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Polymerization of Methyl Methacrylate Initiated by Ultrasound

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ABSTRACT: Irradiation of methyl methacrylate with high-intensity ultrasound produces radicals which can initiate polymerization, although a concurrent degradation reaction occurs. The effect of a number of parameters on the process has been studied and a quantitative model proposed which allows their correlation. Suitable manipulation of the experimental conditions, mainly the temperature and ultrasonic intensity, allows the preparation of polymers with controlled molecular weight, polydispersity, and tacticity. The method offers the possibility of a useful initiation technique although low conversions have been achieved and these will have to be improved before it has commercial application.

Introduction

Despite considerable research into new polymerization techniques,[1] the most common method for the polymerization of vinyl monomers remains that using radical initiation. The initiating radicals are usually produced by thermal or photochemical decomposition either of the pure monomer or of an added initiator such as an azo compound or an organic peroxide.[2] Redox systems may also be used for aqueous reactions. A major focus of current work in this area is the control over the structure and properties of the resulting polymers.

Sonication—the application of high-intensity ultrasound—produces high concentrations of $H^\bullet$ and $OH^\bullet$ radicals in water,[3,4] and the possibility of using ultrasound to initiate polymerization was suggested some years ago when Henglein produced poly(acrylonitrile) in aqueous solution using this method.[5] Most of the physical and chemical effects caused by ultrasound are due to the process of cavitation, or the formation and collapse of microscopic bubbles as the sound wave passes through the liquid. Although the origin of chemical effects has been attributed to electrical discharge processes,[6] the most widely accepted treatment, first suggested by Noltingk and Neppiras,[7] assumes the generation of very large temperatures and pressures during an adiabatic bubble collapse. On a simplified treatment,[8] the maximum temperature generated, $T_{\max}$, is given by

$$T_{\max} = T_{\text{bulk}} P_{\text{m}}(\gamma - 1)/P_{\text{v}} \qquad (1)$$

where P_{m} is the pressure generated on collapse, γ is the ratio of the specific heat capacities of the solvent vapor, and P_{v} is the vapor pressure of the solvent at temperature T_{bulk}. This equation predicts temperatures in the region of several thousand kelvin, and there is also considerable experimental evidence to support this.[9] Clearly, this is sufficiently high to dissociate solvent vapor entering the bubble, leading to bond breakage and radical formation.

Over the past few years, ultrasound has become an extremely useful tool in synthetic organic and organometallic chemistry.[10,11] Ultrasonics have also been applied in a number of areas of polymer science. For example, high-frequency, low-intensity ultrasound has been used for following the course of polymerization reactions[12] and for monitoring conformational changes in polymers.[13] The intensities used in these applications are too low to cause chemical changes. The major use of high-intensity ultrasound has been in the degradation of polymers to lower molecular weights and its use to control their molecular weight distribution and to produce block copolymers.[14]

Although the molecular weights of polymers produced by radical initiation can be controlled, for instance, by the addition of chain-transfer agents, one of their major problems, caused by the high and indiscriminate reactivity of the growing radical, is the stereochemical control of the resulting polymer structure, namely, the tacticity. Clearly, if the ultrasonic method could be applied to vinyl monomers, it would provide an alternative method of initiation with the possibility of a great deal of control over the process. However, cavitation is much less efficient in organic liquids, and it was suggested that polymerization would not take place in organic systems unless the reaction was "seeded" with polymer.[15] Despite this, Kruus and co-workers[16-18] showed that this was not so and polymerized styrene (St) and methyl methacrylate (MMA), monomers also studied by the present authors.[19,20]

We are studying ultrasonic initiation from the point of view of producing polymers with predetermined structures and properties such as molecular weight, polydispersity, and tacticity. Although high molecular weight polymers have been produced, the main limitation of previous work has been the very low conversions, up to a few percent, achieved, and this paper describes our recent work aimed at further characterizing the process, particularly the initiation, and increasing the conversions obtained. We also address the microstructures of the polymers produced and correlate our results with a range of system parameters.

Experimental Section

Materials and Reagents. Methyl methacrylate monomer was a commercially available sample (Aldrich, U.K.) from which the stabilizer (hydroquinone) was removed immediately prior to polymerization by successive washings with a dilute sodium hydroxide solution, water, and a saturated sodium chloride solution, drying with anhydrous sodium sulfate, and molecular sieves, following which it was vacuum distilled and stored under oxygen-free nitrogen. Gas liquid chromatographic analysis showed the resulting purity to be in excess of 99.5% PMMA standard polymers were obtained from Polymer Laboratories Ltd. (U.K.), and GPC was performed with chromatographic-grade THF from BDH Ltd. Azobis(isobutyronitrile) (AIBN; BDH Ltd.) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) were used as received as were reagent-grade methyl butyrate, ethyl acetate, and *n*-propyl acetate (Aldrich).

Polymerizations. Two commercially available ultrasound generators were used, both employing piezoelectric oscillators operating at a nominal frequency of 22 ± 1 kHz. Most of the results described were obtained with a Sonic Systems (U.S.A.) VC50 apparatus, while the intensity study utilized a MSE "Soniprep" generator (Fisons, U.K.). The ultrasonic intensities

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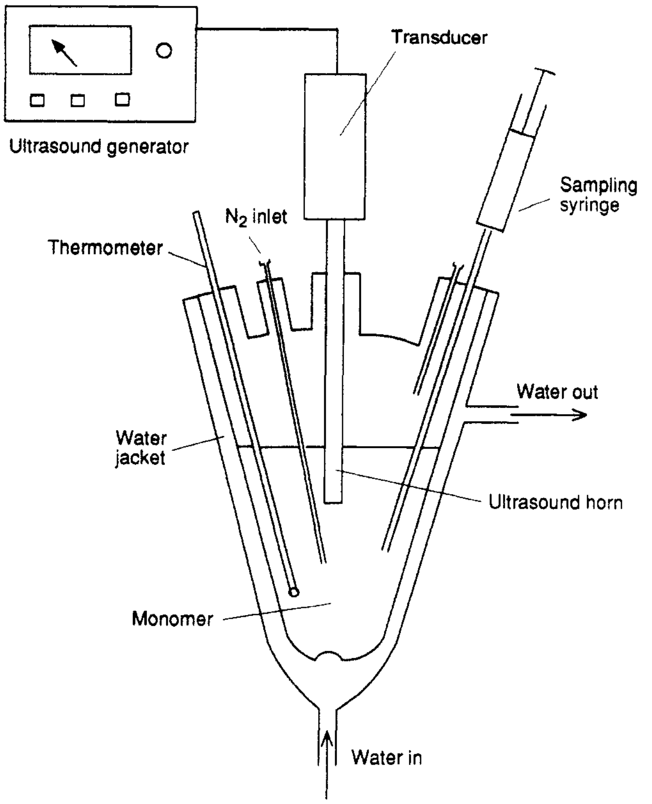

Figure 1. Schematic diagram of the sonication apparatus.

were measured calorimetrically and are quoted in the following section. The polymerization vessel, shown schematically in Figure 1, was designed and made "in-house" and consisted of a 100-cm^3 four-necked pear-shaped flask, modified by the addition of a jacket through which thermostated water, or a water–glycol mixture for subambient work, was circulated to maintain a temperature constant to ±0.1 °C. A secondary effect of the ultrasound is to cause rapid streaming and hence efficient mixing of the monomer so that no extra stirring was required.

Approximately 50 cm^3 of freshly purified MMA was introduced into the vessel and deoxygenated by bubbling with oxygen-free nitrogen gas for 30 min. The ultrasound was then switched on and a nitrogen atmosphere maintained throughout the reaction. Periodically 1.00 cm^3 of monomer was removed using a gas-tight syringe and the polymer precipitated into an excess of ice cold methanol. The polymer was filtered, washed, dried, and weighed to ascertain the conversion gravimetrically in the usual way. Molecular weights were determined using a Bruker LC21/41 gel permeation chromatograph using tetrahydrofuran as the eluent at a flow rate of 1.0 cm^3 min^{-1}. Eight PMMA standards covering a range from 1950 to 1.4×10^6 were used to calibrate a Polymer Laboratories 60-cm "Linear PL-Gel" column. NMR spectra (^{1}H and ^{13}C) were recorded in a $CDCl_3$ solution on a JEOL GX270 spectrometer.

To prevent photochemical initiation, the vessel was wrapped in aluminum foil. Confirmation that ultrasound was responsible for initiation was achieved by assembling the apparatus in an identical fashion for a polymerization except that the ultrasound was not switched on. Over an 18-h period, no detectable polymerization occurred under any of the conditions employed.

Radical Trapping. To more closely investigate some of the initiation reactions, sonications were performed in the presence of a stable radical species, DPPH. Solutions of DPPH were prepared to give an initial absorbance of approximately 0.9 in methyl butyrate and mixtures with other acetate solvents, filtered to remove undissolved solids, and placed in the sonication cell where they were degassed and sonicated under the same conditions as described above. Periodically, 1.00-cm^3 aliquots were removed and their absorbances at 520 nm measured using a Pye Unicam SP6-250 spectrophotometer. This wavelength corresponds to a peak maximum in the absorption spectrum of DPPH at which an extinction coefficient of 1.012 m^2 mol^{-1} was measured.

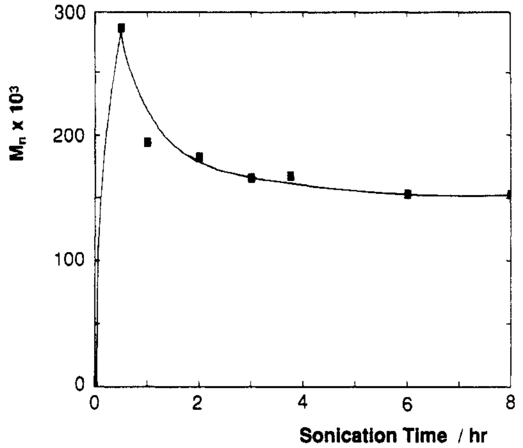

Figure 2. Molecular weight variation during ultrasonic polymerization of MMA at 25 °C.

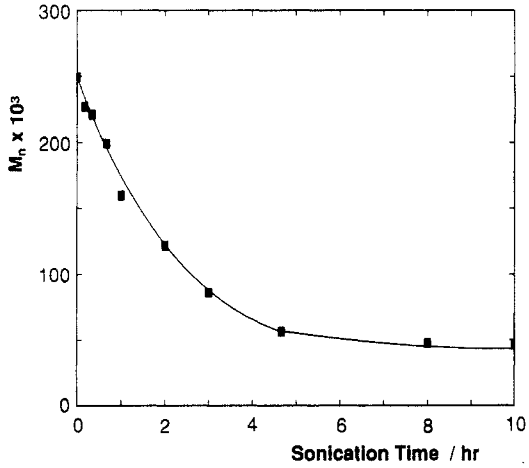

Figure 3. Ultrasonic degradation of a 5 wt % PMMA solution in methyl butyrate at 25 °C.

Results and Discussion

Our initial interest was to investigate the possibility of using ultrasound as a method of controllable, ambient-temperature initiation in vinyl monomers. To illustrate the general features of the process, Figure 2 shows a plot of the number-average molecular weight during the sonication of pure MMA at 25 °C at an ultrasonic intensity of 15.4 ± 0.5 W cm^{-2}. This indicates that a high molecular weight polymer is formed at early stages of the reaction but that this falls at longer times. This is not the same plot as found with conventionally initiated radical polymerization[1] where M_n increases throughout the process. The shape of the later part of the curve, with M_n falling exponentially to a limiting value, is characteristic of the ultrasonic degradation process[14,22,23] as demonstrated in Figure 3 for a 5 wt % solution of PMMA in methyl butyrate, sonicated under the same conditions used for the polymerization. The behavior is similar in the two systems except that the limiting molecular weight is lower in the latter solution which would be expected since the methyl butyrate solution was more dilute than the final solution during polymerization, a factor known to lead to higher rates of degradation,[14] and also the absence of monomer which can add to the ends of the broken polymer chains.

The rate of polymer production and final yield for the reaction in bulk MMA at 25 °C is shown in Figure 4. A conversion of ~12% was achieved after 6 h, similar to that achieved by Kruus et al. It was noticed that cavitation in the solution essentially stopped, shown by a marked changed in the sound of the sonication, at this time, and no further conversion to polymer occurred thereafter. We

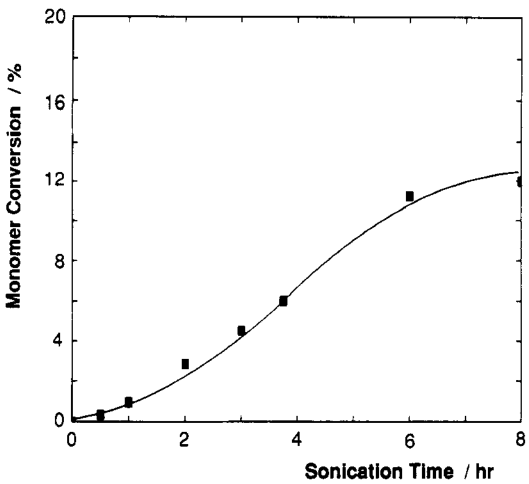

Figure 4. Ultrasonically initiated polymerization of MMA at 25 °C.

Table I
Physical Properties[a] of Solvents at 25 °C

property	methyl methacrylate	methyl butyrate
mol wt	100.13	102.12
boiling point (°C)	100.5	102.3
density (g cm^{-3})	0.9440	0.8984
vapor pressure (Torr)	35.58	31.86
viscosity (cP)	0.56	0.541

[a] References 24 and 25.

ascribe this to be increased viscosity of the solution restricting movement of the solvent molecules and suppressing cavitation, hence preventing formation of radicals. It also demonstrates that cavitation is necessary for the production of polymer.

There are a large number of factors that influence polymerization in an ultrasound field. The major ones are those such as the temperature and nature of the solvent which influence the cavitation in the liquid and also the intensity of the ultrasound which determines the number of cavitation events. Our aim is to completely characterize and develop a quantitative model of the polymerization so that we commenced with an in-depth study of the ultrasonic initiation.

Initiation Process. To assist with determining the mechanism and in modeling the initiation, we needed a solvent that would behave to an ultrasound field in an identical manner to MMA except for the polymerization. The cavitation behavior of a solvent is determined chiefly by its physical properties[8,21] such as viscosity, surface tension, and, often considered to be the most important, vapor pressure. The liquid most closely matching MMA is methyl butyrate as shown in Table I although the lack of a vinylic double bond prevents polymerization, confirmed by performing blank experiments. Thus, the application of ultrasound to these "cavitationally similar" liquids would be expected to produce similar behavior of dissolved polymers and similar numbers of radicals on sonication.

The rates of initation were estimated by trapping the radicals formed as a result of cavitation using an excess concentration of DPPH. Methyl butyrate (MeOBu) was used as the model solvent to avoid complications from reactions with MMA and growing or degrading polymer chains. Obviously, there will be a degree of radical recombination and other side reactions, but since the radical must escape the cavitation bubble and solvent "primary cage" whether to initiate polymerization or to be trapped by DPPH, we feel that the rate trapping will closely mimic the rate of initiation.

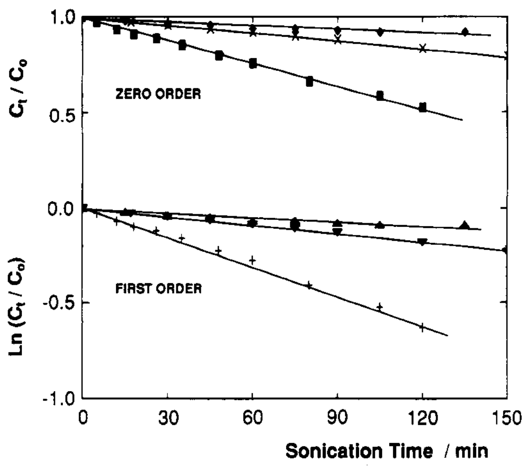

Figure 5. First- and zero-order rate plots for DPPH consumption in methyl butyrate: (+, ■) −10, (▼, ×) 25, (▲, ♦) 60 °C.

Table II
Rate Constants for DPPH Trapping at 25 °C

solvent	temp (°C)	rate constant (×10^5 s^{-1})
MeOBu	-10	6.35
MeOBu	25	2.21
MeOBu	60	1.03
MeOBu + 0.1% AIBN	25	9.13
50:50 MeOBu-EtOAc	25	0.63
50:50 MeOBu-*n*-PrOAc	25	4.03

Plots for the consumption of DPPH at −10, +25, and +60 °C are shown in Figure 5 in the form of both first- and zero-order kinetic plots. In fact, the zero-order plots give marginally better fits to the data as we have found with other systems. However, the first-order fits are also good, and, to facilitate comparison with literature results in the absence of ultrasound, they will be employed here. The rate constants calculated from the slopes of the graphs are shown in Table II together with those measured in other systems as described below.

The rate constant for radical formation in methyl butyrate at 25 °C of 2.3×10^{-5} s^{-1} can be compared with that in MMA in the absence of ultrasound. Few studies of the thermal polymerization of MMA have been made, but the rate of initiation has been estimated[26] to be 7×10^{-16} s^{-1} at 100 °C which is obviously negligible in comparison to the ultrasonic process. It may also be compared with the corresponding value for the thermal decomposition of AIBN in MMA at 25 °C, obtained by extrapolating data from higher temperatures,[25] of $\sim 2 \times 10^{-8}$ s^{-1}. Indeed, the literature value for AIBN in MMA at 70 °C is 3.1×10^{-5} s^{-1} so that, simply by using ultrasound, we can achieve at 25 °C similar rates of initiation as are usually found in thermal polymerizations. To further compare with more conventional experiments, we also sonicated a solution of 0.1 wt % AIBN in MeOBu, a concentration typical of that usually employed for polymerizations, the rate constant also being shown in Table I. This is some 3 orders of magnitude higher than that expected for AIBN at this temperature so that the sonication process is clearly able to accelerate the decomposition of AIBN in solution as well as producing radicals directly.

An Arrhenius plot of the results in methyl butyrate is shown in Figure 6, and this leads to an apparent activation energy of −18.9 kJ mol^{-1}. Kruus and co-workers[27] report this value to be −15 kJ mol^{-1} for styrene but, by considering their polymerization data, report[17] the initiation to be insensitive to temperature in MMA. These values may be compared with that of 159.8 kJ mol^{-1} for the decom-

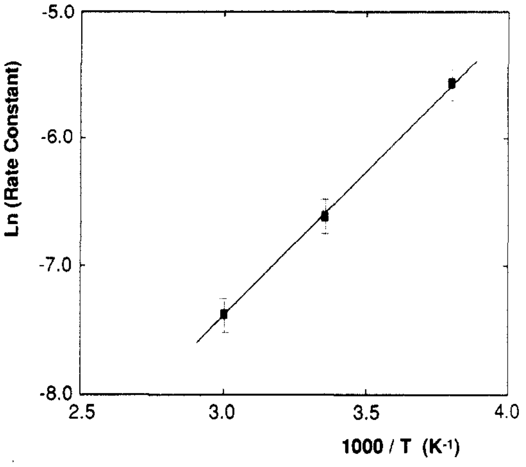

Figure 6. Arrhenius plot for DPPH consumption in methyl butyrate.

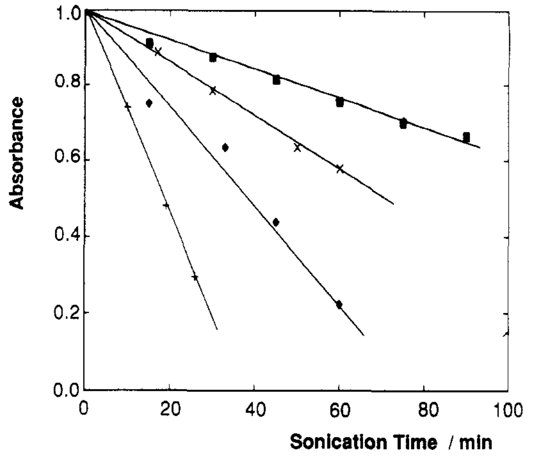

Figure 7. Effect of ultrasonic intensity on DPPH consumption in methyl butyrate at 25 °C. Intensities (W cm^{-2}): (■) 14.6, (×) 29.2, (♦) 35.0, (+) 58.4.

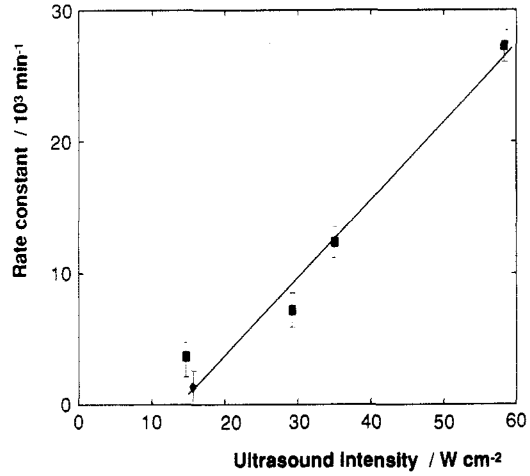

Figure 8. Effect of ultrasonic intensity on the rate constant for DPPH consumption in methyl butyrate at 25 °C.

position of AIBN in the absence of ultrasound[25] and 92 kJ mol^{-1} for solely thermal initiation in MMA at high temperatures.[26] The acceleration of reactions at lower temperatures indicates that the normal Arrhenius behavior of chemical reactions is not obeyed, but this is not unusual in sonochemical reactions[28] and is a consequence of the solvent properties being more favorable to cavitation at lower temperatures as explained below. Some workers[29,30] have correlated the temperature dependence of sonochemical reactions in terms of the maximum temperature generated during the cavitational collapse, given by eq 1, rather than using the bulk temperature in the Arrhenius equation. However, this treatment did not give consistent results in this work.

To study the effect of the physical properties of the solvent, and hence of the monomer, on the initiation process, we also measured rate constants using mixtures of methyl butyrate with ethyl or *n*-propyl acetate at 25 °C. These solvents were chosen so as to give vapor pressures considerably above and below that of methyl butyrate and MMA, the values being 82.73 Torr for ethyl acetate and 5.43 Torr for *n*-propyl acetate at 25 °C. It is usually considered in sonochemistry that cavitation bubbles in a more volatile solvent contain higher pressures of solvent vapor so that their collapse will be cushioned and any effects lessened. It can be seen that this is also the case in this reaction, production of radicals being faster in the less volatile mixture with *n*-propyl acetate. This also explains the unusual temperature dependence of the radical formation remarked on above.

The main parameter influencing the number of cavitation bubbles produced is the ultrasonic intensity, I'_{us}.[31] The effect of I'_{us} on radical production in methyl butyrate at 25 °C is shown in Figure 7. It would be expected that the number of radicals produced would be proportional to the number of cavitation bubbles, leading to a linear dependence of the rate of DPPH consumption on I'_{us}, and this is confirmed from the results in Figure 8 which include results from both of the ultrasound generators used. The results also show that there is a minimum intensity of approximately 12–13 W cm^{-2} below which no production of radicals takes place, presumably corresponding to the cavitation threshold in this system.

In polymerizations with an added initiator, the rate of initiation, R_i, is given by[32]

$$R_i = k_d f[\mathrm{In}] \qquad (2)$$

where [In] is the concentration of the initiator, f is a factor to account for the efficiency of a radical in initiating polymerization, and k_d is the rate constant for the decomposition of the initiator, compared with which the rate of addition of a radical to a monomer molecule is assumed to be so rapid as to be negligible in determining the overall rate. For the ultrasonic process, [In] can be represented by the number of active cavitation bubbles per unit volume of solution, [CS], in turn dependent on the ultrasonic intensity, I_{us}. Thus in this case, we may write

$$R_i = (k'_d f)[\mathrm{CS}] = (k'_d f)AI_{us} = k_{us}I_{us} \qquad (3)$$

where k'_d is the decomposition rate of the initiator (or monomer for a bulk reaction) in the presence of ultrasound and A is a constant for each particular system which accounts for the proportionality between the number of cavitation bubbles and the volume of monomer or solution used. Now I_{us} is defined as the ultrasonic intensity in excess of the threshold value. Clearly, k_{us} is a composite rate constant accounting for all the terms in the initiation reactions which, from the plot in Figure 8, was 5.681 × 10^{-4} dm^3 mol^{-1} min^{-1} in the current work.

Polymerization Process. To develop a model of the polymerization, it is necessary to understand the effect of each of the factors described above on the process, including the propagation and termination reactions as well as initiation since these will determine the structure of the resulting polymer. In addition, while the conversion shown in Figure 4 is adequate to study the mechanism of the process, it is too low to be considered viable in a commercial sense so that we also considered various ways to increase the yield of polymer.

From consideration of the kinetics of thermally initiated radical polymerization using a steady-state type treatment, it may be shown[2,32] that the rate of polymerization, R_p, can be represented by

$$R_p = (2k_ik_p^2/k_t)^{1/2}[M][I]^{1/2} \tag{4}$$

where [M] and [I] are the concentrations of monomer and initiator, respectively, and k_i, k_p, and k_t are the rate constants for initiation, propagation, and termination, respectively, k_i accounting for both the rate and efficiency of the initiator decomposition ($k_i = fk_d$) and k_t accounting for all modes of termination. The corresponding expression for the average chain length of the polymer, DP, is

$$\mathrm{DP} = (k_p^2/k_ik_t)^{1/2}[I]^{-1/2}[M] \tag{5}$$

The same type of treatment has been applied to the ultrasonically initiated process. Using a somewhat simplified treatment, we can apply the following mechanism for the concurrent polymerization and degradation reactions. In the following, CS represents an active cavitation site and P a polymer chain

$$\mathrm{M} + \mathrm{CS} \xrightarrow{k_1} 2\mathrm{R}^\bullet \tag{A}$$

$$\mathrm{R}^\bullet + \mathrm{M} \xrightarrow{k_2} \mathrm{RM}^\bullet \tag{B}$$

$$\mathrm{RM}_n^\bullet + \mathrm{M} \xrightarrow{k_3} \mathrm{RM}_{n+1}^\bullet \tag{C}$$

$$\mathrm{RM}_n^\bullet + \mathrm{RM}_n^\bullet \xrightarrow{k_4} \mathrm{P} \tag{D}$$

$$\mathrm{P} + \mathrm{CS} \xrightarrow{k_5} 2\mathrm{RM}_n^\bullet \tag{E}$$

The process in (E) accounts for the degradation of polymer chains in the ultrasound field once they are formed. Introducing the usual assumptions, the expression for the rate of polymerization is

$$R_p = k_3/(2k_4)^{1/2}[M]\{2[CS](k_1[M] + k_5[P])\}^{1/2} \tag{6}$$

Introducing the expression for [CS] as above leads to

$$R_p = k_3/(2k_4)^{1/2}[M]\{2A(k_1[M] + k_5[P])\}^{1/2}I_{us}^{1/2} \tag{7}$$

Assuming that the amount of monomer involved in the initiation step is insignificant compared to that in the progagation, then eq 7 predicts that the rate is directly proportional to the monomer concentration and to the square root of the ultrasound intensity. Integration of eq 3 for the conventional process predicts that the monomer conversion will be a linear function of time during the early stages of the reaction (up to ~5%). However, eq 7 suggests a nonlinear, quadratic function due to the second initiation process arising from the cleavage of polymer chains to give two macromolecular radicals. The corresponding equation for the chain length in the ultrasonic polymerization is

$$\mathrm{DP} = k_3/(2k_4)^{1/2}[M]\{2A(k_1[M] + k_5[P])\}^{-1/2}(I_{us})^{-1/2} \tag{8}$$

so that it should be proportional to [M] and inversely proportional to $I_{us}^{1/2}$. However, quantitative use of this expression is not straightforward since [P] will change continually throughout the reaction and the rate constant for the degradation, k_5, is known to be dependent on a number of factors, including [P].

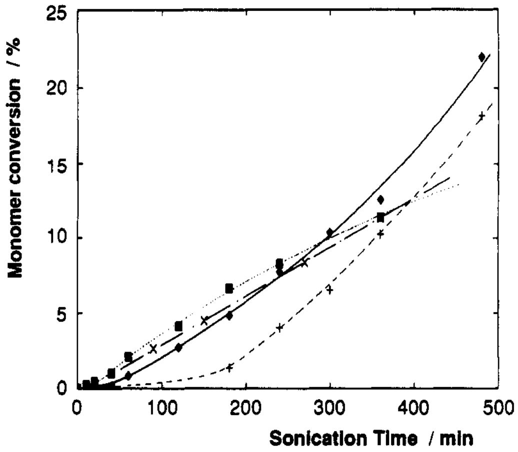

Figure 9. Monomer conversion during the ultrasonic polymerization of varying solution compositions of MMA at 25 °C. Solution composition (% MMA): (···■···) 100, (–×–) 75, (–◆–) 50, (- + -) 25.

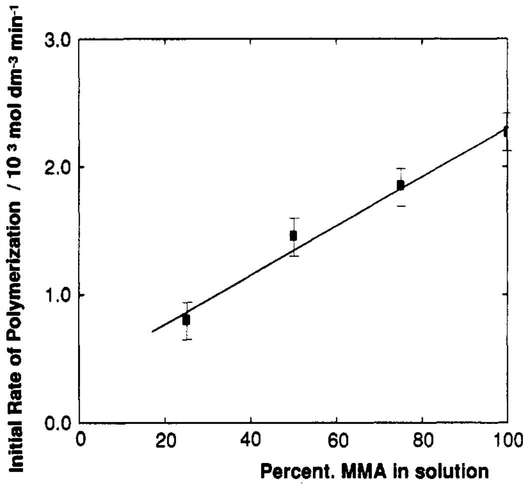

Figure 10. Variation of the initial rate of polymerization with solution composition for the ultrasonic polymerization of MMA at 25 °C.

The next step is characterizing the polymerization was to confirm the applicability of these equations. We first studied the effect of the monomer concentration. As described above, to keep the rate of radical production and initiation constant, mixtures of MMA and methyl butyrate were used. The similarity of the liquid densities means that the percentage composition proportional to the monomer concentration. As well as determining the applicability of eq 7, this would reduce the viscosity of the polymer solution without modifying the cavitational behavior. Since it was felt that the solution viscosity was suppressing the initiation, higher conversions were expected from the solution polymerizations. The conversions to polymer are shown in Figure 9 and display considerably different forms to those from conventional bulk polymerization.

Initially, the behavior is in accord with eq 7 and the rate of polymerization is faster in the solutions containing more monomer. The predicted linear relation is followed to within experimental error as shown in Figure 10. Kruus and Patraboy[17] showed that the conversion was a linear function of sonication time but only studied conversions up to ~3%. This work shows that, as the solutions become more concentrated during the polymerizations, the conversions deviate from the simple model. We interpret the shapes of the plots as follows. In the case of bulk monomer,

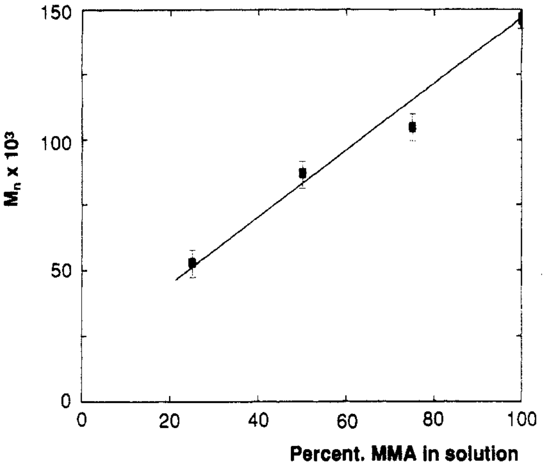

Figure 11. Variation of the final polymer molecular weight with solution composition for the ultrasonic polymerization of MMA at 25 °C.

Table III
Properties of Polymers Produced after 8 h of Sonication at Various Intensities at 25 °C

intensity (W cm^{-2})	mol wt	polydispersity	convn (%)
12.6	144 000	2.3	2.4
29.2	131 000	1.9	10.9
35.0	96 700	1.8	13.5
58.4	35 000	1.5	12.3

polymer is produced rapidly initially, but this leads to an increase in viscosity and consequent reduction in the rate of initiation and hence of polymer. In the dilute solutions, polymerization is initially slow but increases due to the chain scission of the small amount of polymer formed, giving an increased concentration of initiation sites. The degradation is much more efficient in dilute solutions. The lower viscosity also allows the reaction to proceed for longer times and hence to higher conversions before the viscosity limitation comes into effect.

The effect of the monomer concentration on the final molecular weights of the polymers produced is shown in Figure 11 and follows an approximately linear relation as predicted by eq 8. However, as noted above, there are two effects taking place. First, the changing monomer concentration affects the molecular weight. However, also of great importance in this situation is the effect of the degradation of the growing chains caused by the sonication. The limiting molecular weight depends on the solution concentration albeit rather a small effect for solutions with concentrations higher than 8–10% by weight.[14,33]

The next parameter investigated was the ultrasonic intensity since it was hoped that an increase in the intensity would lead to increased conversion. The properties of the polymers produced are given in Table III and show that this is not the case. The conversion does increase with ultrasonic intensity but only up to a limit beyond which no further benefit is obtained, as is commonly the case in sonochemical reactions.[34] The $I_{us}^{1/2}$ dependence of the initial rate of polymerization predicted by eq 7 is confirmed by the results shown in Figure 12.

An increase in intensity leads to a considerable lowering of the molecular weight and polydispersity of the polymer, as has been found in degradation studies on other polymers. This is a consequence of both the nonrandom nature of the degradation with chain cleavage occurring preferentially near the center of the chain and also the molecular weight dependence of the process, longer chains degrading at a faster rate, leading to a narrowing of the distribution. Thus, by suitably modifying the ultrasound conditions,

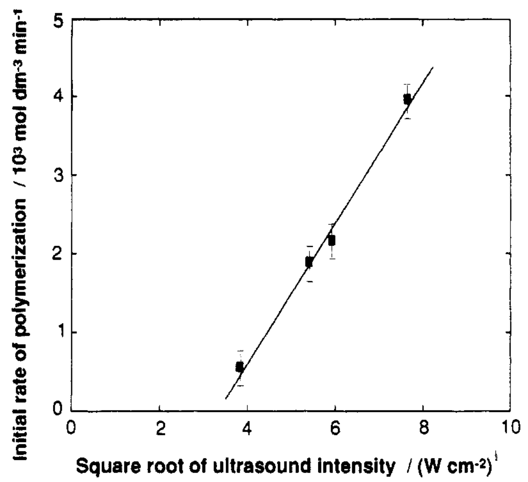

Figure 12. Effect of ultrasonic intensity on the initial rate of polymerization for the ultrasonic polymerization of MMA at 25 °C.

Table IV
Properties of Polymers Produced after 8 h of Sonication at Various Temperatures

temp (°C)	initial rate (10^5 mol dm^{-3} s^{-1})	mol wt	polydispersity	convn (%)
−10	3.28	107 300	1.8	11.0
0	4.17	119 400	1.7	10.0
25	6.12	146 700	1.9	11.4
40	7.61	241 300	1.6	11.3
60	9.68	355 600	1.4	13.0

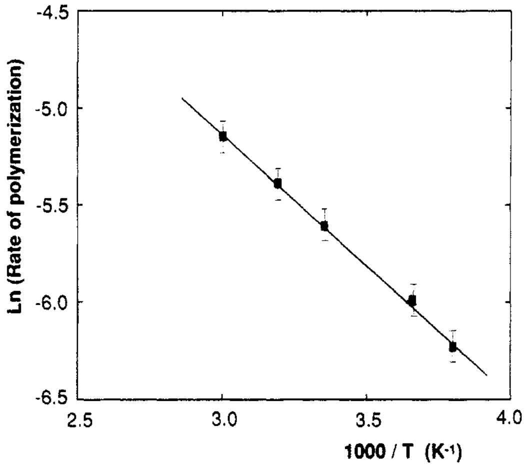

Figure 13. Arrhenius plot for the rate of polymerization in the ultrasonic polymerization of MMA.

considerable control over the structure of the polymers can be obtained.

The effect of temperature on the ultrasonic polymerization is shown in Table IV, and, as expected, higher temperatures lead to an increase in the rate of polymerization.

The termination reactions, both recombination and disproportionation, are relatively insensitive to temperature so that the effect on the propagation reaction is dominant. Despite the effect on the rate, there is little variation in the final conversion achieved. Again, this supports our suggestion that the polymerization is limited by the suppression of cavitation as the solution viscosity rises. The faster propagation reaction at 60 °C, assisted by a less efficient degradation process, leads to higher molecular weights. Conversely, the degradation is more efficient at low temperatures. An Arrhenius type plot for the rate of polymerization is shown in Figure 13 and yields an activation energy of 11.1 ± 1.5 kJ mol^{-1} which can be

Table V
Stereochemical Tacticity Ratios for Radically Initiated PMMA

polymn conditions	ratio i	ratio a	ratio s	av σ
bulk[a] 100 °C	8.9	37.5	53.9	0.27
solution[a] 50 °C	6.3	37.6	56.0	0.25
ultrasound 60 °C	4.3	41.0	54.7	0.25
ultrasound 40 °C	4.0	40.4	56.4	0.24
ultrasound 25 °C	2.8	34.3	62.9	0.20
ultrasound 0 °C	1.7	33.8	64.6	0.18
ultrasound −10 °C	0.8	25.6	73.6	0.13

[a] Using benzoyl peroxide as initiator. Reference 42.

compared with ~67.2 kJ mol^{-1} found for the thermally initiated bulk polymerization.[26,35] The overall activation energy, E_{act}, for the polymerization can be expressed in terms of those for the initiation, E_i, propagation, E_p, and termination, E_t:

$$E_{act} = E_i/2 + E_p - E_t/2 \qquad (9)$$

Using the result of $E_i = -18.9$ kJ mol^{-1} from above, then $E_p - E_t/2 = 20.5$ kJ mol^{-1} from this work, which is in excellent agreement with the literature values of 20.9 kJ mol^{-1}. The polymerization rates in Table IV can also be compared with those in the absence of ultrasound. The solely thermal polymerization of MMA is too slow to be reliably measured at these temperatures, but Walling and Briggs[26] estimated $R_p = 6.2 \times 10^{-7}$ mol dm^{-3} s^{-1} at 100 °C and 8×10^{-6} mol dm^{-3} s^{-1} at 150 °C. For the benzoyl peroxide initiated polymerization, Mackay and Melville[35] obtained 5.56 and 10.51 mol dm^{-3} s^{-1} at 23.6 and 50.5 °C, respectively, in very close agreement with this work.

Under more usual polymerization conditions, further quantitative data could be obtained by combining eqs 7 and 8 since, knowing [M] for bulk MMA, the product of DP and R_p allows calculation of $(k_3/(2k_4))^{1/2}$. However, care must be exercised here since R_p refers to the initial stages of the reaction where only polymerization will be occurring, while the DP value will be determined by concurrent polymerization and degradation, casting doubt on the conclusions. The values obtained in this work agree to within a factor of 2 with previously published values.[35-38] These results give further confirmation of our suggested mechanism and that the rates of the propagation and termination reactions are little affected by the ultrasound field.

To further characterize the ultrasonic process, we then investigated the microstructure of these polymers using NMR spectroscopy.[39] Bovey[40-42] has assigned the resonances due to the α-methyl groups in isotactic, syndiotactic, and atactic polymers and defined a parameter σ to characterize the tacticity, where σ is defined as the probability that a monomer molecule adds with the same stereochemistry as the group at the end of the growing chain so that $\sigma = 1$ for purely isotactic polymers and $\sigma = 0$ for purely syndiotactic. The results from the current work are shown in Table V.

As can be seen, conventional radical initiation leads to a σ value of ~0.25, leading to predominantly syndiotactic polymers although there are also significant sequences of atactic and isotactic groups. Polymerizations under an anionic mechanism using, for example, *n*-butyllithium as the initiator gives a σ of 0.7–0.8 and 60–70% isotactic polymer. Our ultrasound-promoted reactions at higher temperatures produce polymers with similar stereochemistry, confirming that sonication has little or no effect on the propagation reaction. However, lowering the temperature raises the proportion of syndiotacticity along the chain. This can be explained since syndiotactic addition is thermodynamically more favorable due to steric hindrance between the bulky ester groups although the difference is small. As the temperature is lowered, the propagation rate is slowed and there is more chance of the thermodynamically favored addition taking place. Thus, ultrasound offers a chance to control the structure of the polymers.

Finally, following the increased rate of initiation under ultrasound illustrated above, reactions were carried out in the presence of added initiator. A polymerization was carried out as above using a solution of 0.1 wt % AIBN in MMA. As expected from the foregoing discussion, the rate of polymerization was faster than in the absence of AIBN, with a conversion of ~13% being achieved in 4 h. However, as in the reactions described above, polymerization essentially ceased at this point, again indicating that the process is viscosity limited.

Conclusions

We have demonstrated that high-intensity ultrasound offers the possibility of a useful method of initiating radical polymerization in MMA at low temperatures. The process can be described in terms of a conventional treatment of the process kinetics by introducing appropriate ultrasound parameters for the initiation. Suitable manipulation of the conditions allows control over the molecular weight, polydispersity, and tacticity. However, although the initiation proceeds at an acceptable rate and in a controllable manner, it seems that the limiting factor for ultrasonic polymerization lies in the low conversions achieved thusfar. Further investigation of the process to optimize this is underway.

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