Ziegler–Natta polymerization under high intensity ultrasound

Gareth J. Price* and Ali M. Patel
School of Chemistry, University of Bath, Bath BA2 7AY, UK
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Ziegler–Natta polymerization of styrene using a titanium tetrachloride/triethyl aluminium catalyst system has been performed in the presence of high intensity ultrasound. The polymers are produced in better yield and with more control over the molecular weight distribution than in the conventional, unsonicated process.

(Keywords: Ziegler–Natta polymerization; sonochemical polymerization; ultrasound; molecular weight control)

Introduction

Over the past decade or so, the use of high intensity ultrasound has become an important tool in synthetic chemistry[1–3]. As well as very efficient mixing of reactants, a number of chemical effects have been shown to result from the process of cavitation or the rapid rise and collapse of microbubbles as the sound waves pass through the liquid. Among the beneficial effects have been enhanced rates of reaction, the use of less forcing conditions and, in a few cases, a switching of the reaction mechanism. A number of reaction types have been shown to benefit from sonication, particularly those involving a single electron transfer process and those utilizing heterogeneous catalysis[3].

We are involved in a programme studying applications of ultrasound in polymer chemistry and have used it to modify the structure of existing polymers[4,5] as well as to initiate radical polymerization[6,7]. This paper presents a preliminary communication of the effect of ultrasound on the heterogeneous, Ziegler–Natta polymerization of styrene, chosen as an easily characterizable model system. A small number of reactions of this type have been carried out with the aim of determining whether ultrasound could influence the rate and yield of the polymerization and also any effect on the molecular weight distribution and microstructure of the polymer.

Experimental

A titanium tetrachloride/triethyl aluminium ($TiCl_4$/Et_3Al) catalyst system was prepared[8] by adding, under nitrogen gas, 3.0 cm^3 of a 1 mol dm^{-3} solution of $TiCl_4$ in decalin and 1.0 cm^3 of a 1 mol dm^{-3} solution of Et_3Al in cyclohexane to 50 cm^3 of dry decalin. The resulting mixture was heated to 180–185°C for 1 h while the colour changed to a deep violet. The solution was cooled to room temperature and a further 6.0 cm^3 of the Et_3Al solution added along with 200 cm^3 of cyclohexane. Styrene (10 cm^3) was then added. All reagents were used as received from Aldrich Ltd (UK) except for decalin and styrene which were redistilled immediately prior to the polymerizations.

For these preliminary experiments, a laboratory cleaning bath was used as the source of the ultrasound[9]. The reaction flask was immersed in a Ney 2.8 L ultrasound bath operating at a nominal frequency of 35 kHz and power output of 110 W. The flask was contained in a thermostatically controlled bath for those experiments conducted in the absence of ultrasound. The polymer was recovered by precipitation into 500 cm^3 of ice cold methanol followed by redissolving in toluene and reprecipitation into 2-propanol.

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}. Ten polystyrene standards covering a range from 1950 to 1.4×10^6 were used to calibrate a Polymer Laboratories 60 cm 'Linear PL-Gel' column. N.m.r. spectra (^1H and ^{13}C) were recorded in $CDCl_3$ solution on a Jeol GX270 spectrometer.

Results and discussion

The polymerizations were first carried out using the conventional, stirred method, having prepared the catalyst both with and without ultrasound. Although the catalyst was not characterized directly, there were no significant differences in the polymers produced using either catalyst in a conventional polymerization. We then used the same catalyst in polymerizations at 30 and 60°C in the presence and absence of ultrasound. Some of the results are shown in *Table 1*; these results refer to reactions carried out for 18 h.

It can be seen that maintaining the sonication throughout the polymerization increased the rate of the reaction, leading to increased yields in comparable times and that the effect is more apparent at the lower temperature. However, it should be stressed that these

Table 1 Effect of ultrasound on Ziegler–Natta polymerization of styrene

	Temperature (°C)	Yield (%)	M_n	Polydispersity
Stirred	30	~5	53 650	11.90
Ultrasound	30	24	45 700	2.48
Stirred	60	20	8 100	40.50[a]
Ultrasound	60	56	39 800	2.59

[a] Bimodal distribution centred at ~10^6 and ~9000

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* To whom correspondence should be addressed

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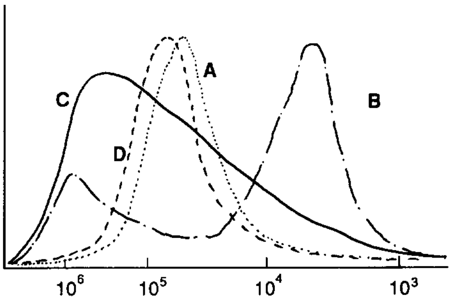

Figure 1 Gel permeation chromatograms of polystyrene: (A) ultrasound, 30°C; (B) stirred, 30°C; (C) stirred, 60°C; (D) ultrasound, 60°C

reactions were not optimized and our yields are rather low (optimization of the stirred reaction should lead to yields in excess of 95%)[8]. Rather, we reproduced reaction conditions (amounts of reactant, temperature, time, etc.) exactly except for the presence or absence of ultrasound to isolate the effect of the sonication.

The n.m.r. spectra of the polymers showed them, as expected, to be almost exclusively isotactic[10,11] (the quaternary phenyl carbon appears at 146.3 ppm in each spectrum with no peak at ~145 ppm in the ^{13}C spectrum) and differences induced by ultrasound in the ^1H n.m.r. spectra are insignificant. The g.p.c. chromatograms are shown in *Figure 1*, and the molecular weights and polydispersities are given in *Table 1*. The differences caused by sonication here are obvious. The stirred reactions give very broad distributions and it should also be noted that there was a substantial amount of toluene-insoluble polymer produced, as is common with this catalyst system[8]. In total contrast, the sonicated reactions gave no toluene-insoluble polymer and a narrower, well defined molecular weight distribution. It is possible that, particularly at the higher temperature, some radically initiated, thermal polymerization took place. However, blank experiments showed that any amount would be very small and the ultrasound intensities employed were too low to cause radical formation in any significant amount so that we attribute the results to the effect of ultrasound.

The reasons for the increased yields and rates of reaction are not totally clear but are probably related to sonication causing efficient mixing and faster mass transfer of monomer to the reaction site on the surface of the catalyst. There may possibly also be a reduction in the particle size and consequent increase in active area of the catalyst. One explanation for the usefulness of ultrasound in heterogeneous reactions has been that it has a cleaning action on the surface, resulting in a more homogeneous distribution of active sites. In our case, this would explain, at least in part, the more even distribution of molecular weights found. A second factor leading to a lower polydispersity is the well known ultrasonic degradation process[4] which produces uniform distributions although it would not be expected to be a particularly efficient process at the intensities generated in a cleaning bath.

Other work in our group[7,12] has shown that molecular weights during polymerization can be controlled by varying the properties of the ultrasound so that this may represent a method of molecular weight control during Ziegler–Natta polymerization, a factor that is difficult to control by current techniques. Further work is under way to more fully characterize the process with a wider range of monomers.

Conclusions

This work suggests that application of ultrasound can have a beneficial effect on Ziegler–Natta polymerizations. The stereochemistry appears to be unaffected but the resulting polymers have relatively narrow, well defined molecular weight distributions so that the method may prove to be a useful way to control the structure of polymers produced by this method.

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