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Recent Developments in Sonochemical Polymerisation

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Abstract

High intensity ultrasound has been applied to two classes of step-growth polymerisation. The ring-opening polymerisation of cyclic lactones to polyesters was accelerated under 20 kHz ultrasound but, in the case of δ-valerolactone, sonication also promoted a depolymerisation reaction so that the molecular weight fell during later stages of the reaction. Sonication was also applied to the preparation of polyurethanes from a number of diisocyanates and diols. In all cases, the sonochemical reactions proceeded faster in the early stages and led to higher molecular weight polymers. The effect of changing the ultrasound intensity is discussed and some speculation as to the mechanisms of the reaction enhancements is given.

Introduction

High intensity ultrasound has been used to enhance polymerisation reactions for a number of years [1][2]. Most published work refers to the radical polymerisation of vinyl monomers where sonication can obviate the need for thermal initiators and allow some control over the molecular weight, tacticity and polydispersity [3][4]. A number of other polymerisation mechanisms have been investigated [1].

Considering the large number of industrially important polymers and plastics prepared *via* step-growth reactions (including condensation reactions) there have been relatively few publications dealing with the use of ultrasound in this area. Among these are by Long [5] who described reactors with vibrating walls which was used to control when and where polymerization took place for several polyurethane systems. There has also been some interest in ring-opening reactions. For example, Stoessel [6] has also reported the use of ultrasound at very high intensities to promote the polymerisation of small cyclic polycarbonate oligomers. Other ring-opening reactions involve the polymerization of cyclic siloxanes to silicones [7].

Most sonochemical effects can be attributed to cavitation [8], the growth and explosive collapse of microscopic bubbles as the sound wave propagates through the fluid. This can result in extreme conditions of temperature (> 2000K) and pressure (>500 bar) on a microsecond timescale [9] leading to the formation of reactive intermediates such as radicals. The motion of fluid around the bubbles is rapid resulting in very efficient mixing and the formation of liquid jets. The rapid motion can result in effective shear degradation of polymer chains in the vicinity of cavitation bubbles [10] as long as they are over a certain molecular weight. Thus, there are a number of effects which may be exploited.

Recent work in the author's laboratory has been concerned with step-growth reactions and two classes will be used to illustrate the results. Firstly, the polymerisation of cyclic lactones to give aliphatic polyesters will be described. These materials have a number of applications since they are biodegradable to relatively harmless products and hence have potential as biomaterials. In these reactions, the monomer conversion and the ultimate chain length are limited by a ring-chain equilibrium so it was of interest to determine whether operating under ultrasound could influence the yields and the achievable molecular weights. A major impetus for this study comes from the work of Ragaini [11] *et al.* who showed that ultrasound enhanced the ring opening of ε-caprolactam to form nylon-6, allowing a single step polymerization. High molecular weight materials with narrower distributions were formed in shorter reaction times than when using the conventional process.

Secondly, a preliminary investigation into the effect of ultrasound on the formation of polyurethanes is described. Polyurethanes are amongst the most widely applied polymers in use [12]. Variation of the diisocyanates and diols used together with the inclusion of various chain extenders allows a huge range of properties to be achieved. Again, the rates, yields and molecular weights were of interest as was the possibility of using ultrasound to control the reaction.

Experimental

Sonication techniques: The main sources of ultrasound used were a Fisons 'Soniprep 150' or a Sonics and Materials VC50 sonic horn system, both operating at 23 kHz and used in the usual configuration whereby the horn was immersed to a depth of $\sim$ 1.5 cm in the reaction mixture. Thermostatting around ambient temperature was achieved to $\pm$ 1 $^{\circ}$C by circulating water through a jacket surrounding the reaction vessel although this degree of control could not be achieved during some highly exothermic polymerisations. At higher temperatures a non-jacketted reaction vessel was placed in a heated silicone oil bath. Sonication intensities were measured calorimetrically [13]. For comparison purposes, some reactions were carried out by immersing a beaker containing the reagents into a Ney 'Ultrasonik 300' ultrasonic cleaning bath. Reactions conducted without ultrasound were performed under the same conditions while replacing the ultrasound horn with vigorous stirring from a mechanical motor, glass rod and Teflon stirring paddle.

Materials: A number of diisocyanates were used. For the work discussed in this paper, H_{12}MDI (4,4'-dicyclohexylmethane diisocyanate) was from Bayer Ltd; VM10 from ICI. The structures are shown in Scheme 1. Appropriate safety precautions were taken to minimise exposure to these compounds. The diol compounds were all obtained from Aldrich in the purest form available. Two lactones were used in the study; δ-valerolactone, VL, (99 %) was obtained from Lancaster chemicals and ε-caprolactone, CL, (99+ %) from Aldrich. All solvents and other reagents used were of Reagent grade or better and were obtained from Aldrich Ltd. For both reaction systems, dibutyltin dilaurate (Aldrich) was used as a catalyst at levels of 0.1 – 0.5% by weight.

Analytical methods: Infra-red spectra were recorded as films on NaCl plates using a Perkin-Elmer PE983 spectrometer. Molecular weights were estimated using a Bruker LC21/41 Gel Permeation Chromatograph using standard methods for the polymers being investigated.

Results and Discussion

Polyurethanes are formed from the reactions of diisocyanates and di- or poly- functional alcohols. An example involving $H_{12}MDI$ and an aliphatic diol is shown in Scheme 2, these polymers being used in a range of surface coatings. To exemplify the initial part of the work to survey the potential for ultrasound [14] to influence diisocyanate/diol systems used in commercial polyurethane production, Figure 1 shows the time taken for this system to form solid polymer under a variety of conditions. In each case, a brittle, transparent polymer was produced except for the catalysed reaction with the ultrasonic horn where some foaming was observed. There is a clear acceleration of the reaction under ultrasound in both catalysed and uncatalysed reactions. At the higher intensity the polymerisation time was less than one-third that of a "silent" reaction at 80 °C. 'Blank' reactions of non-polymerising systems indicated that the temperature rise caused by sonication - the maximum temperature reached in the cleaning bath was ~ 26 °C and in the uncatalysed reaction ~ 50 °C – was not sufficient to explain the acceleration.

VM10, a mixture of MDI and TDI isomers, is used in a range of polyurethane plastics. Table 1 shows the polymerisation times for this monomer with butane diol and with two poly(ethylene glycols). Again, it is noticeable that the use of ultrasound greatly speeds up the initial phase of the reaction even in the absence of a catalyst. In commercial uses, the reaction mixture is typically poured into a mould and simply cured in an oven. To compare with the sonochemical work, reactions were also performed with vigorous mechanical stirring. Stirring also decreases the time taken to start the polymerisation although a hard product similar to that from an oven cure was only obtained after long times. This suggests that the enhanced mixing of reagents caused by ultrasound is at least a contributory factor in the rate acceleration. Other factors include which might contribute to the acceleration are the formation of and modification of action of catalytic species and these are discussed below.

To obtain further information on the process, the reaction of $H_{12}MDI$ was studied in more detail. Figure 2 shows the effect of ultrasound on polymerisations with seven diols. All reactions were started at 25 °C, the non-ultrasound reactions being agitated vigorously with a mechanical stirrer. The polymerisation time was again taken as that required for the system to gel or solidify. This was usually accompanied by a significant exotherm.

The reaction time in the absence of ultrasound increased with the viscosity of the diol. However, this was not the case when ultrasound was used. It was also noted in the reactions with the

PEG's that, after the system gelled, the temperature rose to around 45 °C in the stirred reactions while in the sonochemical polymerisations, > 100 °C was observed. Again, this indicates that a greater degree of reaction is occurring under sonochemical conditions.

The effect of increasing the ultrasound intensity is shown in Figure 3. Larger intensities indicate greater ultrasonic energy entering the system and a consequent increase in the number of cavitation bubbles and sonochemical effect. As might be expected, higher intensities lead to shorter reaction times. Figure 4 shows the molecular weights of the polyurethanes formed in these experiments. In each case the polymers produced ultrasonically have higher molecular weights. Similar results were seen with the other diols investigated.

Thus, it has been convincingly shown that the use of high intensity ultrasound can significantly enhance reactivity in these polymerisations. The reasons for the enhancement will be discussed below but now it is appropriate to consider the effects in the ring-opening polymerisation of lactones.

This reaction is represented by Scheme 3. The reaction may be initiated by anions or cations but industrially polymerisation of the bulk lactone is often achieved by heating with a tin catalyst and it is this system that has been studied here.

To illustrate the effect of ultrasound, Figure 5 shows a comparison of the molecular weight evolution during the polymerisation of caprolactone, CL. The ultrasonically promoted reaction proceeded somewhat faster under the same conditions than the "silent" reaction and the molecular weights were similar. After approx. 150 min, the sonicated system became too viscous to support cavitation so that the reactions were terminated. It would appear that, at this point in the reaction, the maximum molecular weight achieved was again similar under the two sets of conditions. Thus, the effect is much less than has been reported with caprolactam [11].

Figure 6 shows molecular weight results for polymerisation of valerolactone, VL, at an intensity of 25.4 W cm^{-2} at 150 ºC and 170 ºC. In related work [15], it was shown that the yield of polymer was larger in each case, for the sonochemical reaction at the same reaction time. Initially, the rise in chain length or molecular weight mirrors that in the thermal reaction although the chain growth occurs more rapidly under sonication. In contrast to the "silent" polymerisations the average molecular weight reaches a pronounced maximum and then falls steadily during prolonged sonochemical reaction. At the higher temperature, the maximum value was reached earlier in the reaction.

Similar behaviour was observed for experiments at four different ultrasound intensities as shown in Figure 7 although the effect is more pronounced at higher intensities. Also shown are the values from a conventional polymerisation. As the intensity of the ultrasound was increased, the maximum in the molecular weight occurred earlier in the reaction. There was no evidence of the molecular weight lowering degradation process in the thermal polymerisations.

A number of factors associated with sonication of polymer systems could account for these results. Sonication can promote very efficient mass transfer and mixing. In other polymerisations [7], it has been demonstrated that this can lead to good distribution of catalysts through reactants leading to efficient initiation of polymerisation. However, in these lactone systems the catalyst is soluble and, with the experimental procedures used, should be well dispersed prior to the reaction commencing. The harsh conditions of temperature and shear generated around collapsing cavitation bubbles could lead to **breakdown of the monomer**. This has been invoked in other ring-opening reactions [6] but this would seem to be more likely to generate radical species and this polymerisation is not very sensitive to radical species. Ragaini [11] showed that caprolactam could be melt polymerised without the addition of the usual initiator, water, suggesting that reactive intermediates could be generated by sonication alone. Thus, the faster reactions reported here are probably due to a combination of sonochemically generated intermediates combined with extremely efficient mixing and mass transfer.

Another possible explanation of the results would involve the well known shear degradation [10] associated with cavitational collapse to explain the molecular weight profile during the polymerisation. However, work on a wide range of polymer – solvent combinations suggests that this only becomes significant when the molecular weight exceeds $\sim$ 20000 – 25000 depending on the intensity used. Taking into account the observed molecular weights it is unlikely that these polymers included material of this length.

Further discussion

One explanation for the rate acceleration seen in both polymerisation systems would be the heating caused by sonication. However, the bulk temperature of the reaction mixture never rose to temperatures greater than $\sim$ 50 $^{\circ}$C and the sonochemical rates at low temperatures were faster than the "silent" versions at this temperature.

Among the chemical effects due to cavitation is the formation of radicals due to breakdown of the vapour entering the cavitation bubbles. However, this is unlikely to be an effect in these reactions.

Another possibility is that the catalyst action is modified in some way. Ligand exchange processes can be promoted under insonation and the formation of compounds with unusual oxidation states has been reported [16]. However, considerable sonochemical rate enhancements were observed in reactions with no catalyst so that this cannot be a complete explanation. It may play a part but other effects must also occur.

A number of attempts were made to follow the kinetics of the polyurethane formation. However, the experimental set-up made it very diffficult to achieve reproducible results due to the difficulty in obtaining consistent samples from the viscous mixture. To illustrate the effects, Figure 8 shows infra-red spectroscopic data for the reaction of $H_{12}MDI$ with butane diol at (initially) 25 °C. The reactions were sonicated or stirred for 30 min after which a small amount of the reacting mixture was spread onto a NaCl plate and mounted in the spectrometer and the reaction followed by the loss of the isocyanate carbonyl peak at 2256 cm^{-1} compared with the rise in the urethane carbonyl at 1695 cm^{-1}. The reaction initiated under ultrasound still proceeds at a faster rate even though sonication is not continued.

Thus, there are two main possibilities to explain the rate acceleration. Firstly, better distribution of the catalysts through the system due to the efficient microscopic mixing facilitated by ultrasound and secondly the possible formation of reactive intermediates at the catalyst site. As noted above, the former of these is unlikely to play a major part in the lactone polymerisation. In this case, there is the additional factor of the fall in chain length to explain.

It is known [17] that thermolysis of the backbone ester groups can occur during heating and that CL is more stable to this than VL. Indeed, with VL, the equilibrium mixture contains significant amounts of cyclic lactone in addition to the polymer. If the sonochemical enhancement of the reaction is due to efficient dispersal and/or activation of the catalysts, this may also promote the degradation. It is likely that a sonochemical acceleration of these processes means that the system approaches equilibrium faster under ultrasound. The mechanism of the tin catalysis of the reaction has been investigated by several workers. Kricheldorf [18] and Duda et al. [19] showed that the reaction proceeds by breakage of the Sn — OR bond at the catalyst and that propagation occurs via an acyl — oxygen bond scission in the lactone following a coordination-insertion reaction at the catalyst. With a number of active tin species formed. One effect that the sonochemical enhancement might occur is by promotion of these active species. A number of unusual ligand insertion reactions generating unusual coordination species have been reported [16] to occur under sonication and it may be that

sonochemical decomposition of either the catalyst (less likely) or the monomer leads to attack onto the

tin and activation of a tin — alkoxide bond. Further studies of the polymer structure including the

nature of the end-groups will be necessary to determine this mechanistic detail.

Conclusions

This work has show that the rates of reaction in step growth reactions can be accelerated by the use

of high intensity ultrasound. The source of the effect seems to be related to local heating around

collapsing cavitation bubbles together with the enhanced mass transfer caused by the fluid motion but

it is likely that an effect takes place to modify the mode of action of the catalysts in these systems.

This is currently under further investigation to ascertain the precise mode of action.

Acknowledgements

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Table 1. Preparation of polyurethanes containing VM10 (uncatalysed reactions)

Diol	Reaction Conditions	Polymerisation Time / min	Product
1,4 butane diol	Heat, 50 °C	60	Brittle material
1,4 butane diol	Heat, 80 °C	30	Brittle material
1,4 butane diol	Stir, 50 °C	10	Friable foam
1,4 butane diol	U.S., 20.1 W cm^{-2}	1	Friable foam
PEG300	Heat, 50 °C	120	Hard white polymer
PEG300	Heat, 80 °C	55	Hard white polymer
PEG300	Stir, 50 °C	10	Very viscous; hardens overnight
PEG300	U.S., 20.1 W cm^{-2}	1	Very viscous; hardens 5-10 min
PEG600	Heat, 80 °C	25	Hard, transparent material
PEG600	Stir, 50 °C	20	Very viscous; hardens overnight
PEG600	U.S., 20.1 W cm^{-2}	1	Tacky, transparent material. Hardens 5-10 min

CAPTIONS FOR SCHEMES AND FIGURES

Scheme 1. Structures of the diisocyanates used for polyurethane formation.

Scheme 2. Example of the repeat-unit formation during formation of polyurethanes.

Scheme 3. Polymerisation of cyclic lactones to the repeat-units in polyesters.

Figure 1. Comparison of polymerisation times (H_{12}MDI and 1,4-Butanediol) under varying reaction conditions.

Figure 2. Comparison of polymerisation times for H_{12}MDI with various diols.
Key: EG – ethylene glycol; Di – diethylene glycol; Tri - Triethylene glycol;
PEG – polyethylene glycol with the indicated average chain length.

Figure 3. The effect of ultrasound intensity on polymerisation time for H_{12}MDI polyurethanes.
Key: as Figure 2

Figure 4. Comparison of molecular weights for H_{12}MDI polymerised with various diols.
Key: as Figure 2

Figure 5. Comparison of poly(caprolactone) molecular weights for thermal and sonochemical (I = 18.4 W cm^{-2}) reactions at 150 ºC.

Figure 6. Poly(valerolactone) molecular weights for polymerisations at the indicated temperatures (ºC)
(See text for experimental conditions)
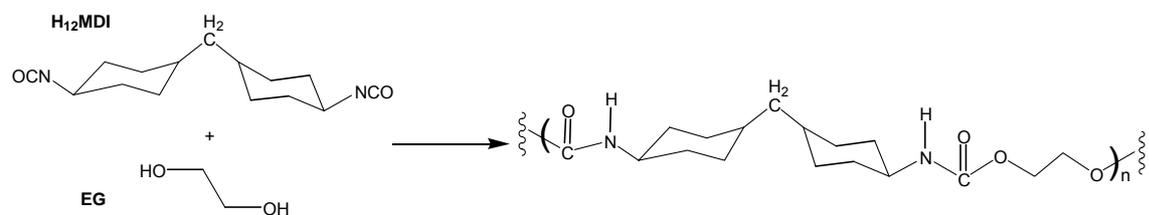
Figure 7. The effect of ultrasound intensity (indicated in W cm^{-2}) on the molecular weight of poly(valerolactone)s polymerised at 150 ºC.
(See text for experimental conditions)

Figure 8. Infra-Red spectroscopic monitoring of kinetics of formation of a polyurethane.
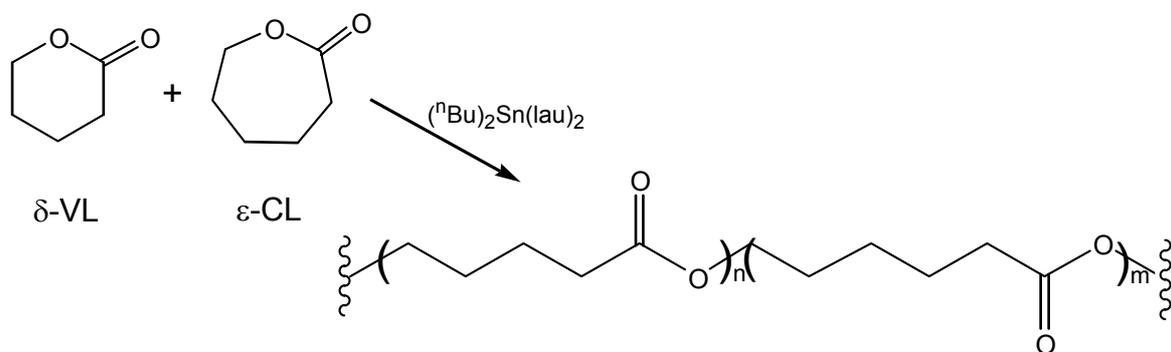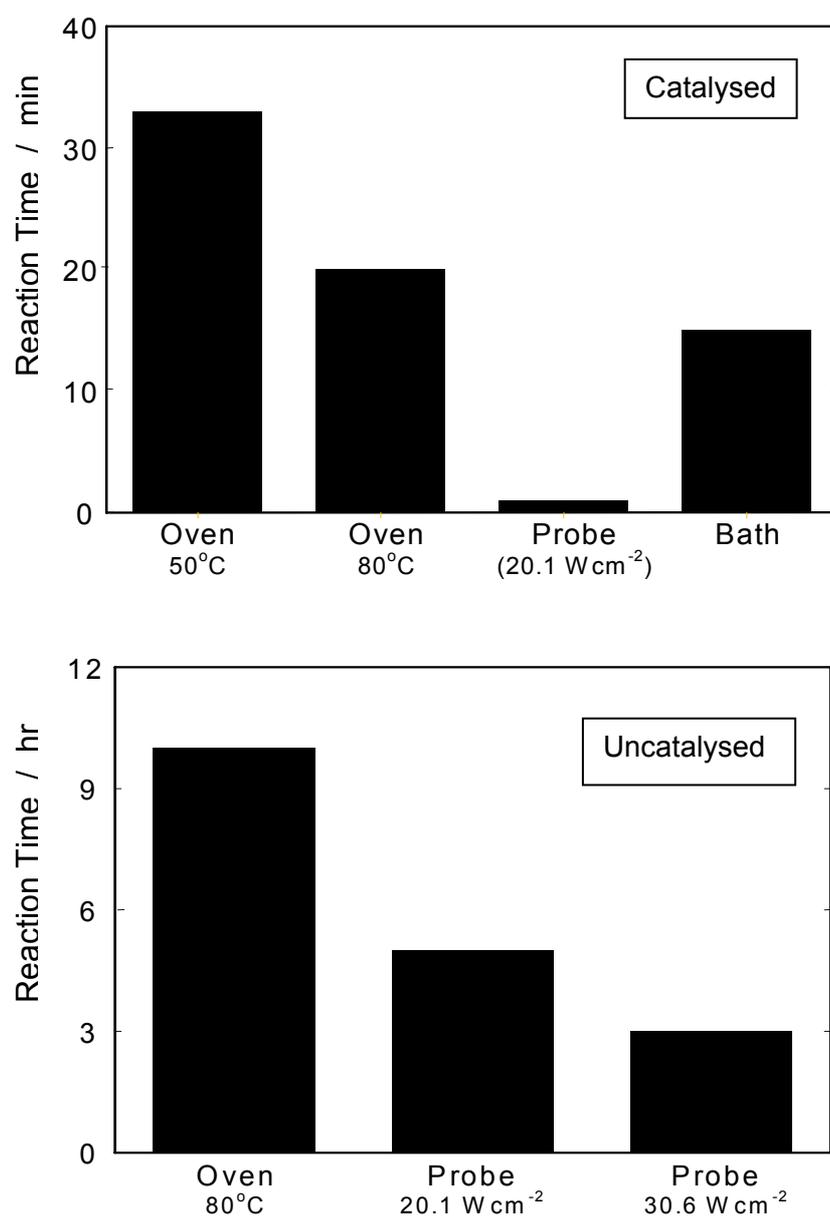(See text for experimental conditions)

Scheme 1

MDI

OCN—⬡—CH$_2$—⬡—NCO

TDI

OCN—⬡(—CH$_3$)(—NCO)

H$_{12}$MDI

OCN∿—⬡—C(H$_2$)—⬡—∿NCO

Scheme 2

H₁₂MDI

OCN — [cyclohexyl ring] — CH₂ — [cyclohexyl ring] — NCO

+

EG   HO—CH₂CH₂—OH

→

[polymer structure: $\{C(=O)-NH-[cyclohexyl]-CH_2-[cyclohexyl]-NH-C(=O)-O-CH_2CH_2-O\}_n$]

Scheme 3

[δ-valerolactone structure] + [ε-caprolactone structure] → (ⁿBu)₂Sn(lau)₂

δ-VL   ε-CL

[polymer structure: poly(valerolactone-co-caprolactone)]
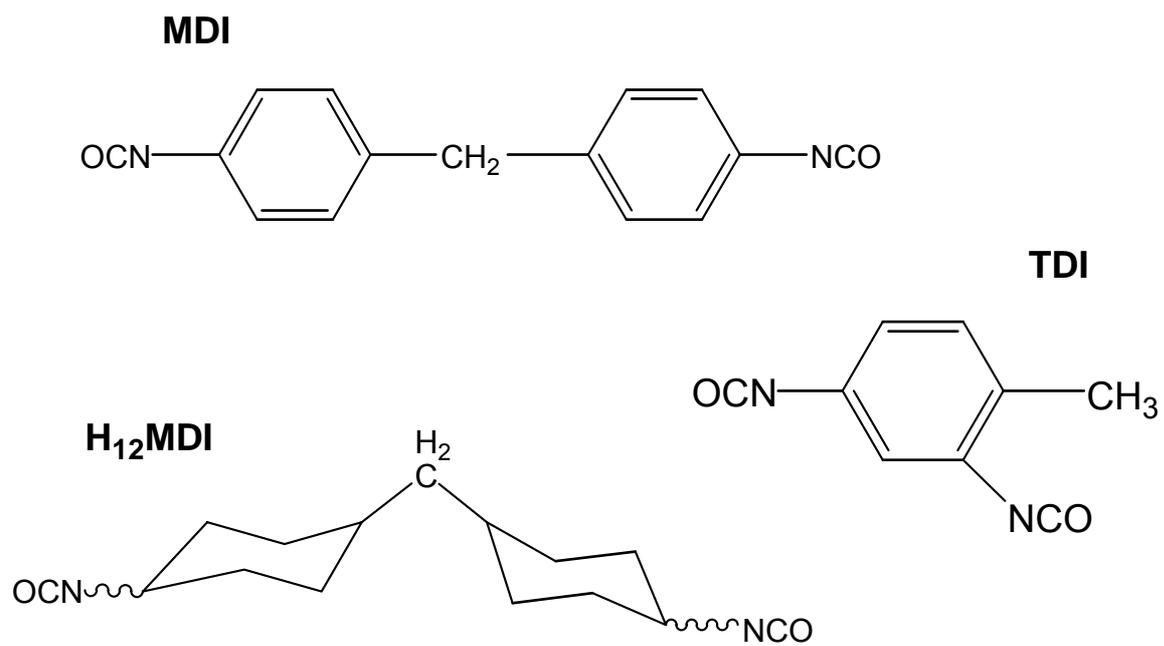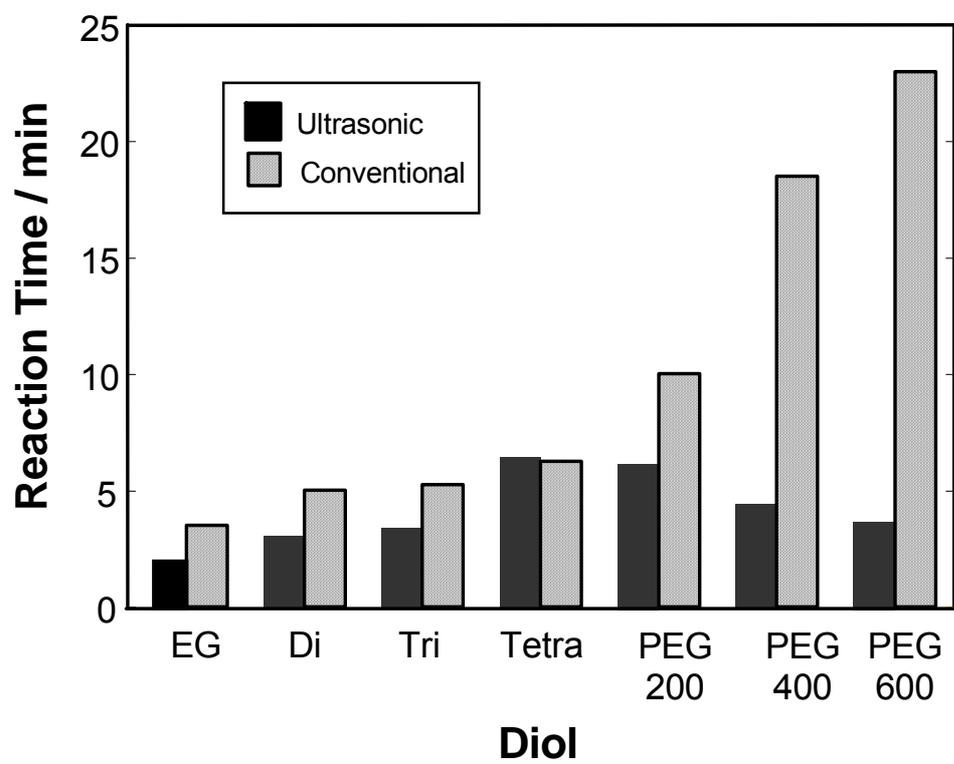
Figure 1

Figure 2

Figure 3
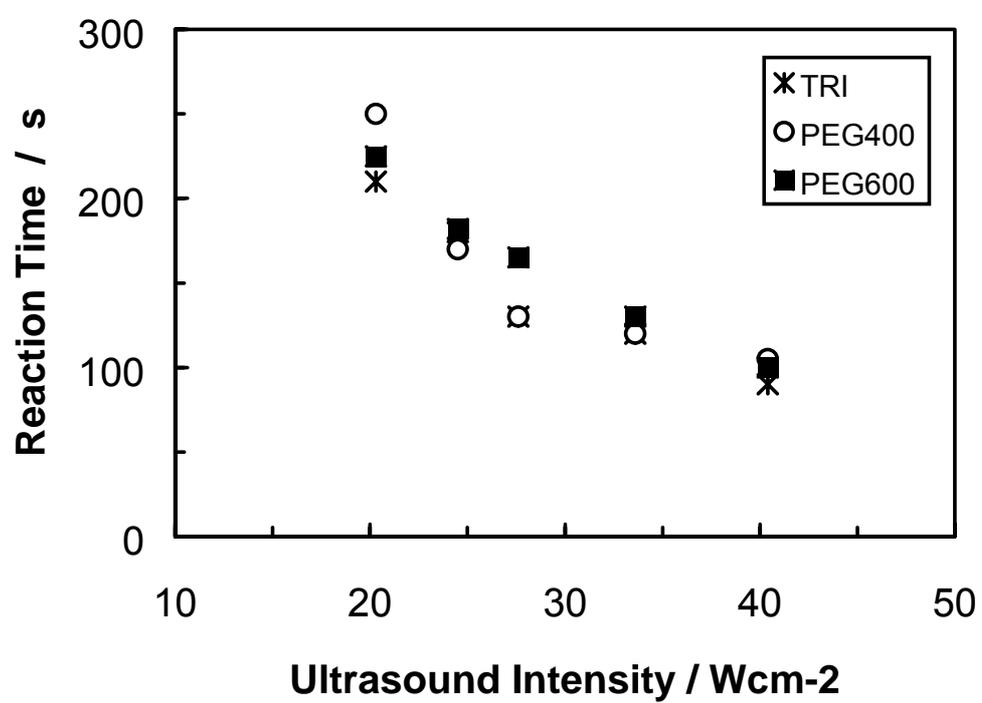
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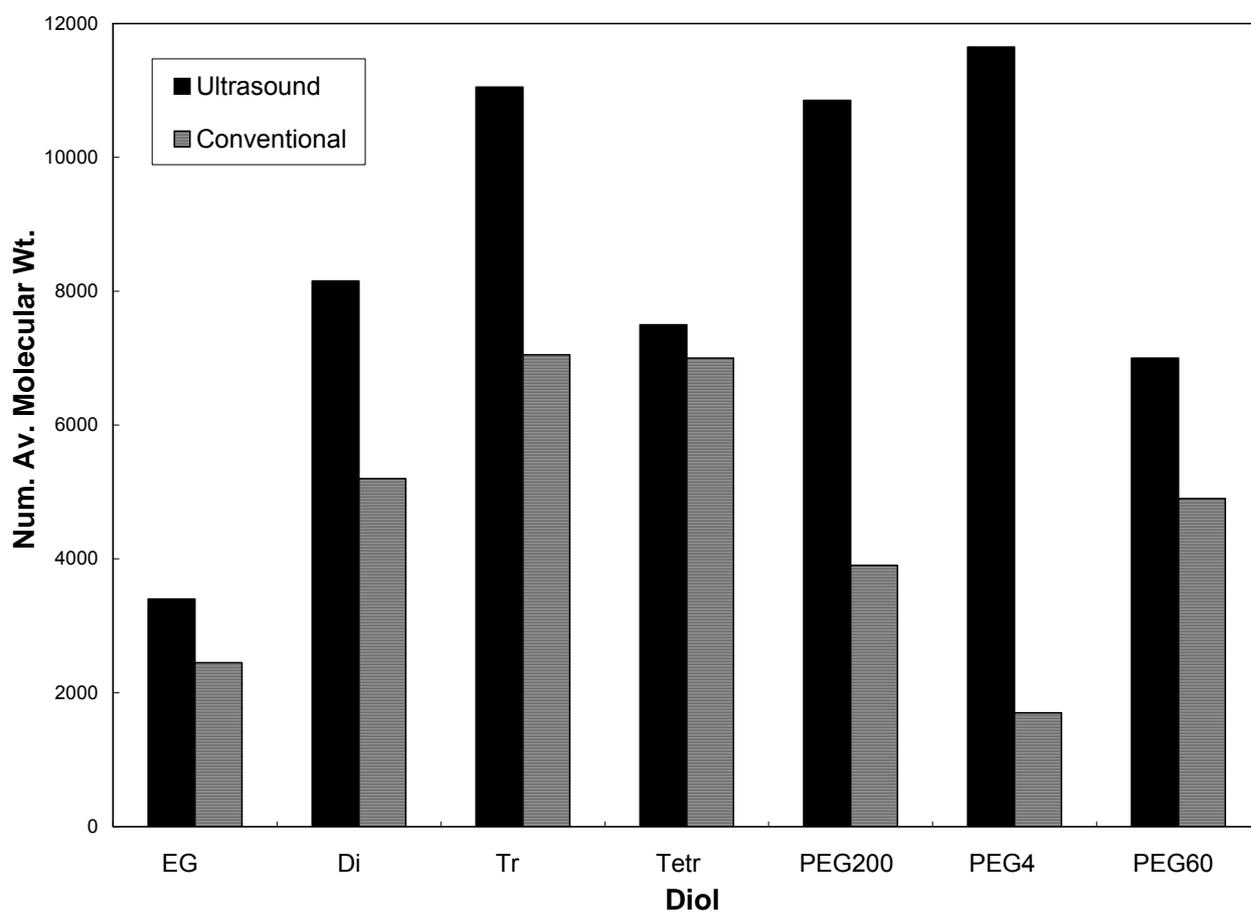
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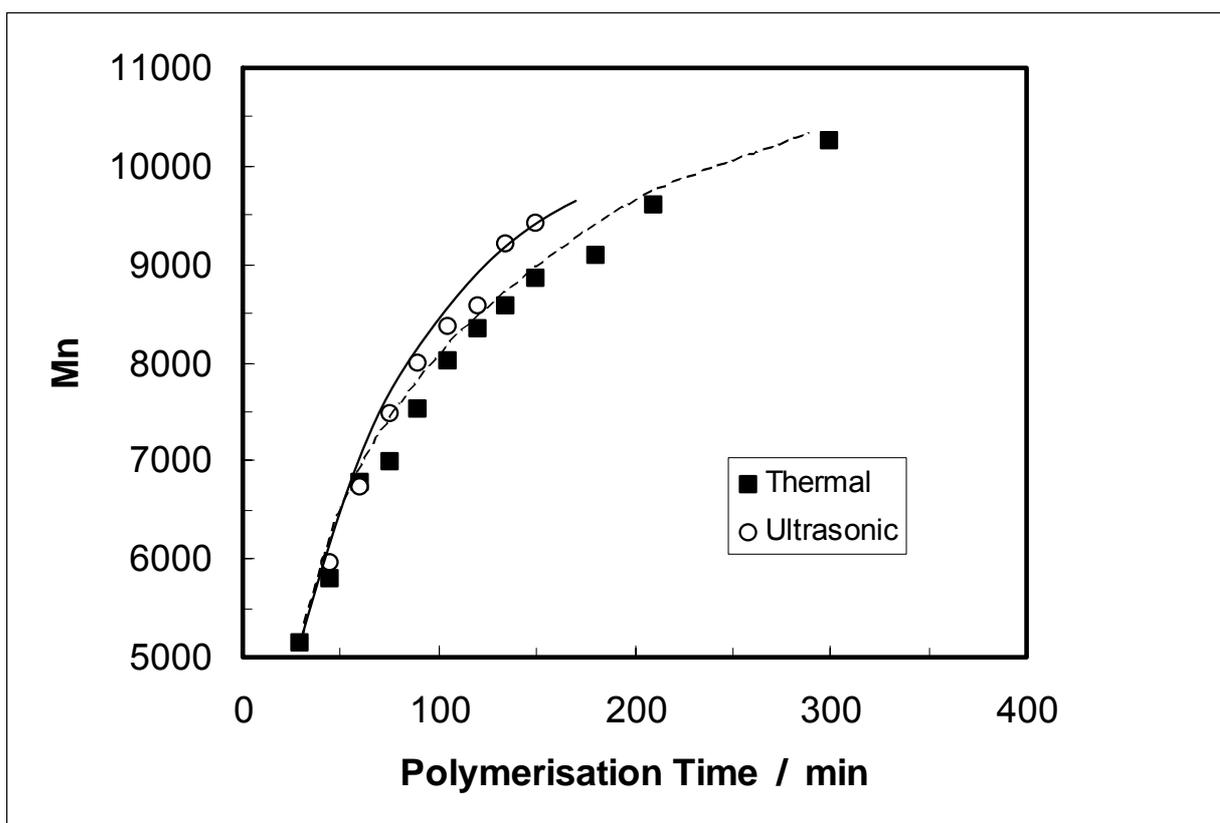
Figure 6

Figure 7

Figure 8