The use of ultrasound and a thermolabile radical initiator in the polymerization of acrylate monomers

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A standard laboratory ultrasonic bath can be used to greatly enhance polymerization of acrylate monomers in the presence of a thermolabile initiator (AIBN) and at a much lower temperature than is otherwise practicable. Initiation appears to result from the action of ultrasonic irradiation on the initiator. Water has also been shown to produce radicals under similar conditions.

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The application of ultrasound is a relatively new but expanding topic in organic chemistry, and an excellent general review of sonochemistry and its laboratory applications has been given by Mason[1]. In polymer chemistry, studies have been carried out into polymerization, depolymerization and grafting under the influence of ultrasound irradiation. These are generally radical processes in which the radicals are initiated either through the formation of cavities in the bulk monomer, or through the homolysis of existing polymer molecules.

Ultrasound appears to have been studied mainly as an alternative to, rather than in conjunction with, other methods of initiating polymerization. The main chemical effect of ultrasound is thought to be due to the formation of microbubbles or cavities. When these cavities collapse, local temperatures or 'hot spots' are generated of at least 5000 K. Such drastic conditions would seem to make the use of the usual thermolabile initiators superfluous. The cavitation process is influenced by many factors, such as temperature, vapour pressure of the medium, dissolved gases, and the power and frequency of irradiation, but changes in these parameters may lead to unexpected results. For instance, a decrease in bulk temperature may lead to increased temperature generated when cavities collapse, and hence greater reactivity, due to lower pressure in the cavities. Increasing the ultrasonic intensity can result in increased reaction but only up to a point, since collapse times also increase; once this exceeds one half the period of the ultrasound, cavities may not collapse completely in each acoustic period, resulting in less reaction. If no cavities form, these effects cannot take place.

Intense ultrasound in which a sonic horn is placed directly in the medium has been shown to initiate polymerization in both pure methyl methyacrylate[2–4] and in the presence of 2,2′-azobisisobutyronitrile (AIBN)[4]. Studies at higher temperature and in the presence of AIBN have been carried out in which ultrasound was switched on after polymerization had started[5]. An increased rate of polymerization was observed, which was attributed to radicals formed on breaking polymer chains, the presence of AIBN having no further effect. In contrast to these findings, this report presents evidence indicating that thermolabile initiators can be effective in promoting radical reactions at lower temperatures with the use of less intense ultrasound.

Whereas previous studies have generally made use of a sonic horn which is placed directly in the reaction medium, in the study presented here an ultrasonic bath of 2.3 l capacity was employed, generating a frequency of about 50 kHz with a power of 235 W. This bath is typical of those used in many organic chemistry laboratories for cleaning and extraction purposes.

Flasks were purged with nitrogen and stoppered before ultrasound was applied. During ultrasonic irradiation the bath temperature increased to about 40°C, though in some experiments cooling water was applied. The temperature attained in the bath and duration of irradiation are given in *Table 1*. A direct comparison with equipment used in other studies is not possible where frequency, power, temperature and volumes differ. The fractional conversion was estimated by evaluating the amount of unreacted or residual monomer; this was measured by removal of the monomer from a thin film of the reaction mixture under vacuum and confirmed by quantitative gas chromatography.

The systems investigated were methyl methacrylate (MMA), and a mixture of 2-ethylhexyl acrylate (2EHA) and acrylic acid (AA). The conditions and results are summarized in *Table 1*. MMA(2), and a mixture of 2EHA:AA(10), polymerize in the presence of initiator during ultrasonic irradiation. Similar results are obtained when methyl ethylketone (MEK) is used as a solvent (7). When no initiator is used (5) or ultrasound is absent (1 and 6) little or no polymerization takes place. These results show that radical initiation is greatly enhanced in the presence of AIBN by the use of ultrasound. Increasing the duration of ultrasonic irradiation has only a slight effect (2 and 3), whereas increasing the level of initiator added initially (9) or by further addition (8) increases the fractional conversion substantially. This indicates that initiation is due mainly to the action of ultrasound on AIBN, and not directly on the monomer or through homolysis of existing polymer molecules. This is in accordance with other findings, where no significant effect on initiation by acoustic depolymerization has been

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Table 1 Experimental conditions and polymerization results

No.	Composition (w/w)[a]	AIBN (% w/w)[b]	Time (h)	Temp. (°C)	Ultrasound	Conversion to polymer (%)
1	MMA	0.1	17	42	No	5
2	MMA	0.1	17	38	Yes	15
3	MMA	0.1	24	38	Yes	17
4	MMA	0.1	17	30	Yes	0
5	AA:2EHA:MEK, 1:9:15	0	17	39	Yes	0
6	AA:2EHA:MEK, 1:9:15	0.1	17	42	No	0.8
7	AA:2EHA:MEK, 1:9:15	0.1	17	39	Yes	41[c]
8	Product from 7	0.1	17	39	Yes	71
9	AA:2EHA:MEK, 1:9:15	1	17	38	Yes	92[d]
10	AA:2EHA, 1:9	0.1	19	39	Yes	38
11	AA:2EHA, 1:9	0.1	17	42	No	1.5
12	AA:2EHA:H_2O, 1:9:10	0	17	38	Yes	25 (gel)
13	MMA:H_2O, 1:1	0	17	42	Yes	0
14	AA:H_2O, 1:1	0	17	38	Yes	4.3
15	2EHA:H_2O, 1:1	0	17	38	Yes	22
16	2EHA:H_2O, 1:1	0	17	44	Yes	3.2

[a] Total monomer, 20 g
[b] Percentage of initial total monomer
[c] Residual monomers: 2EHA, 55%; AA, 4%. M_w, 240280; M_n, 23870; M_w/M_n, 8
[d] Residual monomers: 2EHA, 7%; AA, 0.7%. M_w, 143130; M_n, 17480; M_w/M_n, 8

observed[3] or, where observed, the effect is only slight[5]. On decreasing the bath temperature the initiating effect is lost (4). Lowering the temperature can increase the effect of cavitation, but in this case it may be that cavitation is no longer taking place.

It is well known that water can produce radicals under ultrasonic conditions[1]. This is clearly demonstrated in sample 12, in which a mixture of 2EHA and AA have polymerized in the presence of water but no AIBN. Mixing caused by the action of the ultrasonic bath effectively makes this a reaction in suspension. However, the 2EHA:AA copolymer, unless substantially cross-linked, is normally a soft, sticky material. The product in this case is a gel (12), which on drying gives a much harder, slightly sticky solid, indicating that substantial cross-linking has taken place. This is probably due to the action of highly reactive or so-called 'hot' hydroxy radicals, and indicates that aqueous extractions using ultrasound may be accompanied by reaction of radicals formed in the solvent.

When AA(14) and 2EHA(15) are treated separately, only 2EHA polymerizes to a substantial degree. MMA under similar conditions does not react (13), and when a slightly higher temperature is used, polymerization of 2EHA is greatly reduced (16). It is of interest to note that under different conditions methacrylic acid was found to polymerize easily, but MMA did not react[6]. It is apparent that small changes in conditions can have a significant effect on the degree of reaction observed.

Conventional use of thermolabile initiators requires heating, whilst the polymerization reaction is highly exothermic. There is a consequent difficulty in controlling the temperature throughout the reaction medium as the viscosity increases, especially when carried out on production scales. For commercial and environmental reasons there is an increasing interest in solventless systems where these problems become more severe. The procedure described here offers the advantage of the lower temperature employed, and the degree of control of the reaction. Once turned off, the effect of ultrasound stops[3]. This method could be more widely applied to other radical reactions, particularly where heat-sensitive materials are concerned, since the bulk temperature of the medium is much lower than is usually practicable when using conventional thermolabile initiators.

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