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A convenient route to high molecular weight highly isotactic polystyrene using Ziegler–Natta catalysts and ultrasound

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Abstract

Ziegler–Natta ($TiCl_4/AlEt_3$) catalysts and ultrasound were used to prepare highly isotactic polystyrene (ca. 99%) with a molecular weight of 4.7×10^6 mol g^{-1} and low molecular weight distribution ($M_w/M_n = 1.6$) via a convenient method. Ultrasound was most effective if applied only during an initial stage in the polymerisation, most likely permitting dispersion of catalyst particles which were subsequently coated and separated by growing polymer chains. Yields could be improved by varying the amount of catalyst and reaction time. © 2002 Published by Elsevier Science Ltd.

Keywords: Ziegler–Natta catalysts; Isotactic polystyrene; Ultrasound

1. Introduction

Since Ziegler–Natta catalysts, based on $TiCl_4/AlEt_3$, were used to prepare highly isotactic polystyrene [1–4], iPS, not inconsiderable amount of work has gone into both ameliorating and simplifying the use of these aggressive reagents [5,6]. While composition and 'ageing' of catalysts have been shown to be determinate in yielding highly iPS [6], iPS formed via this route has a high molecular weight distribution, or high MWD (ca. 8) necessitating time-consuming polymer fractionation to recover monodisperse high molecular weight iPS.

Alternate systems have been discovered. Anionic polymerisation of styrene at low temperatures, in the presence of ^{t}BuOLi or LiOH, has been shown [7,8] to yield iPS with only 90% *mm* triads of high molecular weight but again with a high MWD. A Solvay-type catalyst ($TiCl_3$–Cp_2TiMe_2) yielded highly iPS (>99%) with a high molecular weight (ca. 1.2×10^6 g mol^{-1}) but also high MWD (8.5) [9]. $TiCl_4$–$PCl_3/MgCl_2$–$AlEt_3$ based catalyst yielded 94% iPS with a high molecular weight (ca. 2×10^6 g mol^{-1}) of unknown MWD [10]. Nickel based catalysts combined with methylaluminoxane have promisingly yielded extremely iPS (99%), but molecular weights have been limited with MWDs increasing with masses attained [11–14]. Neodymium based catalysts have also shown use in forming iPS, although to our knowledge, iPS molecular weights have not been described in this method [15].

It was with interest therefore that the paper of Price and Patel [5] was studied, as it described the formation of iPS of low MWD with convenient Ziegler–Natta catalysts using ultrasound. While the methodology has been considered as non-optimised, and the iPS formed was of a medium molecular weight (ca. 1.1×10^5 g mol^{-1}, MWD ca. 2.5), this system was seen as being modifiable to yield high molecular weight and highly iPS. Ultrasound disperses particles in heterogeneous mixtures and forms micro-jets of reagents against solid catalyst particles, aiding mass transfer and yielding homogeneous polymer chain growth. But it also facilitates radical and single electron step reactions and, at high powers, may indeed rupture polymer chains and form radical initiating centres from styrene, solvent and PS due to the formation of rapidly expanding and collapsing micro-cavities in a process of 'cavitation' [16–18].

In our laboratory, iPS of high mass (>10^6 g mol^{-1}), high tacticity and low MWD (<2) was required for further studies, for example, characterising the influence of tacticity on rheological properties in the melt state. We followed the work of Price and Patel [5] with the aim of increasing the mass and decreasing the MWD of iPS thereby obtained. Thus, modifications were made to their methodology which incidentally resulted in a more convenient synthesis of iPS.

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Table 1
Polymerisation parameters and molecular weight distributions of resulting iPS

Sample	Styrene (g)	Toluene (ml)	Catalyst (ml)	Duration (h)	Yield (%)	M_w	Mp	M_w/M_n
1	4.6	4	0.6	3	4.5	752 000	892 000	1.7
2	4.6	4	6	3	64	1 155 000	1 732 000	10.6
3	4.6	30	6	3	19	88 100	1 394 000	7.4
4	4.6	60	6	3	17	80 200	1 031 000	8.0
5	4.6	4	12	3	68	1 035 000	1 632 000	11.0
6	4.6	0	8	3	49	756 000	341 000	12.4
7	4.6	4	0.6	18	14	2 400 000	1 710 000	1.6
8[a]	360	300	49	18	9.6	4 720 000	4 190 000	1.6
9[b]	4.6	4	0.6	18	45	2 220 000	2 000 000	1.5
10[c]	4.6	4	0.6	18	50	1 710 000	1 560 000	1.4

[a] Ultrasound applied for initial 2 h only, during which time T raised from 30 to 60 °C.

[b] Ultrasound applied for initial 15 min only, during which time T raised from 30 to 60 °C.

[c] Ultrasound applied for initial 30 min only, during which time T raised from 30 to 60 °C.

2. Experimental

2.1. Ultrasound equipment and application with various samples

A 400 W Vibra Cell™ (Bioblock Scientific, France) was used at maximum amplitude to supply ca. 100 W for Samples 1–7. A 500 ml water bath was used to transfer ultrasound energy from the probe to the reaction vessel and to maintain a constant temperature. Both Schlenk tube and probe (radiating diameter of 13 mm operating at 20 kHz) were immersed to a depth of ca. 4 cm. Sample 8 was prepared using a 2.2 l, 60 W standard cleaning ultrasonic bath operating at 47 kHz (Branson 2200, France). Samples 9 and 10 were prepared using the former apparatus at ca. 60 W.

2.2. General

Schlenk techniques were used throughout unless otherwise stated: vessels were flame dried and flushed with dried nitrogen. Toluene (JT Baker, France) was distilled from over molten sodium under nitrogen. Styrene (Aldrich, France) was distilled from over CaH_2 under nitrogen. Triethylaluminium (1.0 M solution in hexanes), titanium(IV) chloride (99.9%) and butan-2-one were used as supplied (Aldrich, France).

2.3. Catalyst preparation

$TiCl_4$ (0.11 ml, 1×10^{-3} mol) was injected into a 50 ml Schlenk tube and cooled to 0 °C with an ice bath. $AlEt_3$ (3×10^{-3} mol), as a 1.0 M solution in hexanes (3 ml), was slowly added to the stirred $TiCl_4$ during a period of 5 min (caution, this reaction may be extremely violent unless the $AlEt_3$ is added slowly). The mixture was left to 'age' for 30 min at 25 °C [6].

2.4. Polymer preparation

The following is a standard method. To a 100 ml Schlenk tube equipped with a stirring bar, styrene (5 ml, 4.6 g) freshly distilled under vacuum from over CaH_2 was injected. Toluene (4 ml) was injected and the mixture stirred at 25 °C for 1 min. Catalyst (0.6 ml, 1.9×10^{-4} mol with respect to Ti) was quickly added, the ultrasound started immediately, and the mixture warmed slowly to 60 °C. Table 1 shows variations in reaction duration and quantities of reagents used. In the case of Sample 8, a 1 l Schlenk tube was used to accommodate the reagents.

2.5. Recovery of isotactic polymer

The resulting black, highly viscous mixture was transferred into toluene (1 l) with ethanol (50 ml; to neutralise catalyst) and stirred at 100 °C for 4 h. Insoluble, yellow material was removed by centrifuge, and the polymer precipitated in ethanol (4.5 l). Once recovered, the polymer was washed repeatedly with acetone, dried in air during 1 h, and placed in a 250 ml vessel equipped with a condenser and containing methyl ethyl ketone (butan-2-one) (150 ml). After refluxing for 3 h, to remove most atactic polystyrene, the white polymer was again washed with acetone and dried under vacuum for 12 h. Sample 8 was recovered in a similar manner with the exception that 5 l of toluene was used to recover polymer which was subsequently precipitated in ethanol (15 l) and was purified with refluxing butan-2-one (2 l) for 3 h.

2.6. Characterisation

Molecular weight determinations by gel permeation chromatography relative to polystyrene standards were carried out using a bank of four columns (HR 0.5, 2, 4 and 6®) of 300 mm × 5 μm Styragel at 40 °C, with THF eluent at a flow rate of 1.0 ml min^{-1}, controlled by a Waters® 2690 pump equipped with an ERC® INC 7515A refractive index detector and a Waters® 996 multiple wavelength

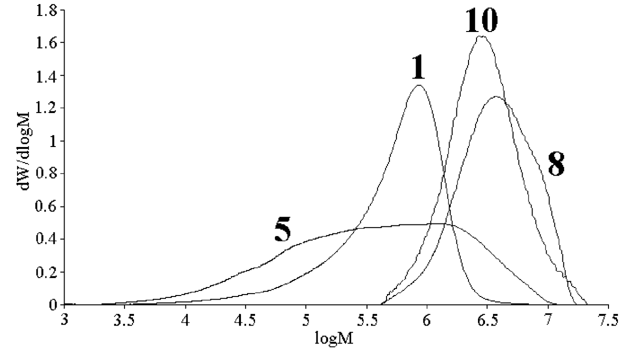

Fig. 1. GPC resolved molecular weight curves of representative samples. Samples 1, 5, 8 and 10 as referred to in Table 1.

UV–Vis Photodiode Array Detector. ^{13}C (100 MHz) NMR spectra were recorded on a Bruker® Avance 400 spectrometer at 100 °C in deuterated tetrachloroethane.

3. Results and discussion

One of the main aims of this work was to provide a convenient route to iPS. Thus, toluene was used as a solvent (being safer to handle than the more normally used benzene), classical Ziegler–Natta catalysts were used and iPS work-up was restricted to precipitation from toluene in ethanol and subsequent refluxing of the reaction products in butan-2-one to remove atactic (and remaining oligomeric) polystyrene.

The work of Price and Patel [5] used the same catalytic system, i.e. $TiCl_4/AlEt_3$, however, their preparation of catalyst was different: 1 M solutions of $TiCl_4$ and $AlEt_3$ were mixed in decalin at ca. 180 °C, then cooled and additional $AlEt_3$ was added up to make up the stoichiometric ratio $TiCl_4/AlEt_3 = 1/3$. We found that mixing reagents in their concentrated state and ageing the catalyst at room temperature [6] to be a more convenient and reliable route, regardless of other experimental conditions.

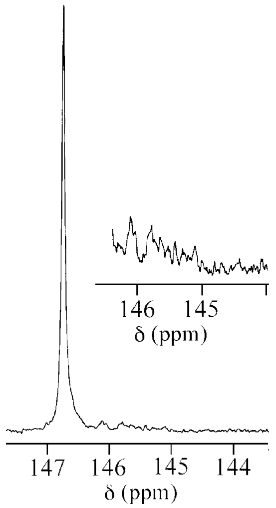

Fig. 2. Representative ^{13}C NMR of iPS (Sample 7), prepared using ultrasound throughout reaction, showing peak due to quaternary carbon at 146.7 ppm (inset zoom 4 × vertical scale).

It should be stressed that this was an initial study on the effect of varying reaction conditions on the MWDs of resulting polymers and does not attempt to optimise this system. We concentrated on varying amounts of catalyst and solvent with respect to styrene used and considered the period of ultrasound application. Samples 1–7 were prepared with continuously applied ultrasound, whereas Samples 8–10 were subjected to ultrasound during the initial reaction stage. Ultrasound was not used during preparation of catalysts as this has been shown to have no noticeable effect [5].

Ziegler–Natta catalysts used without ultrasound typically yield iPS with high, multi-modal MWDs, and this is generally thought to arise from variations in catalyst particles within a heterogeneous mixture [5]. With ultrasound, catalyst particles are dispersed and micro-jets of styrene and solvent move against the particles increasing mass transfer of reagents and resulting in a more homogeneous mixture and iPS with lower MWD [5,17]. Sample 1, as shown in Fig. 1, verifies this statement. However, it can be seen in Table 1 that increasing the amount of catalyst (e.g. Sample 1 versus Sample 2) improved the yield, but also the MWD increased from below 2 to above 10. It is interesting to note that in the case of Samples 2–6, even with ultrasound, iPS was formed with a MWD noticeably more multi-modal than polymer formed without ultrasound at the same temperature [5]. This result may have been due to incomplete catalyst particle dispersion and particles participating in violent cavitation processes giving rise to surfaces against which aggressive jet-streams [18] of solution may break down iPS. Visual inspection of shoulders and peaks of the MWD curve of Sample 2 (Fig. 1) showed that each peak is approximately one-half the molecular weight of the preceding peak. As it is known that the cavitation process tends to rupture polymers at their midpoint [17], the idea is therefore not completely without foundation.

Increasing the amount of solvent did not greatly affect the reaction, except that the molecular weights and MWDs decreased slightly (Samples 2–4). When a high excess of toluene was used, the recovered polymer solution retained a slight yellow colour indicative of the presence of 'coloured compounds', probably oligomers formed from styrene and toluene radical species induced by ultrasound rupturing molecules [16]. This effect was noticeable in Sample 4 and was most likely due to low catalyst concentration reducing the effective rate of styrene consumption (and therefore increasing the time during which styrene remained in solution), and the lower vapour pressure of styrene/toluene mixture allowing a more aggressive micro-cavitation process (and therefore forming a higher concentration of radical species) [16]. Although not completely exact, due to carbon atoms being decoupled from protons, integration over peaks from quaternary carbons in near identical environments in the ^{13}C NMR of a representative

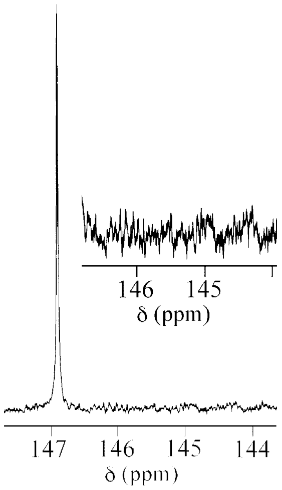

Fig. 3. Representative ^{13}C NMR of iPS (Sample 8), prepared using ultrasound for initial period of reaction, showing peak due to quaternary carbon at 146.9 ppm (inset zoom 4 × vertical scale).

low MWD iPS (Fig. 2) showed that the polymer contained a proportion (ca. 5–10%) of atactic segments, as evidenced by peaks between 145.7 and 146.2 ppm (peaks at 146.1 and 145.8 ppm indicated the presence of *mr* triads) [14,19,20]. This may have been due to the incorporation of radically polymerised styrene into the polymer mixture, initiated either by low molecular weight species or by cleaved iPS.

While retaining the same quantities of catalyst as used for Sample 1, Sample 7 was prepared by increasing the duration of polymerisation, from 3 to 18 h. Both yield and molecular weights increased and MWD slightly decreased, indicating that active catalytic sites were neither formed nor depleted during the course of the reactions. The ultrasound, in dispersing catalyst and 'jet-streaming' styrene formed a homogeneous size distribution of polymer covered particles which could not recombine; and any further chain growth must occur at sites already used. This brings to mind the original work of Natta et al. [1], which showed that after an initial period of agitation, the reaction products did not vary, independently of whether or not agitation was continued.

Realising that (i) high catalyst concentration coupled with relatively high power ultrasound could be rupturing formed iPS and introducing atactic PS via radical polymerisations; (ii) radical polymerisation of styrene by ultrasound is known to stop once ultrasound is arrested [21]; (iii) ultrasound may only be effective in the earlier stages of the reaction, a polymerisation was attempted using a lower power ultrasound only during an initial stage. Sample 8 shows the result of applying this thinking. Catalyst was used at a low concentration, possibly explaining the low yield of iPS. The molecular weight of the resulting iPS is extremely high, while maintaining a low MWD. It should be noted that the GPC curve of Sample 8 has a high molecular weight shoulder resulting either from additional polymerisations starting during the 'silent' period, rupturing of polymer by ultrasound or a discontinuous breakdown of catalyst and polymer particles. iPS (Sample 8) was extremely isotactic (ca. 99% indicated by integration over a single peak at 146.9 ppm and indistinguishable peaks in the region associated with *mr* triads as shown in Fig. 3) indicating a limitation of radical based reactions. These results therefore show that the polymerisation occurred as previously reasoned.

In an attempt to prepare high molecular weight iPS without a minor secondary peak, the polymerisation was performed again using low power ultrasound but only for 15 or 30 min (Sample 9 or 10, respectively, Table 1). As for Sample 7, the former yielded a polymer with a bimodal MWD, while the latter a mono-modal MWD (Fig. 1), which shows that reaction can be optimised with respect to duration of ultrasound. This would indicate that proper catalyst dispersion, rather than polymerisations started under ultrasound or 'silent' conditions, is the determining factor when aiming for mono-disperse iPS. Sample 10 results from 'optimum' timing of ultrasound and silent periods given the nature of the equipment used (which was different to that used for Sample 8), and resulted in a reasonable yield of high molecular weight and low MWD iPS. This result is caused by good catalyst dispersion which probably did not occur in case of Sample 9 and minimised polymer and polymer/catalyst particles rupturing unlike that found for Sample 8.

4. Conclusions

The method described is a convenient route to extremely iPS with mass over 10^6 g mol^{-1} and MWD below 2 without resorting to complex polymer fractionation techniques. It has been found that the use of ultrasound is effective in synthesising high molecular weight polymers, but only when it is used during initial stages of the heterogeneous reaction. Most probably, ultrasound disperses catalyst particles throughout the reaction medium, while 'jet-streams' of monomer against catalyst particles ensure that polymerisation sites are occupied and that catalyst particles do not recombine. It is expected that this technique may be extended to other heterogeneous systems but in each case, the reaction conditions should be modified appropriately with respect to the materials and equipment used.

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References

[1] Natta G, Pino P, Mantica E, Danusso F, Mazzanti G, Peraldo M. Chim Ind 1956;38:124.
[2] Danusso F, Sianesi D. Chim Ind 1958;40:450.

[3] Danusso F, Sianesi D, Calcagno B. Chim Ind 1958;40:628.
[4] Danusso F, Sianesi D. Chim Ind 1958;40:909.
[5] Price GJ, Patel AM. Polymer 1992;33(20):4423.
[6] Kern RJ, Hurst HG, Richard WR. J Polym Sci 1960;45:195.
[7] Cazzaniga L, Cohen RE. Macromolecules 1989;22:4125.
[8] Makino T, Hogen-Esch TE. Macromolecules 1999;32:5712.
[9] Soga K, Yanagihara H. Makromol Chem Rapid Commun 1988;9:23.
[10] Sun Q, Fan Y, Liao S, Liu J, Wan F, Xu J. Polymer 2001;42:4087.
[11] Ascenso JR, Dias AR, Gomes PT, Romão CC, Pham Q-T, Neibecker D, Tkatchenko I. Macromolecules 1989;22:998.
[12] Crossetti GL, Bormioli C, Ripa A, Giarrusso A, Porri L. Macromol Rapid Commun 1997;18:801.
[13] Po R, Cardi N, Santi R, Romano AM, Zannoni C, Spera S. J Polym Sci A, Polym Chem 1998;36:2119.
[14] Longo P, Grassi A, Oliva L, Ammendola P. Makromol Chem 1990;191:237.
[15] Liu L, Gong Z, Zheng Y, Jing X. J Polym Sci A, Polym Chem 1998;36:1773.
[16] Kruus P, McDonald D, Patraboy TJ. J Phys Chem 1987;91:3041.
[17] Price GJ. In: Ebdon JR, Eastman G, editors. New methods of polymer chemistry, vol. II. Glasgow: Blackie, 1995. Chapter 9.
[18] Price GJ. Ultrason Sonochem 1996(3):S229–38.
[19] Kawamura T, Toshima N. Macromol Rapid Commun 1994;15:479.
[20] Chen TK, Harwood HJ. Makromol Chem Rapid Commun 1983;4:463.
[21] Kruus P. Adv Sonochem 1991;2:1.