plots of weight-average chain length, $\overline{DP}_w$, as a function of irradiation time for ultrasonic (70 W, 20 kHz) solution (2%) degradations of poly(methyl methacrylate) and poly(isopropyl methacrylate) in toluene at 27°C and in THF at -20°C.

TABLE 1. Ultrasonic Solution Degradation of Various Poly(Alkyl Methacrylates) (PRMA) where R = Methyl, Ethyl, n-Butyl, and Cyclohexyl

			Methyl			Ethyl			n-Butyl			Cyclohexyl		
Irradiation time, min	Temperature, °C	Solvent	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$
Non-irradiated	-	-	6.70	1.60	4.20	3.35	1.20	2.80	2.48	0.93	2.66	3.10	1.30	2.40
60	27	Toluene	2.55	1.23	2.07	1.90	1.05	1.80	1.25	0.70	1.80	2.01	1.20	1.68
120	27	Toluene	1.77	1.00	1.77	1.54	0.94	1.64	1.10	0.64	1.72	1.58	0.99	1.58
180	27	Toluene	1.45	0.92	1.58	1.40	0.87	1.62	1.12	0.59	1.90	1.56	1.04	1.50
240	27	Toluene	1.17	0.80	1.46	1.04	0.71	1.48	1.07	0.60	1.80	1.39	0.93	1.49
360	27	Toluene	0.98	0.68	1.45	0.89	0.58	1.54	1.00	0.60	1.66	1.40	0.96	1.46
480	27	Toluene	0.80	0.58	1.38	0.80	0.56	1.43	0.86	0.53	1.62	1.40	0.96	1.46
30	-20	THF	2.68	1.32	2.00	2.27	1.14	2.00	1.85	0.85	2.18	2.10	1.25	1.68
60	-20	THF	2.07	1.14	1.80	1.75	0.90	1.94	1.27	0.71	1.78	2.01	1.2	1.68
120	-20	THF	1.17	0.76	1.54	1.12	0.75	1.50	0.99	0.63	1.57	1.58	1.04	1.52
180	-20	THF	0.92	0.63	1.46	0.95	0.68	1.40	0.85	0.55	1.54	1.41	0.98	1.44
240	-20	THF	0.84	0.57	1.48	0.81	0.60	1.36	0.71	0.50	1.40	1.22	0.85	1.43

TABLE 2. Ultrasonic Solution Degradation of Various Poly(Alkyl Methacrylates) (PRMA) where R = Isopropyl, Isobutyl, and Isodecyl

			Isopropyl			Isobutyl			Isodecyl		
Irradiation time, min	Temperature, °C	Solvent	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$
Non irradiated	-	-	9.95	2.35	4.23	3.95	1.32	3.00	2.54	1.12	2.27
60	27	Toluene	3.28	1.19	2.76	2.39	1.28	1.87	1.63	0.87	1.87
120	27	Toluene	2.05	1.01	2.00	1.97	1.13	1.74	1.44	0.79	1.82
180	27	Toluene	1.49	0.89	1.67	1.58	1.03	1.53	1.28	0.75	1.70
240	27	Toluene	1.19	0.76	1.56	1.41	0.96	1.47	1.09	0.72	1.51
360	27	Toluene	1.15	0.79	1.45	1.23	0.94	1.31	1.07	0.71	1.50
480	27	Toluene	1.03	0.75	1.37	1.08	0.84	1.29	1.06	0.70	1.50
30	-20	THF	3.60	1.20	3.00	2.42	1.22	2.00	1.56	0.92	1.70
60	-20	THF	2.22	0.97	2.30	1.93	1.12	1.72	1.05	0.66	1.59
120	-20	THF	1.67	0.91	1.84	1.37	0.90	1.52	0.90	0.60	1.50
180	-20	THF	1.40	0.80	1.75	1.29	0.86	1.50	0.90	0.64	1.41
240	-20	THF	1.05	0.70	1.50	1.24	0.86	1.45	0.90	0.62	1.42

TABLE 3. Ultrasonic Solution Degradation of Various Poly(Alkyl Methacrylates) (PRMA) where R = Hexyl, Lauryl, Hexadecyl, and Octadecyl

			Hexyl			Lauryl			Hexadecyl			Octadecyl		
Irradiation time, min	Temperature, °C	Solvent	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$
Non-irradiated	-	-	3.85	1.30	3.00	3.20	1.83	1.75	4.60	1.68	2.74	5.50	3.30	1.67
60	27	Toluene	2.27	1.17	1.94	2.55	1.59	1.60	2.70	1.56	1.73	3.23	1.98	1.63
120	27	Toluene	2.05	1.14	1.80	2.16	1.51	1.43	2.31	1.41	1.64	2.65	1.65	1.60
180	27	Toluene	1.83	1.09	1.68	2.10	1.50	1.40	2.19	1.40	1.56	2.42	1.71	1.41
240	27	Toluene	1.62	0.96	1.69	2.00	1.50	1.33	1.98	1.32	1.50	2.20	1.60	1.38
360	27	Toluene	1.70	1.05	1.62	1.90	1.40	1.35	1.70	1.21	1.40	2.00	1.51	1.32
480	27	Toluene	1.64	1.04	1.58	1.77	1.36	1.31	1.75	1.24	1.41	1.90	1.46	1.30
30	-20	THF	2.50	1.30	1.92	2.46	1.70	1.45	2.53	1.48	1.71	2.75	1.97	1.40
60	-20	THF	1.88	1.06	1.77	1.79	1.33	1.35	2.15	1.37	1.57	2.19	1.69	1.30
120	-20	THF	1.79	1.09	1.64	1.52	1.15	1.32	1.74	1.20	1.45	1.77	1.36	1.30
180	-20	THF	1.54	0.97	1.60	1.43	1.10	1.30	1.53	1.11	1.38	1.58	1.20	1.32
240	-20	THF	1.26	0.81	1.56	1.35	1.05	1.30	1.40	1.06	1.32	1.42	1.04	1.37

Poly(methyl methacrylate) ($\overline{DP}_w$ = 6 700) and poly(isopropyl methacrylate) ($\overline{DP}_w$ = 7 770) reached a limiting $\overline{DP}_w$ of 820 ± 20 after 480 min of irradiation in toluene at 27°C, but only after 240 min in THF at -20°C (Fig. 2). Poly(ethyl methacrylate) ($\overline{DP}_w$ = 2 940) and polyisobutyl methacrylate) ($\overline{DP}_w$ = 2 780) reached a limiting $\overline{DP}_w$ of 730 ± 30 after 480 min of irradiation in toluene and after 240 min of irradiation at -20°C in THF. Other poly(alkyl methacrylates) ($\overline{DP}_w$ from 1 125 to 2 265) also reached limiting chain lengths after 480 min of irradiation at 27°C and 240 min at -20°C. These limiting $\overline{DP}_w$ values range from 400 to 750 depending on the initial $\overline{DP}_w$ of the polymer. In general, the limiting chain lengths decrease with increasing bulk size of the alkyl substituent.

Poly(alkyl methacrylates) also degrade faster at -20°C compared to 27°C (Fig. 2). The limiting chain lengths at 27°C for 480 min and at -20°C for 240 min are not necessarily the same. The primary reasons for greater degradations at lower temperatures are considered to be 1) increased chain stiffness or lower chain mobility and 2) enhanced cavitation [25, 39, 40]. Toluene and THF are good solvents for poly(alkyl methacrylates), hence solvent effects have not been considered important. This assumption may be only partly true, and solution viscosity may play some role in determining the degradation. Although the enhancement in cavitation at -20°C accelerates degradation of all poly(alkyl methacrylates) equally, the effect of decreased mobility of chains on degradation is not the same for all of them, the ones with long-chain substituents being affected most. This may explain why the limiting chain lengths for substituents of different chain lengths are not the same at 27 and -20°C. It is also possible that these poly(alkyl methacrylates) have not attained their limiting chain lengths even at -20°C.

Rate Constants

The relation [41, 42] between $\overline{DP}_n$ and time t in a random degradation process is given by

$$-\ln(1 - 1/\overline{DP}_{n,t}) = kt - \ln(1 - 1/\overline{DP}_{n,0}), \qquad (3)$$

where $\overline{DP}_{n,t}$ and $\overline{DP}_{n,0}$ are the number-average degrees of polymerization at t = t and t = 0, respectively, and k is the rate constant.

According to Sato and Nelepa [43], Eq. (3) can be transformed to

$$\frac{1}{\overline{M}_{n,t}} = \frac{1}{\overline{M}_{n,0}} + k't, \tag{4}$$

where $k' = k/M_0$, and M_0 is the molecular weight of the monomer unit. Plots of $1/\overline{M}_n$ versus t will give k', and consequently k (Table 4). For identical $\overline{M}_n$, k values at 27°C in toluene were in the range $(4.2 \pm 2.0) \times 10^{-6}$ min^{-1}, and in THF at -20°C $(5.4 \pm 2.0) \times 10^{-6}$ min^{-1}). For poly(isopropyl methacrylate) and poly(octadecyl methacrylate) with initial $\overline{M}_n$, k values were higher $((9.0 \pm 1.0) \times 10^{-6}$ min^{-1} at 27°C and $(1.0 \pm 1.5) \times 10^{-6}$ min^{-1} at -20°C). This suggests that the alkyl substituent does not play an important role in determining the rate of degradation. The rate constant, however, is dependent on initial $\overline{M}_n$.

The Average Number of Chain Scissions

In random degradations, when the number of scissions are low and no volatile products result, the average number of scissions per chain, S, can be computed from

$$S = (\overline{M}_{n,0}/\overline{M}_{n,t}) - 1. \tag{5}$$

However, as in ultrasonic solution degradations of poly(alkyl methacrylates) with broad molecular weight distributions (MWD), it is the high-molecular weight tail in the MWD which is more prone to scissions. Hence, use of overall molecular weights for calculating S is questionable and a measure of the entire MWD is required. In order to accomplish this, an alternate approach of analysis was developed [39, 40] in which the normalized GPC chromatograms of undegraded and degraded polymers were superimposed. One can now readily visualize the changes resulting from the decomposition of the high-molecular-weight species. By this approach information regarding the weight fraction α involved in a degradation process in a given period, its initial $\overline{M}_w$ and $\overline{M}_n$ as well as the $\overline{M}_w$ and $\overline{M}_n$ values of its resulting counterparts, was obtained (Fig. 3). These data for the solution degradation of various poly(alkyl methacrylates) are presented in Tables 5 to 10. Using $\overline{M}_{n,0}$ and $\overline{M}_{n,t}$ values of that fraction α of the polymer which is involved in degradation, average numbers of scissions S were computed and found to decrease with time. In contrast, when one computes S from the overall values of $\overline{M}_{n,0}$ and $\overline{M}_{n,t}$, S in-

TABLE 4. Rate Constant k for the Degradation of Various Poly-(Alkyl Methacrylates)

Substituent alkyl	Solvent	Temperature, °C	k × 10^6, min^{-1}
Methyl	Toluene	27	3.1
Ethyl	Toluene	27	4.3
Isopropyl	Toluene	27	8.4
n-Butyl	Toluene	27	5.7
Isobutyl	Toluene	27	1.6
Hexyl	Toluene	27	2.4
Cyclohexyl	Toluene	27	5.0
Isodecyl	Toluene	27	4.8
Lauryl	Toluene	27	3.4
Hexadecyl	Toluene	27	3.1
Octadecyl	Toluene	27	9.8
Methyl	THF	-20	4.3
Ethyl	THF	-20	5.1
Isopropyl	THF	-20	16.8
n-Butyl	THF	-20	5.7
Isobutyl	THF	-20	3.5
Hexyl	THF	-20	3.7
Cyclohexyl	THF	-20	5.1
Isodecyl	THF	-20	6.0
Lauryl	THF	-20	6.8
Hexadecyl	THF	-20	6.5
Octadecyl	THF	-20	19.5

creases with time. Furthermore, the values of S (1 to 15) computed for component degradation are far greater than those (< 2.0) based on overall $\overline{M}_n$ values (Tables 1 to 3). Component analyses reveal that S values for poly(methyl methacrylate) (5.5-6.5), poly(ethyl methacrylate (3.5-5.0) poly(cyclohexyl methacrylate) 2-3), poly(hexyl meth-

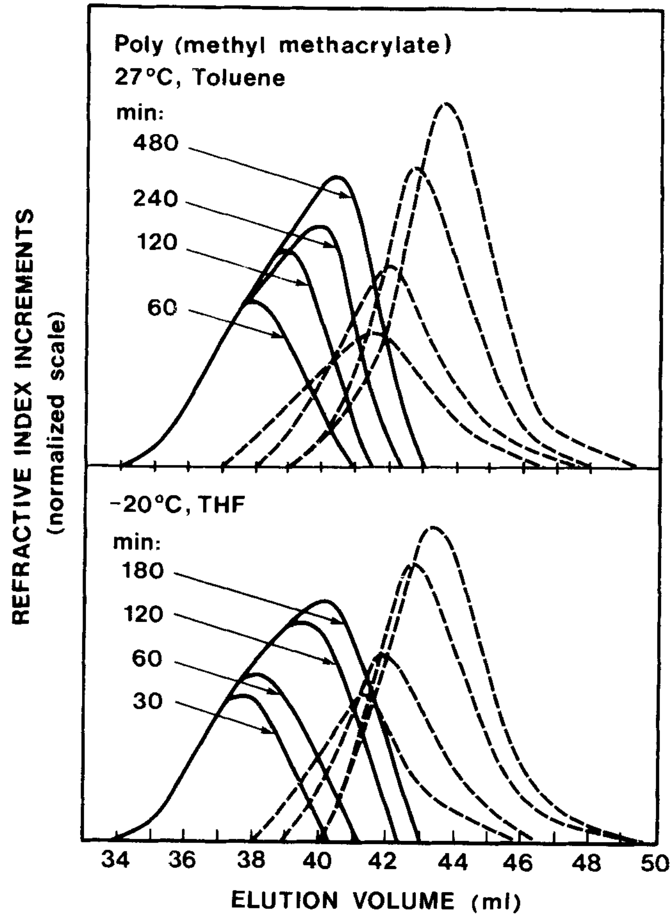

FIG. 3. GPC component analyses for ultrasonic solution degradations of poly(methyl methacrylate).

acrylate) (2-3), poly(lauryl methacrylate) (1.5-2), poly(hexadecyl methacrylate) (2.5-3.0), and poly(octadecyl methacrylate) (3-4) remain constant during the whole period of degradation. This suggests that there are no specific weak links in the backbone chains of these polymers. In the other poly(alkyl methacrylates), the S values are high initially and then these level off to steady-state values. Decrease in S values for poly(isopropyl methacrylate) (15 to 7.0), poly(n-butyl methacrylate) (11 to 3), poly(isobutyl methacrylate) (8 to 4), and poly(isodecyl methacrylate) (6 to 4) may indicate the presence of weak links in the high-molecular-weight tail of these polymers which break more readily than the normal backbone bonds.

TABLE 5. Ultrasonic (70 W, 20 kHz) Solution (2%) Degradation of Poly(Methyl Methacrylate): $\overline{M}_w$ = 6.7×10^5, $\overline{M}_n = 1.6 \times 10^5$

				Before degradation			After degradation				
Irradiation time, min	Temperature, °*C*	*Solvent*	Weight fraction (*α*)	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	*S*	$S/t \times 10^3$, min^{-1}
60	27	Toluene	0.34	152.0	98.5	1.54	29.2	15.0	1.95	5.6	92.8
120	27	Toluene	0.46	123.0	74.8	1.64	19.2	11.1	1.72	5.7	47.8
180	27	Toluene	0.485	118.0	67.3	1.75	12.5	8.9	1.41	6.5	36.4
240	27	Toluene	0.605	103.0	54.5	1.89	11.8	8.1	1.46	5.7	23.9
360	27	Toluene	0.72	89.0	41.7	2.13	10.7	6.9	1.55	5.0	14.0
480	27	Toluene	0.77	86.4	40.8	2.12	9.0	5.9	1.50	5.9	12.3
30	-20	THF	0.28	170.0	118.0	1.44	25.3	15.6	1.62	6.6	218.8
60	-20	THF	0.37	141.0	84.3	1.67	16.1	9.1	1.77	8.3	137.7
120	-20	THF	0.59	104.0	53.5	1.94	10.6	7.2	1.48	6.4	53.6
180	-20	THF	0.70	90.8	42.3	2.15	11.0	6.1	1.80	5.9	33.0
240	-20	THF	0.70	91.5	41.6	2.20	7.7	5.25	1.47	6.9	28.8

TABLE 6. Ultrasonic (70 W, 20 kHz) Solution (2%) Degradation of Poly(Ethyl Methacrylate): $\overline{M}_w$ = 3.35×10^5, $\overline{M}_n$ = 1.20×10^5

				Before degradation			After degradation				
Irradiation time, min	Temperature, °C	Solvent	Weight fraction (α)	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	S	S/t × 10^3, min^{-1}
60	27	Toluene	0.165	103.0	82.1	1.25	14.30	11.10	1.30	6.4	106.6
120	27	Toluene	0.255	84.0	61.7	1.36	12.60	9.75	1.29	5.3	44.4
180	27	Toluene	0.31	76.2	52.8	1.44	12.10	9.27	1.30	4.7	26.1
240	27	Toluene	0.455	60.3	37.1	1.62	9.50	7.10	1.33	4.2	17.6
360	27	Toluene	0.52	55.2	32.3	1.71	7.87	5.83	1.35	4.5	12.6
480	27	Toluene	0.61	49.4	26.7	1.85	7.52	5.69	1.32	3.7	7.7
30	-20	THF	0.13	114.0	76.0	1.50	22.3	16.0	1.40	3.75	125.0
60	-20	THF	0.22	87.7	62.5	1.40	14.7	10.8	1.36	4.8	79.8
120	-20	THF	0.44	61.2	37.7	1.62	10.0	7.55	1.32	4.0	20.8
180	-20	THF	0.53	54.4	31.2	1.74	9.0	6.82	1.32	3.6	19.8
240	-20	THF	0.61	49.4	26.7	1.85	7.6	5.92	1.28	3.5	14.6

TABLE 7. Ultrasonic (70 W, 20 kHz) Solution (2%) Degradation of Poly(p-Isopropyl Methacrylate): $\overline{M}_w = 9.95 \times 10^5$, $\overline{M}_n = 2.35 \times 10^5$

				Before degradation			After degradation				
Irradiation time, min	Temperature, °C	Solvent	Weight fraction (α)	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_n/\overline{M}_n$	S	$S/t \times 10^3$, min^{-1}
60	27	Toluene	0.32	245.0	148.0	1.65	23.8	9.65	2.47	14.4	239.0
120	27	Toluene	0.485	185.0	88.6	2.09	16.1	7.68	2.10	10.5	87.8
180	27	Toluene	0.61	157.0	72.8	2.16	12.8	7.08	1.81	9.3	51.6
240	27	Toluene	0.71	139.6	55.0	2.53	10.7	7.00	1.53	6.9	28.6
360	27	Toluene	0.74	134.0	54.7	2.45	10.8	6.80	1.59	7.0	19.6
480	27	Toluene	0.83	130.0	52.0	2.50	10.5	6.50	1.60	7.0	14.6
30	-20	THF	0.42	205.0	120.0	1.71	18.0	7.27	2.47	15.5	258.4
60	-20	THF	0.535	175.0	89.8	1.95	13.7	7.43	1.84	11.1	100.7
120	-20	THF	0.65	149.0	62.6	2.38	11.7	7.24	1.62	7.4	40.2
180	-20	THF	0.795	127.0	44.0	2.89	9.7	6.30	1.53	6.0	21.4
240	-20	THF	0.87	118.0	38.2	3.10	9.0	5.87	1.53	5.5	15.3

TABLE 8. Ultrasonic 70 W, 20 kHz) Solution (2%) Degradation of Poly(Isobutyl Methacrylate): $\overline{M}_w$ = 3.95×10^5, $\overline{M}_n = 1.32 \times 10^5$

				Before degradation			After degradation				
Irradiation time, min	Tempera-ature, °C	Solvent	Weight fraction (α)	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w / M_n$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w / M_n$	S	$S/t \times 10^3$, min^{-1}
60	27	Toluene	0.15	120.0	93.0	1.29	16.8	12.3	1.37	6.6	109.3
120	27	Toluene	0.23	102.0	76.2	1.34	13.3	11.5	1.16	5.6	46.9
180	27	Toluene	0.34	82.0	57.0	1.44	12.9	10.3	1.25	4.5	25.2
240	27	Toluene	0.40	75.0	50.2	1.50	11.7	9.0	1.30	4.6	19.1
360	27	Toluene	0.49	66.7	40.5	1.65	10.9	8.3	1.31	3.9	10.8
480	27	Toluene	0.54	56.6	37.9	1.49	9.8	7.9	1.24	3.8	7.9
30	-20	THF	0.14	123.0	95.0	1.29	14.3	10.5	1.42	8.0	268.2
60	-20	THF	0.29	86.6	56.9	1.52	16.6	11.0	1.50	4.2	69.5
120	-20	THF	0.44	70.2	43.7	1.61	11.2	7.7	1.45	4.7	39.0
180	-20	THF	0.51	64.0	37.5	1.71	11.7	8.3	1.41	3.5	19.5
240	-20	THF	0.55	60.7	33.8	1.80	11.3	8.3	1.35	3.1	12.8

TABLE 9. Ultrasonic (70 W, 20 kHz) Solution (2%) Degradation of Poly(Hexyl Methacrylate): $\overline{M}_w = 3.85 \times 10^5$, $\overline{M}_n = 1.30 \times 10^5$

Irradiation time, min	Temperature, °C	Solvent	Weight fraction (α)	Before degradation			After degradation			S	S/t × 10^3, min^{-1}
				$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$		
60	27	Toluene	0.22	92.9	75.0	1.24	20.8	16.5	1.26	3.5	59.1
120	27	Toluene	0.31	79.7	61.1	1.30	21.4	17.1	1.25	2.6	21.4
180	27	Toluene	0.38	72.0	52.3	1.38	18.5	15.2	1.22	2.4	13.5
240	27	Toluene	0.475	63.3	42.8	1.48	16.8	13.9	1.21	2.1	8.7
360	27	Toluene	0.50	61.4	40.9	1.50	17.2	14.5	1.19	1.8	5.1
480	27	Toluene	0.50	60.0	40.0	1.50	17.0	14.0	1.20	1.9	3.9
30	-20	THF	0.17	101.0	82.4	1.23	20.4	15.9	1.28	4.2	39.4
60	-20	THF	0.35	74.3	54.1	1.37	18.3	14.0	1.30	2.9	47.7
120	-20	THF	0.41	69.6	47.9	1.45	17.8	14.6	1.22	2.2	19.0
180	-20	THF	0.49	62.5	42.5	1.47	15.9	13.0	1.22	2.3	12.6
240	-20	THF	0.625	54.0	33.6	1.61	13.0	10.3	1.26	2.3	9.4

TABLE 10. Ultrasonic (70 W, 20 kHz) Solution (2%) Degradation of Poly(Hexadecyl Methacrylate): $\overline{M}_w = 4.68 \times 10^5$, $\overline{M}_n = 1.68 \times 10^5$

Irradiation time, min	Temperature, °C	Solvent	Weight fraction (α)	Before degradation			After degradation			S	S/t × 10^3, min^{-1}
				$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$		
60	27	Toluene	0.20	127.0	98.4	1.29	31.2	26.4	1.18	2.7	45.5
120	27	Toluene	0.32	103.0	78.1	1.32	23.5	20.1	1.17	2.9	24.0
180	27	Toluene	0.37	95.4	70.0	1.36	23.2	20.0	1.16	2.5	13.9
240	27	Toluene	0.43	87.3	61.2	1.43	21.1	18.3	1.15	2.3	9.8
360	27	Toluene	0.505	79.5	53.4	1.49	18.4	15.9	1.16	2.4	6.5
480	27	Toluene	0.51	79.0	53.0	1.50	18.0	15.5	1.16	2.4	5.0
30	-20	THF	0.26	115.0	91.0	1.26	24.7	21.0	1.18	3.3	111.1
60	-20	THF	0.37	94.6	69.1	1.37	21.6	18.4	1.17	2.8	45.9
120	-20	THF	0.47	83.8	58.7	1.43	17.7	15.2	1.16	2.9	23.8
180	-20	THF	0.53	77.7	52.3	1.49	15.3	13.1	1.17	3.0	16.6
240	-20	THF	0.585	73.0	47.4	1.54	14.1	12.1	1.17	2.9	12.2

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