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Ultrasonically assisted synthesis and degradation of poly(dimethyl siloxane)

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The effect of ultrasound on the ring opening polymerization of octamethylcyclotetrasiloxane to give poly(dimethyl siloxane), PDMS, is described. Sonication was found to increase the rate of polymerization over conventional stirring and to give higher molecular weights with lower polydispersities. The results are explained in terms of the efficient mixing and dispersal of acid catalyst given by sonication. The basic effects of sonicating dilute PDMS solutions are also described but it was found that, in contrast to other polymerizations, the degradation plays little part in determining the molecular weight during synthesis. Copyright © 1996 Elsevier Science Ltd.

(Keywords: sonochemistry; ultrasound; PDMS; silicones; molecular weight control)

INTRODUCTION

While most research in polymer science continues to concentrate on wholly organic materials, there is rapidly growing interest in polymers with inorganic backbones[1]. There is considerable research activity in the all-silicon chain poly(organosilanes) as well as the polyphosphazenes which are based on phosphorous and nitrogen. The major group of inorganic polymers is undoubtedly the polysiloxanes[2] which have found widespread use as low viscosity, low surface energy fluids and in silicone elastomers. Polysiloxanes are usually based on poly(dimethyl siloxane), PDMS, prepared by ring-opening polymerization of the cyclic tetrameric siloxane. Other substituents can be incorporated to provide chemical functionality, usually via hydrosilylation reactions onto Si–H groups along the backbone.

Over the past two decades, the use of high intensity ultrasound has become a common technique in synthetic chemistry[3–5]. A number of reactions, especially those in heterogeneous systems, have been shown to give enhanced rates and yields under ultrasound, leading to a branch of chemistry sometimes termed *sonochemistry*. Polymer sonochemistry in fact predates synthetic uses, the irreversible cleavage of polymer chains when irradiated in solution being reported in the 1930s[6]. More recently, ultrasound has been applied to polymer synthesis with some success[7]. In addition to rate and yield enhancements, perhaps the major advantage of performing sonochemical polymer synthesis is that it provides an additional means of molecular weight control.

The main effects of sonication are due to *cavitation* or the growth and explosive collapse of microscopic bubbles on a microsecond timescale[8]. This can result in the formation of relatively high concentrations of excited species such as radicals[9] which can diffuse into solution and react. The rapid movement of solvent around the molecule also sets up shear gradients which stretch out and break the chains in a non-random, molecular weight dependent process resulting in a lowering of the molecular weight and polydispersity[10,11]. A second effect of this enhanced molecular motion is very efficient mixing and dispersion of multi-phase systems[12].

In a very brief report on the first study of sonochemical preparation of polysiloxanes, Kogan and Smirnov[13] some time ago demonstrated that reactions under ultrasound showed significant rate enhancements. However, there was no account of the effect on molecular weights. This paper will describe the sonochemical synthesis of PDMS by the acid catalysed ring opening of octamethylcyclotetrasiloxane and in particular the variation of the molecular weight. The effects of sonicating performed PDMS in solution and the properties of the degradation are also described.

EXPERIMENTAL

Sonication methods

Two sources of ultrasound were used. Much of the published sonochemical organic synthesis has been performed by immersing the reaction vessel into an ultrasonic cleaning bath[14]. Considerably higher sound intensities and better temperature control are achievable with a 'horn' type apparatus where the ultrasound vibrations are coupled directly into the reaction via a titanium alloy rod which dips into the reaction medium. In this work, a Kerry Ultrasonics Pulsatron 325 cleaning bath and a MSE 'Soniprep 150' horn apparatus were used. The ultrasound intensities on the latter system were measured calorimetrically in the usual way[14] and temperature control was achieved to ±0.1°C by circulating thermostatted water through a

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jacketted vessel. The apparatus has been described previously[9].

Polymer degradation

For the degradation studies, polymer solutions of 1% (w/v) concentration were prepared in HPLC grade toluene (Aldrich). 100 cm^3 of solution was placed in the jacketted vessel and allowed to attain thermal equilibrium. The sonicator was switched on and small samples ($\sim$0.2–0.3 cm^3) removed periodically for analysis. The polymers used were Dow Corning 'DC' fluids (BDH Ltd.) with viscosities ranging between 50 and 30 000 cs and were used as received.

Polymer analysis

Polymer molecular weights were recorded on a Bruker LC21/41 Gel Permeation Chromatograph using toluene as the eluent for PDMS and refractive index detection. Ten polystyrene standards (Polymer Laboratories Ltd.) with molecular weights between 1020 and 2.65×10^6 were used as calibrants and all values reported below are 'polystyrene equivalents'.

Polymerization procedure

The basic procedure for the preparation of PDMS was that of Sorenson and Campbell[15]. Typically, 20 cm^3 octamethylcyclotetrasiloxane (OMCTS, 98%, Aldrich) was mixed with 10 cm^3 diethyl ether and $\sim$0.5 cm^3 sulfuric acid (95–98%, BDH). This was stirred vigorously for a predetermined time after which 20 cm^3 of diethyl ether and 10 cm^3 of water were added. The organic layer was separated, washed with water and dried over sodium sulfate. The ether and unreacted OMCTS were removed at 60°C under vacuum to leave the PDMS. For the sonochemical experiments, the stirring was replaced by the bath or horn as indicated below.

RESULTS AND DISCUSSION

Sonochemical degradation of PDMS in solution

The chain breakage when polymers above a certain molecular weight in solution are exposed to ultrasound seems to be a universal phenomenon, having been seen in organic, inorganic and aqueous systems[10,11]. The degradation of PDMS was noted some time ago by Thomas and de Vries[16]. The basic properties of the process are shown in *Figure 1* using toluene as the solvent with six PDMS samples at concentrations of 1 g (100 cm^3)$^{-1}$ having different initial molecular weights. Sonications were carried out on the horn system at an intensity of 23 ± 1 W cm^{-2}.

As found with previous studies, the molecular weight falls rapidly during the early stages of the degradation but reaches a limiting value, $M_{\rm lim}$, below which no further change occurs. The polymer with the lowest molecular weight, $\sim$6500, is unaffected under the conditions used. Since all the solutions were sonicated under the same conditions of temperature, intensity and concentration, it would be expected that they would all reach the same value of $M_{\rm lim}$ at long times. Some differences between samples may occur due to the differing starting polydispersities although the molecular weights of the larger samples are still falling so that the same final value may well have been reached had sonication been continued. The initial small increase in molecular weight seen for the highest molecular weight samples is worthy of further comment. We have noted this with a number of organic polymers such as polystyrenes[17] and poly(alkyl methacrylates)[18] and have interpreted the effect as the macromolecular radical generated on chain cleavage attaching to an unbroken chain in solution giving a branched, higher molecular weight chain[18]. Thomas and de Vries suggested that PDMS undergoes heterolytic cleavage, initially leading to an ion-pair. The absence of radical intermediates is also supported by our studies[18] of monitoring trapped radical intermediates by e.s.r. spectroscopy where no signal due to radicals could be detected. Whether a macromolecular ion could attack an adjacent chain in a similar manner without causing further chain breakage is unclear but would explain the observed results. Other possibilities include the formation of large rings which are then readily broken down.

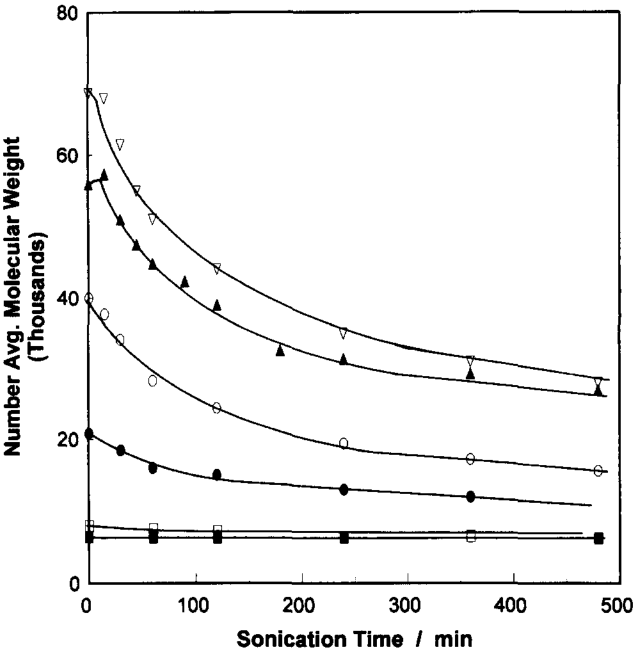

Figure 1 Change in molecular weight on sonication for 1% PDMS solutions in toluene at 25°C

A consequence of the molecular weight dependence is that the polydispersity is altered throughout the degradation. *Figure 2* illustrates this for two polymers where the M_w/M_n ratio is clearly narrowing as sonication proceeds.

To correlate the results from this type of experiment, a number of rate models have been proposed. A number of these have been found only to apply to particular systems and a full examination of these for a number of systems is underway. Some of the earliest models have found widest use and were proposed by Schmid[19] and Ovenall[20]. Schmid assumed that the rate of chain breakage was proportional to the chain length in excess of $M_{\rm lim}$ and, introducing the solution concentration, c, and monomer unit molecular weight m_0, derived the rate equation:

$$\left(\frac{M_{\rm lim}}{M_t}\right) + \ln[M_t - M_{\rm lim}] = -\frac{kM_{\rm lim}^2}{cm_0^2}t + \left(\frac{M_{\rm lim}}{M_i}\right) + \ln[M_i - M_{\rm lim}] \qquad (1)$$

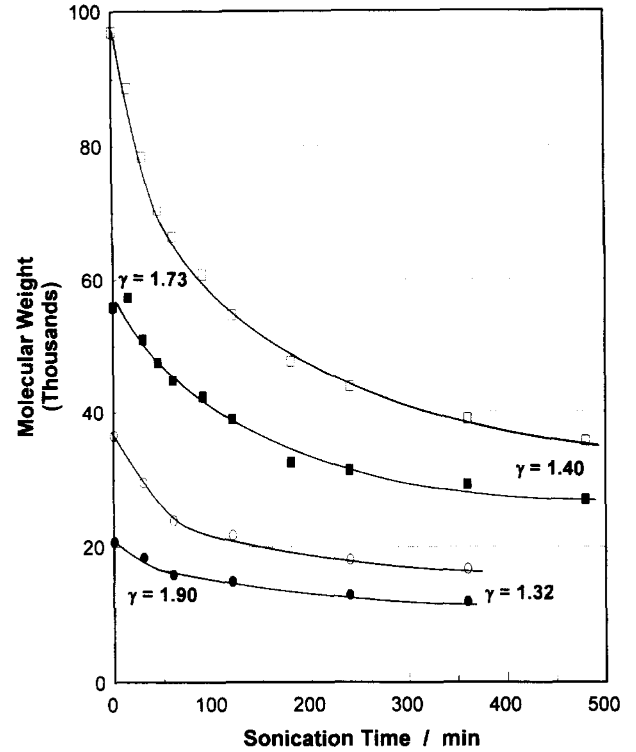

Figure 2 Change in molecular weight on sonication for 1% solutions of two PDMS polymers in toluene at 25°C. (■, ●) Number average; (□, ○) weight average

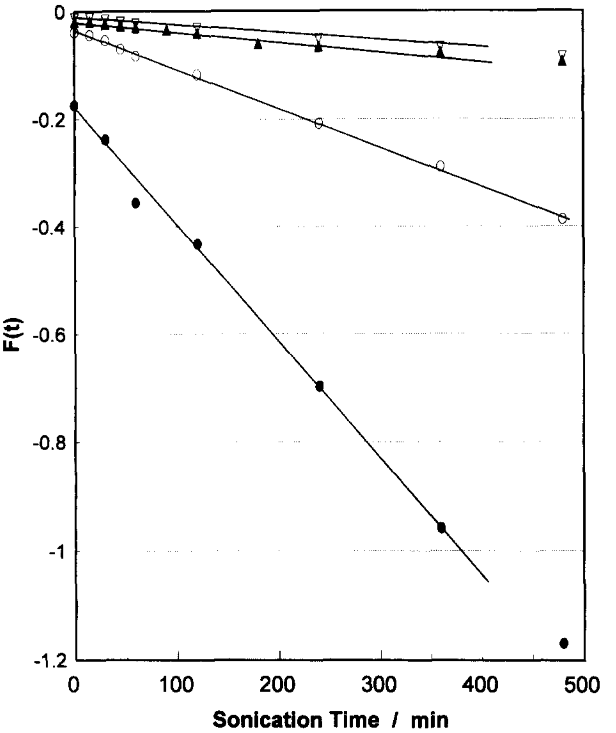

Figure 3 Kinetic plot for Schmid rate model applied to PDMS in toluene. (Conditions as *Figure 1*) $F(t) = [M_{lim}/M_t] + \ln[M_t - M_{lim}]$. Starting molecular weights: (●) 20 800; (○) 40 000; (▲) 56 000; (△) 68 600

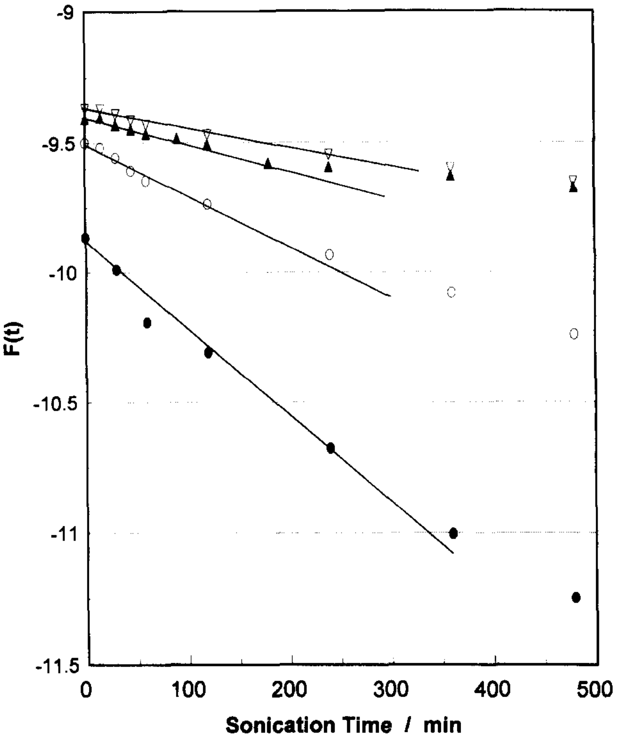

Figure 4 Kinetic plot for Ovenall rate model applied to PDMS in toluene. (Conditions as *Figure 1*) $F(t) = \ln[1/M_{lim} - 1/M_t]$. Starting molecular weights: (●) 20 800; (○) 40 000; (▲) 56 000; (△) 68 600

Table 1 Rate constants, k, for the ultrasonic degradation of PDMS in toluene at 25°C

Initial M_n	Initial γ	Initial rate (min^{-1})	k (Schmid) (10^{11} mol dm^3 min^{-1})	k (Ovenall) (10^6 mol dm^3 min^{-1})
20 800	1.90	78	5.4	25.0
40 000	2.46	194	2.8	16.0
56 000	1.73	165	2.0	7.0
68 600	1.84	225	1.7	5.5

where M_i and M_t are respectively the molecular weight before sonication and at time t during the degradation and k is a rate constant. Although this model was based on the fallacious assumption of an unchanging, monodisperse polymer sample, this equation has been found to fit data from a range of systems and to allow effects to be correlated. Ovenall *et al.* were amongst the first workers to measure the rate of bond breakage of organic polymers by trapping the resultant radicals. They showed that their results fitted a rate equation of the form:

$$\ln\left(\frac{1}{M_{lim}}-\frac{1}{M_t}\right)=\ln\left(\frac{1}{M_{lim}}-\frac{1}{M_i}\right)+k\left(\frac{M_{lim}}{cm_0}\right)t \qquad (2)$$

Figures 3 and *4* show the results for four of the PDMS samples plotted in the appropriate form for both of these rate equations. Both give good linear fits for the data and the rate constants calculated from the slopes are shown in *Table 1*. There are considerable deviations from linearity at longer times in the plots from equation (2), largely caused by the uncertainties in molecular weight being magnified as M_t approaches M_{lim}. Also shown in *Table 1* is the initial rate of degradation taken over the first 30 min.

As expected, the initial rate of degradation is faster at higher molecular weights although the sample with initially $M_n = 40\,000$ is rather anomalous with a rather higher rate than would be expected. This may well be due

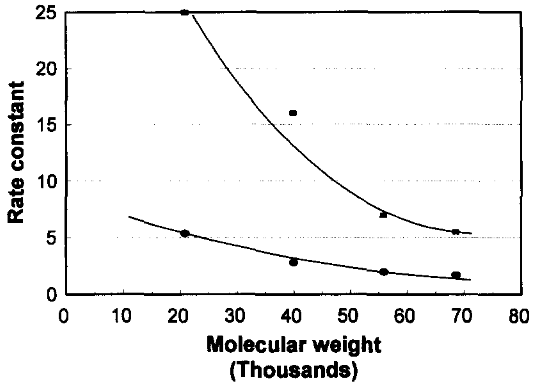

Figure 5 Variation of degradation rate constant with PDMS molecular weight, M_n. (■) Ovenall model (10^6 mol dm^3 min^{-1}); (●) Schmid model (10^{11} mol dm^3 min^{-1})

Table 2 The effect of ultrasound on the synthesis of PDMS at 30°C

Volume of acid(cm^3)	Molecular weight		Polydispersity		Conversion(%)	
	Ultra.	Stir.	Ultra.	Stir.	Ultra.	Stir.
0.5[a]	23 000	17 500	2.3	3.4	71	60
1.5[b]	49 500	17 300	1.6	2.0	68	71

[a] Reaction time 6 h
[b] Reaction time 8 h

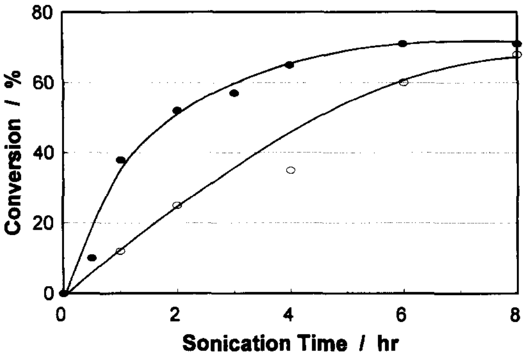

Figure 6 The effect of ultrasound on the yield of PDMS. (Reaction conditions as *Table 1*[b])

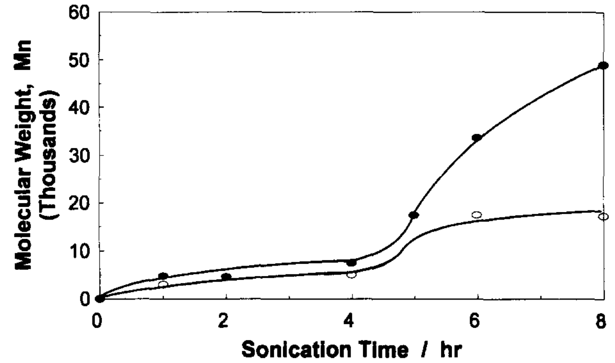

Figure 7 The effect of ultrasound on the molecular weight during sonochemical synthesis of PDMS. (Reaction conditions as *Table 1*[b])

to the higher polydispersity, preferential breakage of the longer chains leading to the observed faster rate. Rather unexpectedly, although the results fit the rate models reasonably well, they give rate constants which fall regularly with increasing molecular weight as shown in *Figure 5*. It is not clear why this polymer–solvent system behaves in this way when, for example, polystyrene, PMMA and similar materials all give the expected increase of k with M_n. One factor which may play a part is the use of 'polystyrene equivalent' rather than 'true' molecular weights but this does not alter the form of the data to any significant fashion and further work is underway to account for these observations.

Although not described here, the degradation of PDMS has also been seen in other solvents such as tetrahydrofuran and the cyclic monomer OMCTS and has similar characteristics to that described here. Thus it would be expected to occur whenever a polymer solution is exposed to ultrasound, including during polymerization. Indeed, during the sonochemical radical polymerization of methyl methacrylate[9], the degradation was found to be the major factor which determined the polymer molecular weight. Hence, the process can offer an additional method of molecular weight control during preparation and this was studied in the next phase of our work.

Ring-opening polymerization of PDMS

The first stage of the work was to carry out sets of reactions under identical conditions except that one was stirred and the other sonicated using the cleaning bath. Examples of the results are shown in *Table 2* although it should be noted that temperature control is more difficult when using the ultrasonic bath and could have varied by ± 5°C. In both cases, the molecular weights of the polymers produced under sonication were higher than those from the conventional reaction. In addition, they had lower polydispersities. The molecular weight dependence in sonochemical polymerizations is often interpreted in terms of the degradation process described above. However, while this might explain the narrower polydispersities, the higher molecular weights cannot be explained. The ultrasound intensity when using a cleaning bath is much lower than when using a horn and sonication of a 1% solution of the PDMS with $M_n = 56\,000$ using the cleaning bath produced only very small changes in M_n and γ. Thus the effect of ultrasound in this case cannot be due to sonochemical degradation.

The higher molecular weights obtained suggest that ultrasound is accelerating the ring-opening so that the kinetics of the reaction were then followed. A number of systems were studied and to illustrate the results, examples are shown in *Figure 6*. These demonstrate that ultrasound gives a clear enhancement of the rate although the final yield of polymer is similar to that in the stirred reaction, an effect noted in all our reactions of this type. *Figure 7* shows the molecular weights of the recovered polymers during polymerization. The plots from both the ultrasonic and conventional reactions are of a rather unusual shape but the former gives higher molecular weights throughout the reaction.

In an effort to determine whether the use of ultrasound could replace some or all of the catalyst, a series of polymerizations were carried out using varying volumes of sulfuric acid. Some results are shown in *Table 3* and it should be noted that no polymer was recovered in the absence of acid. There is obviously a complex dependence of the results on the amount of acid but some

Table 3 The effect of amount of catalyst on the sonochemical preparation of poly(dimethyl siloxane)[a]

Volume of acid(cm^3)	Molecular weight		Polydispersity		Conversion(%)	
	Ultra.	Stir.	Ultra.	Stir.	Ultra.	Stir.
0.25	13 000	6941	4.3	3.3	75	84
0.5	28 700	15 500	4.5	5.5	56	45
0.9	33 600	26 400	2.3	3.1	52	54
2.0	40 500	13 600	1.6	1.8	74	53

[a] Reaction conditions: ultrasound bath or stirred at 18°C for 6 h

Table 4 The effect of ultrasound intensity on the preparation of poly(dimethyl siloxane)[a]

Ultrasound intensity	Molecular weight	Polydispersity	Conversion(%)
18	24 200	1.6	63
23	31 000	1.6	64
32	44 300	1.9	73

[a] Reaction conditions: 90 min using ultrasound horn at 18°C with 1 cm^3 H_2SO_4 catalyst. Intensities in W cm^{-2}

general trends can be seen. In particular, the sonochemical reactions again give higher molecular weights and, with one exception, lower polydispersities. However, it is clear that the amount of catalyst plays a major part in determining the course of the reaction. Attempts were also made to induce polymerization in the absence of acid using the horn system to sonicate bulk OMCTS and also with 1 cm^3 of water. Neither of these resulted in the formation of any polymer. This is perhaps not surprising given the cationic nature of the reaction since ultrasound is most effective in producing radicals and often ineffective in ionic systems[21].

While ultrasonic cleaning baths have been widely used in organic and organometallic synthesis, the available intensity is low and varies depending on the position of the reaction vessel and temperature of the water (also difficult to control) so that reproducibility is poor. In general, the experimental conditions can be more easily controlled using a horn apparatus so that this was employed to determine whether variation of the intensity could be used to control the course of the polymerization. The effect is demonstrated in *Table 4*. Carrying out the reaction at higher intensities than those shown caused a large amount of foaming due to the nature of the 'monomer' and consequently little formation of polymer. The results show the opposite trend to that expected if the degradation process, which is more efficient at high intensity[17], were playing a part.

Further discussion

Clearly, in the PDMS reaction the ultrasound is accelerating the ring opening reaction as well as affecting the molecular weight distribution. In all cases, the use of ultrasound led to faster polymerization and higher molecular weights but, significantly, lower polydispersities. However, it was clear that the amount of catalyst was also a major factor in determining the extent of reaction even under ultrasound.

These results are best interpreted by considering the heterogeneous nature of the polymerization. The OMCTS and acid are immiscible and the catalyst needs to be dispersed by stirring. Sonication is known to greatly enhance dispersion and mixing. Indeed, it has been used to efficiently produce emulsions and has also been used to replace phase transfer catalysts. These effects have been used to enhance emulsion polymerizations[22,23]. In the system here, we consider that the ultrasound leads to much better dispersion of the acid catalyst throughout the reaction. The initial ring opening is thus more rapid than in the 'silent' case, leading to the faster kinetics. The 'initiation' also occurs more evenly through the system so that more chains are growing simultaneously at the same rate, hence giving lower polydispersity. There may also be some acceleration of the propagation steps and/or perturbation of the ring-chain equilibrium in the system. This is currently under further study. In contrast to radical polymerizations, the sonochemical degradation is relatively unimportant in determining the course of this reaction.

CONCLUSIONS

This preliminary study, along with previous work on poly(organosilanes)[24–26], has shown that ultrasound can be a useful tool in the preparation of inorganic polymers. It further confirms its benefits when applied to heterogeneous reaction systems. The major benefit in the preparation of PDMS is that the catalyst is rapidly and evenly distributed throughout the polymerizing system so that faster and more homogeneous initiation and chain growth can occur. This leads to higher yields and molecular weights for a given reaction time but also to lower polydispersities. While ultrasound under the conditions employed here cannot be used to "initiate" the ring opening in the absence of added catalyst, there may well be a place for it in the control of the structure of the polymers arising from the catalysed reaction.

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