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# Polyolefin-polar block copolymers from versatile new macromonomers

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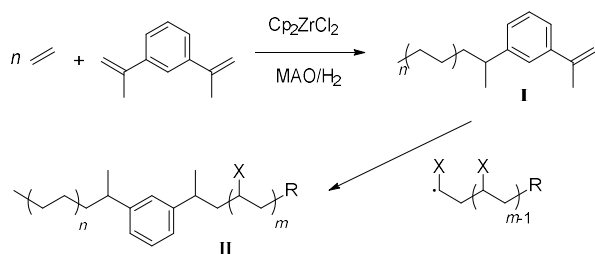
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**ABSTRACT:** A new metallocene-based polymerization mechanism is elucidated in which a zirconium hydride center inserts  $\alpha$ -methylstyrene at the start of a polymer chain. The hydride is then regenerated by hydrogenation to release a polyolefin containing a single terminal  $\alpha$ -methylstyrenyl group. Through the use of the difunctional monomer 1,3-diisopropenylbenzene, this catalytic hydride insertion polymerization is applied to the production of linear polyethylene and ethylene-hexene copolymers containing an isopropenylbenzene end group. Conducting simple radical polymerizations in the presence of this new type of macromonomer leads to diblock copolymers containing a polyolefin attached to an acrylate, methacrylate, vinyl ester or styrenic segments. The new materials are readily available and exhibit interfacial phenomena, including the mediation of the mixing of immiscible polymer blends.

## INTRODUCTION

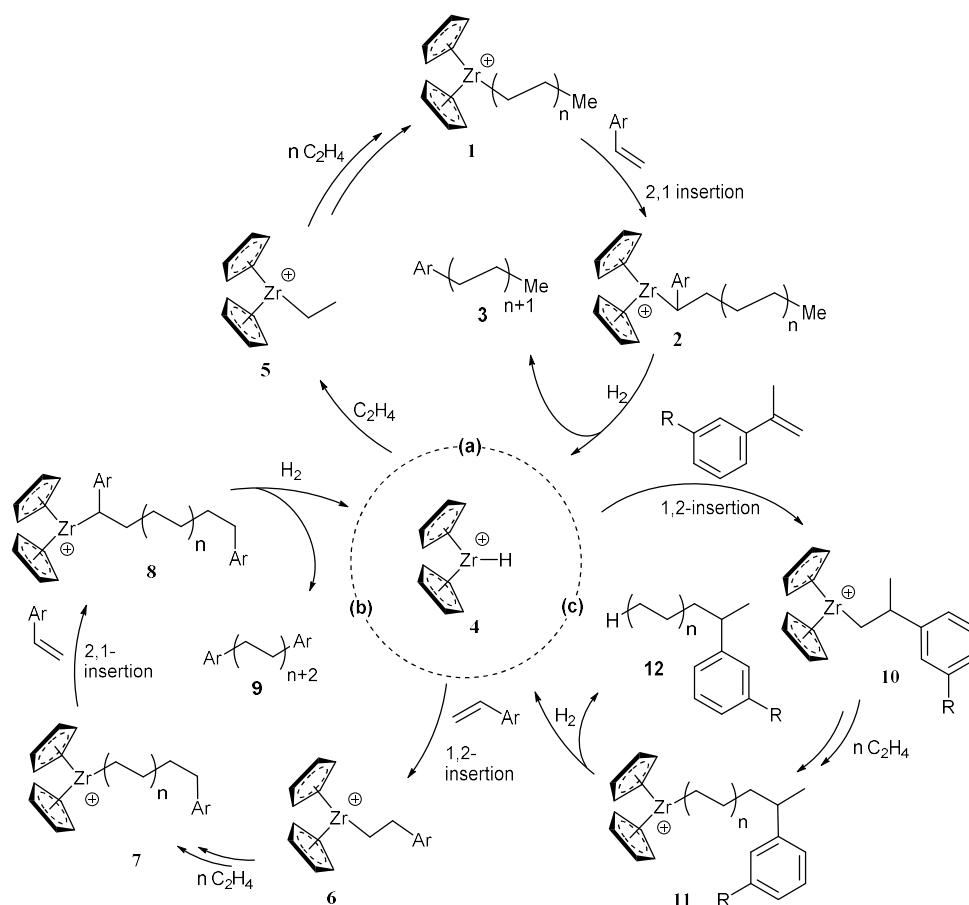
Polyolefins pervade most aspects of modern life, with applications facilitated by their efficient and low cost production, lightness, and durability. They are however almost totally inert and immiscible with other materials and polymers. These features present problems in recycling, printing, coating, adhesion, impact modification, composites manufacture<sup>1, 2</sup> and many other practices that rely on favourable properties of an interface/interphase. There is thus a substantial unmet need for interface-modifying polymer additives.



**Figure 1.** The new block copolymer synthesis described in this work.

Existing commercial polymer systems are largely based on random/statistical copolymers such as poly(ethylene-vinyl

acetate), or grafted systems typically made by reactive extrusion of the base polyolefin with maleic anhydride. These have architectures far from ideal for the purpose because they cannot efficiently span the phase boundary between the two immiscible materials.<sup>3, 4</sup> Ready access to truly amphiphilic copolymers containing polyolefin (PO) and polar polymer (PX) segments, such as diblock copolymers PO-*b*-PX, would present an opportunity to revolutionise the uses of polyolefins in higher value applications as well as for example improving the value of recycled polymers.<sup>5</sup> The production of such interface-active polyolefins remains one of the great technical challenges in polymer synthesis, not least because of the great differences in reactivity of the two monomer types. So, while radical polymerization works well for polar monomers and styrenes, simple olefins usually require very high temperatures and pressures.<sup>6, 7, 8, 9</sup> At the same time, Ziegler-Natta/metallocene methods for polyolefin synthesis are adversely affected by the presence of polar monomers and even styrenes.<sup>10, 11, 12</sup> Long-established anionic polymerization processes are used commercially to make diene/styrene block copolymers, but exacting conditions are necessary, few monomers are tolerated and hydrogenation is required to furnish the polyolefin-like block.<sup>13, 14</sup> A variety of strategies have been described in an attempt to provide such polymers.



**Figure 2. Olefin polymerisations in the presence of dihydrogen.** (a) The Chung mechanism describes ethylene insertion at the hydride cation **4** giving **5** and eventually the dormant (or insertion-resistant) species **2** which is hydrogenated to give the observed product **3**; (b) we find however that **4** must also be susceptible to 1,2-insertion of styrene because some chains (**9**) bear a styrene unit at both ends; (c) this creates a new opportunity to use  $\alpha$ -methylstyrenes to give functionalized polyolefins like **12**.

Living alkene polymerization has been utilized by Yasuda and co-workers in the synthesis of polyolefin block copolymers with alkyl methacrylates and lactones *via* sequential monomer addition using lanthanide catalysts.<sup>15,16</sup> An organometallic-mediated radical polymerization strategy was employed by Detrembleur and co-workers<sup>17</sup> to directly polymerize ethylene with several polar monomers under mild conditions. Catalytic chain transfer to various heteroatoms has also been reported.<sup>18</sup> Yagci and co-workers<sup>9</sup> recently described the thermally-induced controlled radical polymerization of iodo-functionalized PE with methyl methacrylate using  $\text{Mn}_2(\text{CO})_{10}$ .

Various multi-step polymerization strategies have been developed.<sup>1,19,20,21</sup> Catalytic olefin polymerization has been used to produce macroinitiators for ATRP,<sup>22,23</sup> NMP,<sup>24,25</sup> ROP,<sup>26,27</sup> RAFT,<sup>28,29</sup> cationic<sup>19</sup> and anionic<sup>30,31,32,33,34,35</sup> methods. ATRP<sup>36,37</sup> and RAFT<sup>38</sup> systems have also been prepared *via* ROMP methods. The one-pot combination of polyhomologation (or C1 polymerization) with anionic<sup>39</sup> and cationic<sup>40</sup> polymerization to produce PE block copolymers has also been reported.

Although significant advances have thus been made and a good number of examples of block or block-like copolymers with interesting properties have been prepared, all the protocols feature drawbacks such as low productivity, multi-step procedures, or the use of expensive or sensitive reagents or processes.

Here we report the discovery of a simple new polymerization mechanism that provides large quantities of polyolefin macromonomers such as **I** (Figure 1) in high catalytic productivity. These are converted under standard free-radical conditions with a variety of monomers to copolymers **II** with tuneable amphiphilic properties. The chemistry is conducted under scalable conditions with conventional apparatus and reagents. The products show great promise as interface modifiers for the types of application described above.

**Table 1. Ethylene copolymerisations with styrenes in the presence of dihydrogen.**

Run <sup>a</sup>	Comonomer <sup>b</sup>	[Comonomer] (mol/L)	H <sub>2</sub> (psi)	GPC <sup>c</sup>			Yield (g)	Productivity/kg/molZr.h	Styrenic end groups (%) <sup>d</sup>	T <sub>m</sub> (°C)
				M <sub>n</sub> (g/mol)	M <sub>w</sub> (g/mol)	Dispersity (Đ)				
1	STY	1.0	20	3000	6300	2.1	15.0	18000	100	123
2	STY	2.0	20	3200	4800	1.5	10.7	13000	156	118
3	AMS	2.0	20	2900	6100	2.1	9.90	12000	93	123
4	AMS	2.0	40	2800	3800	1.4	11.4	14000	96	120
5	AMS	2.0	60	2500	3600	1.5	12.1	14000	95	117
6 <sup>e</sup>	AMS	7.2	60	2400	3500	1.5	7.40	8900	97	118
7	DIB	1.0	20	3400	5000	1.5	10.4	13000	100	122
8	DIB	2.0	20	2600	6300	2.4	6.30	7500	100	123
9	DIB	2.0	40	3600	4800	1.4	10.5	13000	98	121
10	DIB	2.0	60	2900	4600	1.6	11.0	13000	96	121
11 <sup>f</sup>	DIB	2.0	90	2100	4000	2.0	11.9	14200	94	120
12	DIB/hexene	2.0 / 0.9	60	3300	4700	1.4	11.4	14000	92	100

<sup>a</sup> Reaction Conditions: Catalyst: Cp<sub>2</sub>ZrCl<sub>2</sub>; Catalyst amount = 2.5 × 10<sup>-6</sup> mol.; MAO = 1800 equiv.; C<sub>2</sub>H<sub>4</sub> partial pressure = 32 psi; reaction volume = 90 ml; solvent = toluene; reaction time = 20 min; reaction temperature = 60°C. <sup>b</sup> STY = styrene, AMS = α-methylstyrene, DIB = 1,3-diisopropenylbenzene. <sup>c</sup> Analysed using mixed-D columns and universal calibration. Polystyrene standards were used to calibrate the system. <sup>d</sup> One styrene end-group per chain corresponds to 100% <sup>e</sup> No solvent used. <sup>f</sup> C<sub>2</sub>H<sub>4</sub> partial pressure = 10 psi.

## RESULTS AND DISCUSSION

### Catalytic hydride insertion mechanism

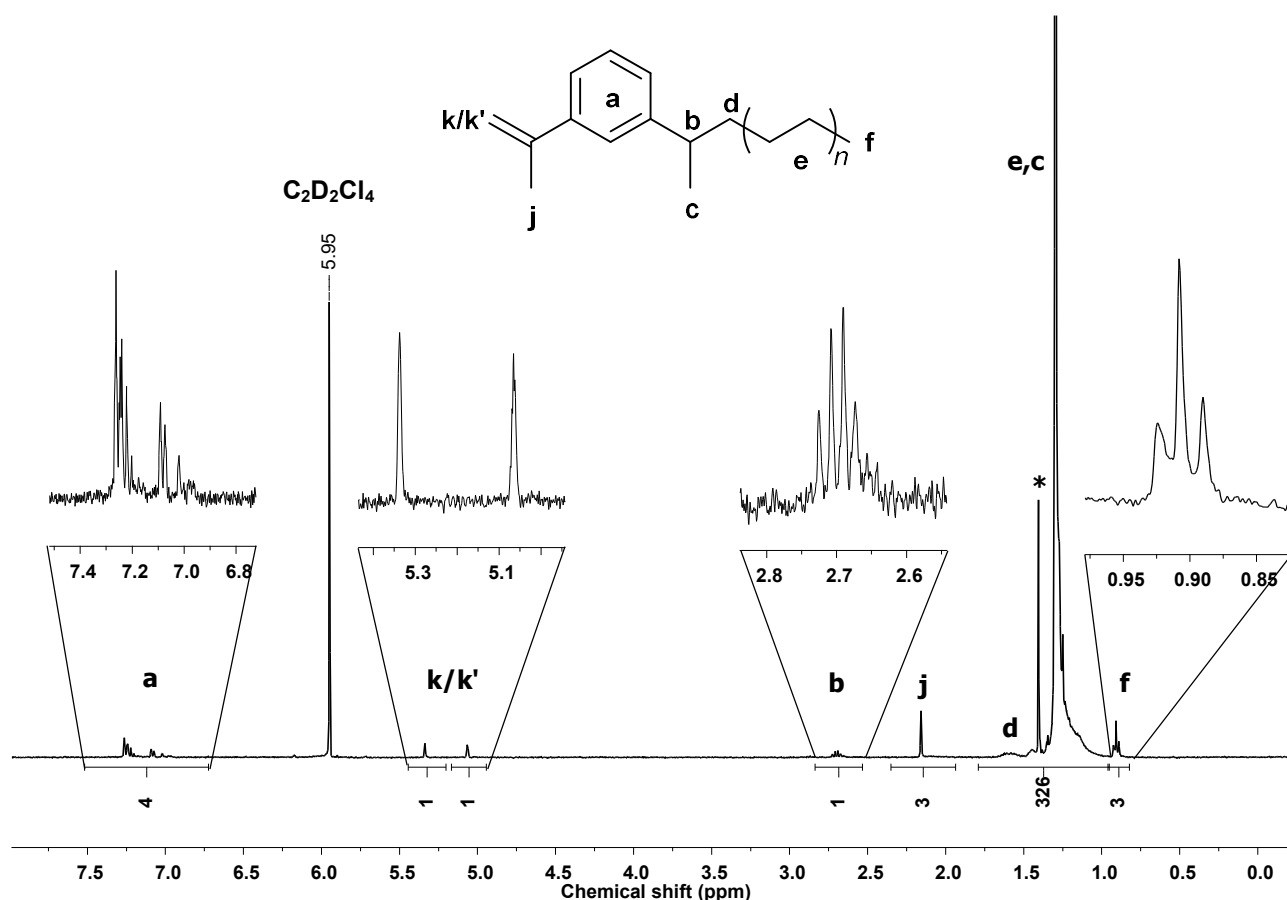
Chung reported<sup>35</sup> that polymerization of ethylene with the classic Kaminsky catalyst system ZrCp<sub>2</sub>Cl<sub>2</sub>/MAO<sup>41</sup> in the presence of *p*-methylstyrene and dihydrogen, led to polyethylene (PE) terminated with a single styrenic unit [Figure 2(a)]. The consecutive chain transfer mechanism shown has also been supported by computations.<sup>42</sup> Thus, the active catalyst **1** bearing a polymeryl chain succumbs to 2,1-insertion of a styrene to give **2**, which does not readily undergo further insertion but is instead hydrogenated to give product **3** (Ar = C<sub>6</sub>H<sub>4</sub>Me) and the cationic zirconium hydride **4** which is recycled *via* **5**.

We successfully reproduced the reported catalysis conditions<sup>35</sup> (e.g. Run 1, Table 1), but discovered that increasing the concentration of styrene beyond the 1.44 mol/L used previously led to apparently more than 100% end groups (Run 2). Hence some chains must bear styrene groups at both the beginning and the end.

A new mechanism is required to explain this observation [Figure 2(b)]. The rate of 1,2-insertion of styrene into the

cationic zirconium hydride **4** must be competitive with insertion of ethylene leading to the *primary* alkyl intermediate **6** – studies by Bercaw<sup>43</sup> and Oliva<sup>44</sup> on related systems indicate that this is highly likely. In contrast, the alkyl **6** (like **5** and **1**) is expected to undergo ethylene insertion far faster than styrene insertion. The subsequent polymeryl intermediate **7** eventually undergoes 2,1-insertion of the styrene to give **8**, analogous to **2**, which halts ethylene insertion as before. Species **8** is hydrogenated to regenerate **4** and yield the double end-capped polymer **9**.

This discovery led us to a new strategy as outlined in Figure 2(c). Comonomers such as α-methylstyrene (AMS) are not expected to react with alkyls like **1** and **5** *etc.* but *are* expected to react with the hydride **4**. Indeed Chirik and Bercaw showed that AMS derivatives, being more sterically demanding than simple styrenes, give exclusively 1,2-insertion into a *neutral* zirconium hydride.<sup>45</sup> Further, a Hammett parameter determined for that reaction ( $\rho = -0.46$ )<sup>45</sup> indicates build-up of positive charge at the benzylic position which would be exacerbated by the cationic nature of the reaction centre in the metallocene-catalysed polymerization. These features should all increase selectivity for 1,2-insertion of AMS at **4** to give alkyl



**Figure 3.**  $^1\text{H}$  NMR spectrum of Run 10 in  $\text{C}_2\text{D}_2\text{Cl}_4$  at  $100^\circ\text{C}$  (400 MHz). The top of the peak at 1.30 ppm corresponding to the PE main chain has been omitted for clarity. Relative integrals are shown under the spectrum.

**10**, rather than the insertion of ethylene. In contrast to **2** and **8**, the primary alkyl **10** is expected to insert ethylene readily, and the growing polymer chain in **11** eventually encounters a molecule of dihydrogen, resulting in the regeneration of **4** and production of PE initiated by AMS. The above mechanistic idea was borne out in experiments (Table 1), and while zirconocene/MAO does not copolymerize AMS with ethylene, introduction of  $\text{H}_2$  leads to production of new polymer **12** ( $\text{R} = \text{H}$ , Runs 3-5). The polymer molecular weights and melting points also fell as the partial pressure of  $\text{H}_2$  was increased, consistent with an increased rate of  $\mathbf{11} \rightarrow \mathbf{4}$  vs  $\mathbf{10} \rightarrow \mathbf{11}$ . Notably, since AMS can only be incorporated at the beginning of the chain and not the end, the proportion of styrenic end groups did not exceed the target 100%. Further, both chain-end incorporation and productivity increased with AMS concentration, and the use of AMS as a solvent is viable (Run 6). This is in stark contrast to the strongly negative comonomer effect generally found in ethylene/styrene copolymerizations.<sup>46, 47</sup> The  $^1\text{H}$  NMR spectrum of polyethylene “initiated” with AMS *i.e.* PE-*i*-AMS (see SI) clearly indicates the presence of a single AMS unit at the chain end.

Other 2-isopropenyl derivatives are suitable substrates for this new mechanism, and we were particularly interested in reactions in the presence of 1,3-diisopropenylbenzene

(DIB); a large-scale commercial monomer that on the basis of the above mechanism should provide us with new macromonomers for radical polymerization (*vide infra*). We were pleased to find that the reactions proceeded smoothly and responded to experimental conditions in the same manner as AMS indicating the same mechanism. High end-group fidelity is observed (Runs 7-10). The  $^1\text{H}$  NMR spectra of PE-*i*-DIB [Figure 3] feature sharp signals at 5.06 and 5.34 ppm for the free isopropenyl group of **12** ( $\text{R} = \text{CMeCH}_2$ ). Thus, in a total reaction volume of 90 ml and operating at 92 psi pressure in a conventional homogeneous metallocene set-up, 11 g of this end-functionalised PE can be produced in 20 min [productivity 13000 kg/mol<sub>Zr</sub>.h] with no reduction in rate of ethylene gas uptake over this time (Run 10). Further, the addition of hexene to this metallocene polymerization also led efficiently to DIB-initiated ethylene/hexene copolymers *i.e.* EH-*i*-DIB (Run 12). Crucially, these polymers are all produced at low enough molecular weight (as determined by universal calibration) to facilitate their use as macromonomers, but high enough to be effective in the intended applications (*vide infra*).

**Table 2. Selected radical copolymerisations incorporating the polyethylene and ethylene/hexene macromonomers PE-*i*-DIB and EH-*i*-DIB.**

Run <sup>a</sup>	Macromonomer/ $M_n$	Comonomer <sup>b</sup> / equiv	Initiator <sup>c</sup>	Yield (g)	GPC <sup>d</sup>			$T_m$ (°C)	$T_c$ (°C)
					$M_n$ (g/mol) <sup>d</sup>	$M_w$ (g/mol) <sup>d</sup>	$\bar{D}$ <sup>d</sup>		
13	PE- <i>i</i> -DIB/2200	<i>n</i> -BA/50	BP	0.37	7000	15700	2.2	120	109
14	PE- <i>i</i> -DIB/2200	<i>n</i> -BA/200	BP	1.46	19200	69200	3.6	116	71
15	PE- <i>i</i> -DIB/2200	<i>n</i> -BA/400	BP	3.43	42500	278300	6.5	114	69
16	PE- <i>i</i> -DIB/2200	MMA/200	BP	0.35	5300	8500	1.6	116	100
17	PE- <i>i</i> -DIB/3000	STY/500	TP	1.49	24400	52000	2.1	119	86
18	PE- <i>i</i> -DIB/2200	VAc/400	BP	0.60	4200	9200	2.1	114	89
19	PE- <i>i</i> -DIB/3000	VAc/500	TP	0.86	8000	19300	2.4	109	69
20	EH- <i>i</i> -DIB/3900	<i>n</i> -BA/50	BP	0.41	5500	13800	2.3	100	89
21	EH- <i>i</i> -DIB/3900	STY/500	BP	0.69	23000	65000	2.7	95	50
22	EH- <i>i</i> -DIB/3900	VAc/500	BP	0.42	4300	14400	3.3	99	83
23 <sup>f</sup>	PE- <i>i</i> -DIB/3100	STY/500	TP	75	56500	130000	2.3	117	64
24 <sup>g</sup>	PE- <i>i</i> -DIB/2200	<i>n</i> -BA/100	BP	6.9	11000	28000	2.6	115	100
25 <sup>h</sup>	PE- <i>i</i> -DIB/2200	<i>n</i> -BA/100	BP	6.5	10200	26300	2.6	117	103

<sup>a</sup> Conditions: macromonomer = 0.20 g; solvent = toluene; reaction volume = 8.2 mL; temperature = 125°C; reaction time = 120 min, unoptimised (*vide infra*). <sup>b</sup> Abbreviations: *n*-BA (*n*-butyl acrylate), MMA (methyl methacrylate), STY (styrene), VAc (vinyl acetate). <sup>c</sup> Abbreviations: BP = dibenzoyl peroxide, TP = di-*tert*-butylperoxide). <sup>d</sup> GPC data obtained in 1,2,4-trichlorobenzene at 160°C using mixed-D columns and universal calibration. Polystyrene standards were used to calibrate the system. <sup>e</sup> Conditions: macromonomer = 10 g;  $M_n$  = 3100  $\bar{D}$  = 2.0; [PE-*i*-DIB] =  $7.4 \times 10^{-3}$  mol/L; [Initiator] =  $7.4 \times 10^{-2}$  mol/L; solvent = toluene; reaction volume = 436 ml; temperature = 125 °C. <sup>f</sup> Conditions: macromonomer = 2.4 g;  $M_n$  2200 g/mol  $\bar{D}$  = 2.1; [PE-*i*-DIB] =  $1.8 \times 10^{-2}$  mol/L; [Initiator] = 0.11 mol/L in 10 ml solvent; solvent = toluene; initial reaction volume = 60 ml; temperature = 110 °C; initiator addition rate =  $1.14 \times 10^{-3}$  mol/hr; monomer addition rate = 0.114 mol/hr. <sup>g</sup> Initiator addition rate =  $1.14 \times 10^{-3}$  mol/hr; monomer addition rate = 0.038 mol/hr.

#### Polyolefin macromonomers in radical polymerization

In a classic patent,<sup>48-49</sup> Moad and co-workers polymerized *n*-butyl acrylate (*n*-BA) at high temperatures in the presence of small amounts of AMS using a cobalt chain-transfer agent such as bis(boron difluoromethylglyoximate)cobaltate(II) (COBF). This led to AMS being incorporated selectively as an end group because the tertiary benzylic AMS radical so formed does not propagate at a significant rate.<sup>50</sup> If our AMS-like macromonomers PE-*i*-DIB [Figure 4(a)] and EH-*i*-DIB were also incorporated terminally in such a reaction, block copolymers of the much sought-after kind described in the introduction would be produced *viz.* Figure 4(b).

In preliminary experiments we attempted copolymerizations of PE-*i*-DIB with excess *n*-BA in toluene at high temperature (125°C) as recommended,<sup>50</sup> using 2,2'-azobis(2-methylpropionitrile) (AIBN) as the initiator and COBF as the chain transfer catalyst. This led to complete conversion of the PE-*i*-DIB starting material and produc-

tion of copolymer (*vide infra*), but interestingly the <sup>1</sup>H NMR spectrum of the product did not show any vinylidene groups at the AMS unit [Figure 4(b)]. We subsequently discovered that the COBF was having no detectable effect on the polymerization and the same copolymers were produced by simply heating PE-*i*-DIB with various polar monomers in the presence of radical initiators.

#### Batch synthesis and purification of copolymers

In Run 13 (Table 2), heating PE-*i*-DIB ( $M_n$  = 2200 g/mol,  $\bar{D}$  = 2.1) in simple one-pot reactions with 50 equivalents of *n*-BA at 125°C in the presence of dibenzoyl peroxide gave complete conversion of PE-*i*-DIB within 20 min and excellent recovery of a copolymer PE-P(*n*-BA) with  $M_n$  = 7000 g/mol and  $\bar{D}$  = 2.2, which is shown to be principally a block copolymer (*vide infra*). Increasing the concentration of *n*-BA (Runs 14, 15) led to higher molecular weights, dispersi-

ties, yields and rates of conversion. The use of higher temperature initiators was less successful, leading to incomplete conversion.

The macromonomer PE-*i*-DIB can also be used in the synthesis of other polar copolymers (Runs 16-19, Table 2) including vinyl ester, styrene and methacrylate. The branched polyolefin based on ethylene/hexene copolymerization (Run 12, Table 1) *i.e.* EH-*i*-DIB behaves similarly (Runs 20-22).

The purification of the copolymers thus formed – removal of any co-produced homopolymer – was achieved most readily in most instances by precipitation; the materials containing the PE or EH blocks have relatively low solubility. The exception was PE-P(MMA) which was most readily purified by Soxhlet extraction with MeOH to remove any P(MMA) followed by precipitation from toluene/MeOH. All samples were analyzed by GPC, NMR and DSC for comparison with the PE-*i*-DIB starting material and homopolymers. The data were not significantly affected by multiple reprecipitations of the samples.

In Run 15 using 0.2 g of PE-*i*-DIB and 4.9 g (400 equiv.) of *n*-BA, it was found that conversion of the PE-*i*-DIB was complete after 5 min and the copolymer fraction contained 64% of the monomer feed. In addition, *ca* 907 mg of homopolymer (19%) was produced. The <sup>1</sup>H NMR spectrum of this P(*n*-BA) coproduct featured prominent peaks at 6.2 and 5.5 ppm indicating vinyl termination as expected from backbiting and subsequent  $\beta$ -scission at temperatures  $\geq 90^\circ\text{C}$ .<sup>51, 52, 53</sup> A control experiment conducted in the absence of PE-*i*-DIB but otherwise under the same conditions gave a more conventional high temperature free-radical P(*n*-BA) polymer, with high molecular weight ( $M_w = 127500$  g/mol) and dispersity (9.1), and in a yield corresponding to 85% of the feed monomer. It would thus appear that the presence of the PE-*i*-DIB macromonomer provides significant control over the *n*-BA homopolymerization under these conditions.

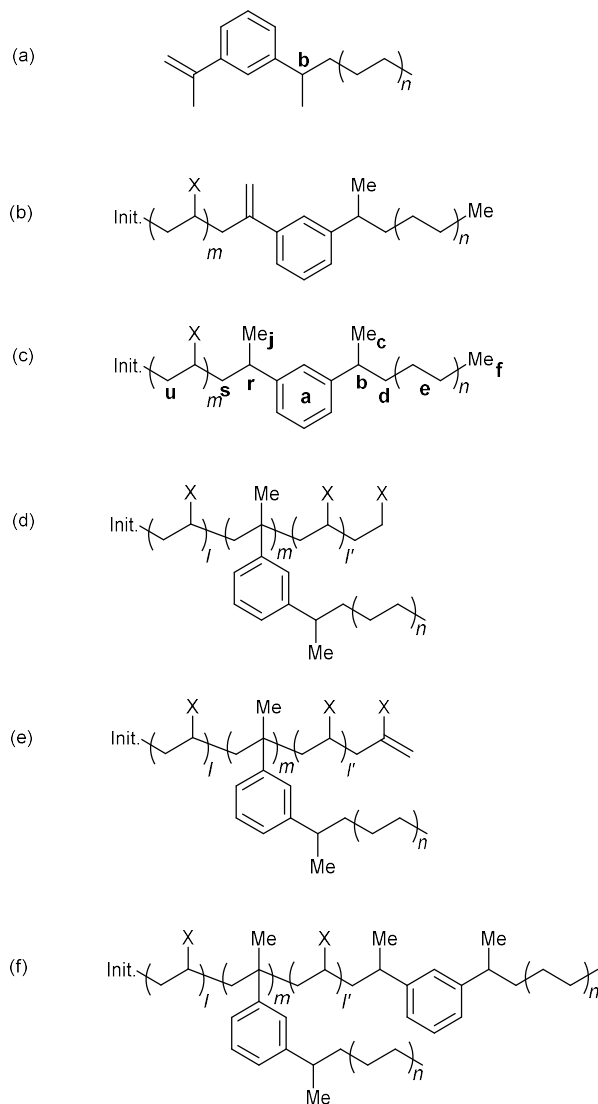
It is perhaps for these reasons why large scale batch reactions proceeded without technical difficulty, and for example 75 g of PE-PS (Run 23) was synthesized for use in polymer blending studies (*vide infra*).

### Semi-batch synthesis of copolymers

Runs 24 and 25 (Table 2) were conducted under semi-batch conditions, feeding monomer and initiator into the reaction vessel containing macromonomer and solvent at the reaction temperature. Such conditions are more suitable for scale-up. Samples were taken periodically and the evolution of molecular weight with time was followed by plotting the GPC traces of the separated copolymer (Figure 5). At a high rate of monomer addition in Run 24 [1.7 equiv/min, (a)] the shift in molecular weight to copolymer product indicates that most of the macromonomer is converted within 30 min, and we note that 48% of the sample collected was homopolymer at  $t = 60$  min. At the lower feed rate of Run 25 [0.56 equiv/min, (b)] conversion of macromonomer is more gradual and here only 20% of the feed was converted to homopolymer. Further optimization of this type of reaction is possible and will be reported in due course.

### Characterization of copolymers – general comments

In the following sections we describe a range of techniques including NMR (DOSY, correlation spectra, variable temperature, end-group analysis, correlation with GPC data), thermal measurements, light scattering and other physical techniques that point strongly towards the presence of principally block copolymer architectures in the above types of sample. A mechanistic rationalization is also presented for the observations.

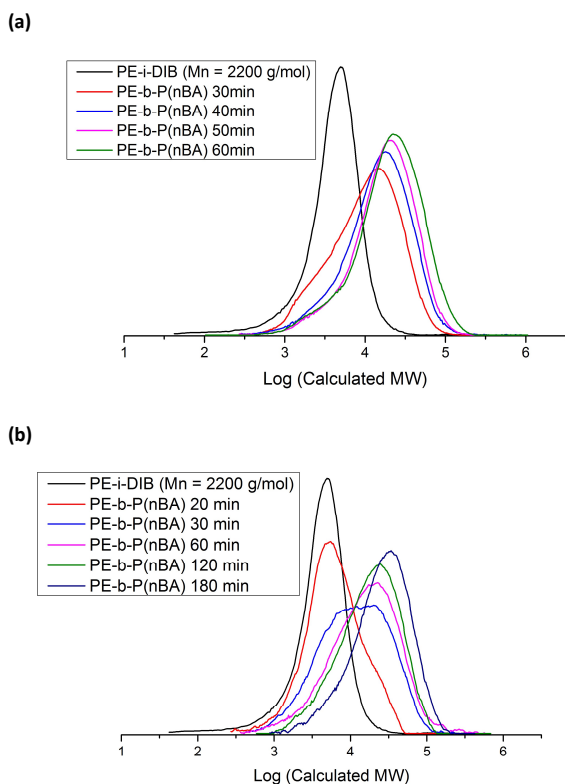


**Figure 4. Possible architectures of PE-*i*-DIB radical copolymer products:** (a) the PE-*i*-DIB macromonomer; (b) the block copolymer product expected from COBF chain transfer agent<sup>54</sup> mediated copolymerization with e.g. acrylates; (c) block copolymer produced by radical polymerization if rate of propagation through the PE macromonomer is slow; (d) “graft through” copolymer with saturated termination from disproportionation of chain end, or chain transfer to solvent. (e) “graft through” copolymer with vinylic termination from backbiting/ $\beta$ -scission; (f) “graft through” copolymer with eventual termination to PE-*i*-DIB.

## NMR spectra of the copolymers

Examination of the NMR spectra of various kinds has allowed us to cast light on the nature of the copolymers of Table 2 which might in principle be block or graft structures of the various kinds shown in Figure 4.

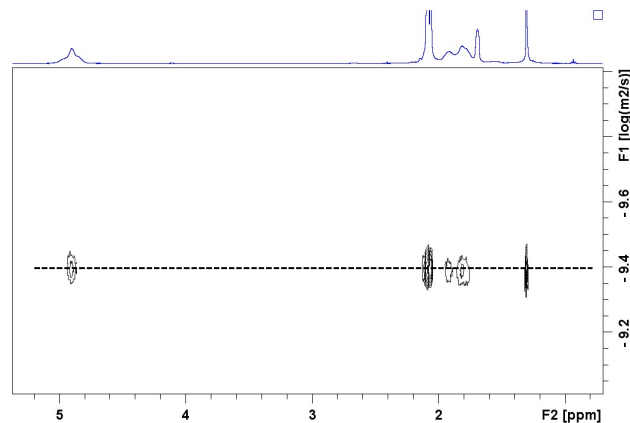
**Diffusion-ordered NMR spectroscopy (DOSY)** This technique,<sup>55, 56</sup> as applied to the analysis of polymers or polymer mixtures in solution,<sup>57, 58, 59, 60</sup> relies on the principle that at a given temperature and viscosity, diffusion rates depend on hydrodynamic radius and molecular weight. This technique can be used to *e.g.* distinguish between copolymers and mixtures of homopolymers, particularly where the analyte is freely soluble in the NMR solvent. If elevated temperatures are required to dissolve the sample, then distinct diffusion rates may not be resolved even if several components are present. It is perhaps for these reasons that we were unable to find any published examples of DOSY analysis of polyethylenes, these materials being only soluble at high temperatures (typically  $\sim 100^\circ\text{C}$  in chlorinated hydrocarbons). Some of the copolymers of Table 2 are however quite soluble at low temperatures and gave excellent DOSY spectra.



**Figure 5. GPC traces following the progress of semi-batch polymerisations.** (a) Run 24 (Table 2), monomer addition rate *ca* 1.7 equiv/min with respect to PE-*i*-DIB macromonomer; (b) Run 25, monomer addition rate *ca* 0.56 equiv/min.

PE-P(VAc) copolymer (Run 19, Table 2) gave a clear solution in  $d^2$ -tetrachloroethane at  $25^\circ\text{C}$ . In the DOSY spectrum at this temperature (Figure 6), signals corresponding to PE

(*ca* 1.3 ppm) and P(VAc) segments aligned tightly around a diffusion coefficient of *ca*  $4 \times 10^{-10} \text{ m}^2/\text{s}$ . Alongside a series of control experiments on samples deliberately contaminated with homopolymers (see SI), this is inconsistent with the presence of a mixture of polymers of different identities and molecular weight ranges, and corroborates the observation from GPC of there being a single molecular weight distribution. Similar results were obtained for lower MW PE-P(*n*-BA) materials which are also soluble at room temperature. Further experiments are detailed in the SI.



**Figure 6. DOSY  $^1\text{H}$  spectrum of PE-P(VAc) in  $\text{C}_2\text{D}_2\text{Cl}_4$  at  $25^\circ\text{C}$  (500 MHz).** The dashed line corresponds to a diffusion coefficient of  $4.0 \times 10^{-10} \text{ m}^2/\text{s}$ .

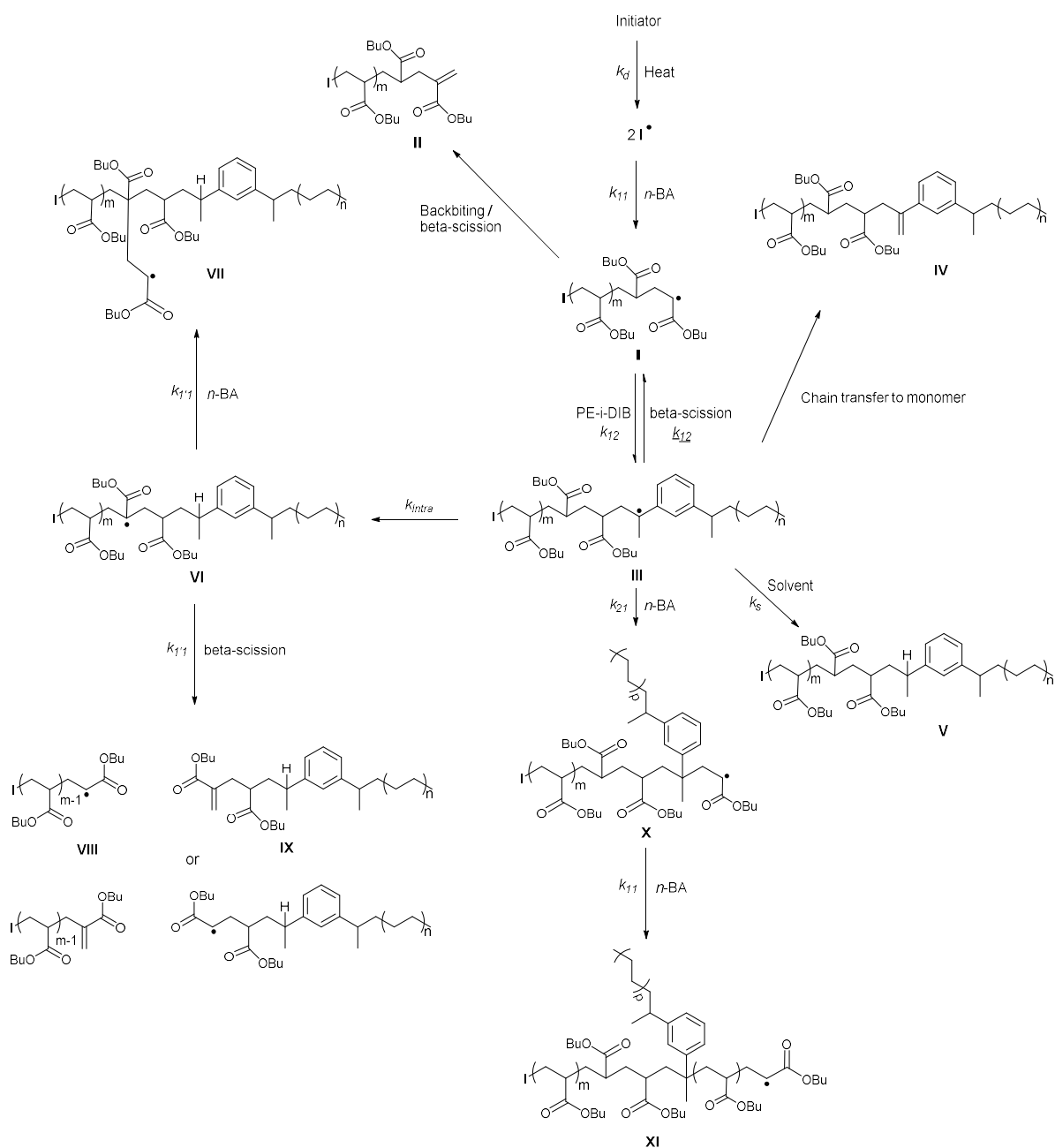
**End-groups** The homopolymer coproducts in most of the above reactions feature end-groups resulting from conventional termination mechanisms: (i) as noted above the P(*n*-BA) homopolymer produced in *e.g.* Runs 13-15 (Table 2) features the expected vinylic end-groups; (ii) in the vinyl acetate system, methylene termination from the expected chain transfer mechanism and vinylic termination from disproportionation<sup>61, 62</sup> was observed in *e.g.* the homopolymer from Run 18 (Table 2); (iii) in the P(MMA) homopolymer isolated from Run 16, vinylic end-groups arising from disproportionation and chain transfer *via* H abstraction from the  $\alpha$ -methyl group – as observed by Davis and co-workers<sup>63</sup> – are seen. In all instances however, such diagnostic end-groups are absent in the spectra of the isolated PE-PX copolymers (SI). This indicates that architectures (d) and (e) of Figure 4 are not significant components.

For the PS materials, deductions of this nature are more difficult because the reaction temperature is insufficient for backbiting to occur at a significant rate<sup>51</sup> and as a result we would not expect to see vinylic end-groups in either copolymer or homopolymer.

### Estimation of molecular weight from NMR spectra

For all the copolymers, the ratio of the integrals of the polyolefin and polar segments increase rapidly (*ca* three-fold) with increase in temperature from  $25^\circ\text{C}$  to  $50^\circ\text{C}$  but more slowly thereafter. Such behavior is consistent with the formation of aggregates at lower temperatures. This aggregation reduces the molecular motion of the relatively insoluble PE segment more than that of the soluble polar blocks.





**Figure 7. Proposed mechanism for the copolymerization of PE-*i*-DIB with *n*-butyl acrylate.**

Consequently, high temperature NMR measurements were routinely made in order to give useful integrals.

For many of the copolymers, signals for the PE chain cannot be fully resolved from those of the polar units. In the  $^1\text{H}$  NMR spectra of PE- $P(n\text{-BA})$  (Runs 13-15, 24, 25) at  $100^\circ\text{C}$  in  $d^2$ -tetrachloroethane for example the signal for the PE chain at  $ca$  1.3 ppm overlaps with a broad  $P(n\text{-BA})$  side-chain  $\text{CH}_2$  multiplet at  $ca$  1.4 ppm. Also, the PE end group methyl and  $P(n\text{-BA})$  side chain methyl groups overlap at  $ca$  1 ppm. While this prevents direct estimation of the  $M_n$ , we can readily compare the degrees of polymerization (DP) indicated by NMR spectra and GPC measurements by assuming for the moment that the copolymer

(*e.g.* Run 24  $M_n = 11000$  g/mol, universal calibration) includes a single macromonomer unit (2200 g/mol).

As detailed in SI for all the polymer systems the DP implied by GPC data sets the well-resolved  $P(n\text{-BA})$  ester  $\text{CH}_2$  signal at  $ca$  4.1 ppm (Figure S5) to be  $ca$  137 H. The relative integrals of the remaining groups correspond with expectations  $\pm 5\%$ . If some comb polymer [Figure 4 (f)] is present, then the in-chain incorporation of macromonomer (*i.e.*  $m$ ) is small.

These calculations are detailed in SI for each copolymer system. The NMR spectra of PE- $P(\text{VAc})$ , PE- $P(\text{MMA})$  and PE- $P(\text{S})$  samples gave similarly consistent measurements between GPC and integration of high temperature NMR. The EH-based copolymers (*e.g.* Run 20) have spectra that are

further complicated by the presence of branched polyolefin chains, but the  $^1\text{H}$  NMR spectra could nevertheless be analyzed similarly. The relative integrals of all peaks are consistent with the copolymers having *ca* one PE segment per chain.

In addition to the above, PE-P(VAc) copolymers gave sufficiently well-separated peaks in the  $^1\text{H}$  NMR spectra for  $M_n$  to be estimated directly. The sample from Run 18 in  $d^2$ -tetrachloroethane at  $100^\circ\text{C}$  displayed P(VAc) methine and the PE main chain  $\text{CH}_2$  resonances in the ratio 1.27:1 hence  $M_n = 4800$  g/mol. This corresponds sufficiently well with the value of  $M_n = 4200$  g/mol from GPC (Table 2).

**$^1\text{H}$ - $^{13}\text{C}$  and  $^1\text{H}$ - $^1\text{H}$  correlation spectra** It was possible in several examples using a series of correlation spectra to detect and assign key peaks consistent only with the block copolymer structure (c). For example, in the  $^1\text{H}$  NMR spectrum of PE-P(VAc) (Run 19) recorded at  $100^\circ\text{C}$ , overlapping signals for  $\text{H}_b$  and  $\text{H}_r$  couple to two benzylic environments in the  $^{13}\text{C}$  spectrum. We can also see separate correlations between: (i)  $\text{H}_b$  and the neighbouring diastereotopic backbone methylene proton environments  $\text{H}_d$  (1.51 and 1.62 ppm); and (ii)  $\text{H}_r$  and methylene proton environments  $\text{H}_s$  (1.88 ppm). See SI for further details.

### Mechanism of formation of copolymer

A consideration of the above observations, as well as the expected rates of the various reactions, leads us to propose the mechanism in Figure 7 using *n*-BA monomer as an example.

At the high reaction temperatures required to dissolve the polyolefin macromonomer ( $> 90^\circ\text{C}$ ) thermal decomposition of the initiator (dibenzoyl peroxide) proceeds at a high rate<sup>64</sup>  $k_d$  followed by fast<sup>50</sup> propagation of *n*-BA ( $k_{11}$ ) to produce growing polar polymer I. The cross-propagation of I with PE-*i*-DIB is expected to have a very high rate coefficient ( $k_{12}$ ), perhaps 5-6 times higher than that of  $k_{11}$ ,<sup>65</sup> noting also that the macromonomer is present at concentrations *ca* two orders of magnitude higher than the control agent in a typical nitroxide-mediated polymerization.<sup>66</sup> The tertiary benzylic radical III formed is expected to have appreciable stability,<sup>50, 53, 67</sup> and taking into account the additional steric protection provided by the mid-chain position of the radical centre it will be resistant to most chain-transfer processes and certainly homopropagation. We noted above that in copolymerizations of AMS with other monomers, the styrene forms a high fraction of end-groups.<sup>68, 49, 69, 70</sup>

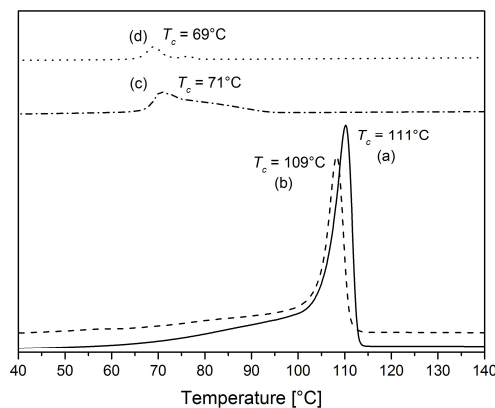
In contrast, unimolecular  $\beta$ -scission of III ( $k_{12}$ ) may be appreciable at high temperature,<sup>69</sup> and thus competitive with irreversible termination, reforming I and in principle permitting further propagation with *n*-BA. After depletion of monomer under batch conditions, backbiting and subsequent  $\beta$ -scission of species I predominate,<sup>51, 52, 53, 69, 71</sup> leading to a propagating P(*n*-BA) radical and the observed unsaturated homopolymer II with relatively low  $\bar{D}$ , as noted earlier.

In any event, the sterically protected nature of III militates against intermolecular chain-transfer reactions, and we propose that this is why attempted COBF-mediated copolymerizations of PE-*i*-DIB and *n*-BA (*vide supra*) did not

give detectable vinylidene units of the type shown in Figure 4 (b). Chain transfer from III to solvent at rate constant  $k_5$ <sup>65</sup> is likely to be the main source of eventual termination and production of the proposed polymer product V, an example of the block structure in Figure 4 (c).

Under these conditions the effective rate of cross-propagation of III with *n*-BA to form X is expected to be low, even before taking into account steric crowding of the radical centre in III by the polymer chain. Nevertheless, this process is feasible and would be followed by further homopropagation at a rate comparable to  $k_{11}$ , so we cannot exclude *a priori* the possibility that a graft copolymer based on XI would be produced.

As mentioned earlier however, this polymer would be expected to contain vinylic termination products [Figure 4(e)], and these are not observed. Addition of P(*n*-BA) monomer or macromonomer to the tertiary carbon would lead to the formation of branches (species VII), but fragmentation could be significant at these high temperatures<sup>52</sup> and quarternary branch points are not detected in the  $^{13}\text{C}$  NMR spectra.<sup>72</sup> We also took into account the possibility of mid-chain radical migration as another consequence of the backbiting reaction, given its significance in *n*-BA homopolymerization.<sup>73</sup> In this case the process would lead to conversion of III to VI with rate coefficient  $k_{\text{intra}}$ . Rapid  $\beta$ -scission would then be expected to follow in two directions,<sup>74, 71</sup> one of which would yield copolymer IX with a vinylic end-group. Since these species are not detected in high temperature NMR experiments, intramolecular chain-transfer of III to another tertiary carbon is, as expected, slow.

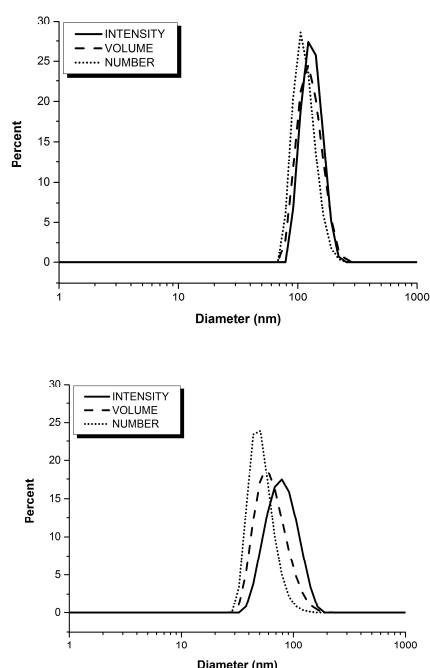


**Figure 8. Crystallization of PE segments.** The crystallization temperature of (a) PE-*i*-DIB ( $M_n = 2200$  g/mol) is typical of low MW HDPE, while addition of increasingly large P(*n*-BA) segments (b), (c) and (d) - total  $M_n = 7000$ , 19200 and 42500 g/mol respectively - leads to a dramatic reduction in  $T_c$  because the polar block kinetically impedes nucleation. The reduction in intensity is a result of there being less PE in the sample as the proportion of the polar polymer increases.

### Thermal properties of the copolymers

Block copolymers display crystallization phenomena associated with differences in the behavior of the individual

segments.<sup>75</sup> In the PE-P(*n*-BA) materials the melting temperature ( $T_m$ ) associated with the PE block fell from that of the macromonomer PE-*i*-DIB (121°C) by up to 8°C as the size of the P(*n*-BA) segment increased (Table 2). This relatively small change would result from reductions in the size of the PE lamellae. At the same time however, the crystallization temperature ( $T_c$ ) fell dramatically [Figure 8] such that the difference between  $T_m$  and  $T_c$  (supercooling or undercooling)<sup>76</sup> increased from 10°C in the PE-*i*-DIB sample to as much as 41°C. This is consistent with increased kinetic inhibition of PE chain nucleation;<sup>76-77</sup> as the non-crystalline block length increases it becomes more difficult for the polyethylene units to orient themselves into lamellae.<sup>78</sup> The other copolymers displayed similar phenomena (Table 2) *i.e.* modest fall in  $T_m$  and large fall in  $T_c$  on addition of a polar block. In contrast, physical blends of the constituent homopolymers behaved as phase-separated mixtures, with *e.g.*  $T_m$  and  $T_c$  as for PE-*i*-DIB.



**Figure 9. Dynamic light scattering analysis.** (upper) EH-b-P(*n*-BA) (Run 20, Table 2) comprising blocks of polyethylene-co-hexene ( $M_n = 3900$ , 6 wt% hexene) and poly(*n*-butyl acrylate), and of total  $M_n = 5,500$ ,  $\bar{D} = 2.3$ , dispersed in THF. Apparent hydrodynamic diameter of *ca* 100 nm; (lower) PE-b-P(*n*-BA) (Run 14, Table 2) comprising blocks of polyethylene ( $M_n = 2200$  g/mol) and poly(*n*-butyl acrylate) and a total  $M_n = 19200$ ,  $\bar{D} = 3.6$ , dispersed in THF. Apparent hydrodynamic diameter of *ca* 60 nm.

### Aggregation properties

Amphiphilic copolymers commonly form micellar dispersions in suitable solvents, and this was found to be the case here. In particular, the less crystalline examples contained branched polyolefin segments (*i.e.* EH blocks) dispersed most readily in THF – a solvent expected to be selective for the polar blocks – and excellent dynamic light scattering

data were collected [*e.g.* Figure 9]. Further DLS data are presented in SI.

### Mediation of immiscible polymer blending

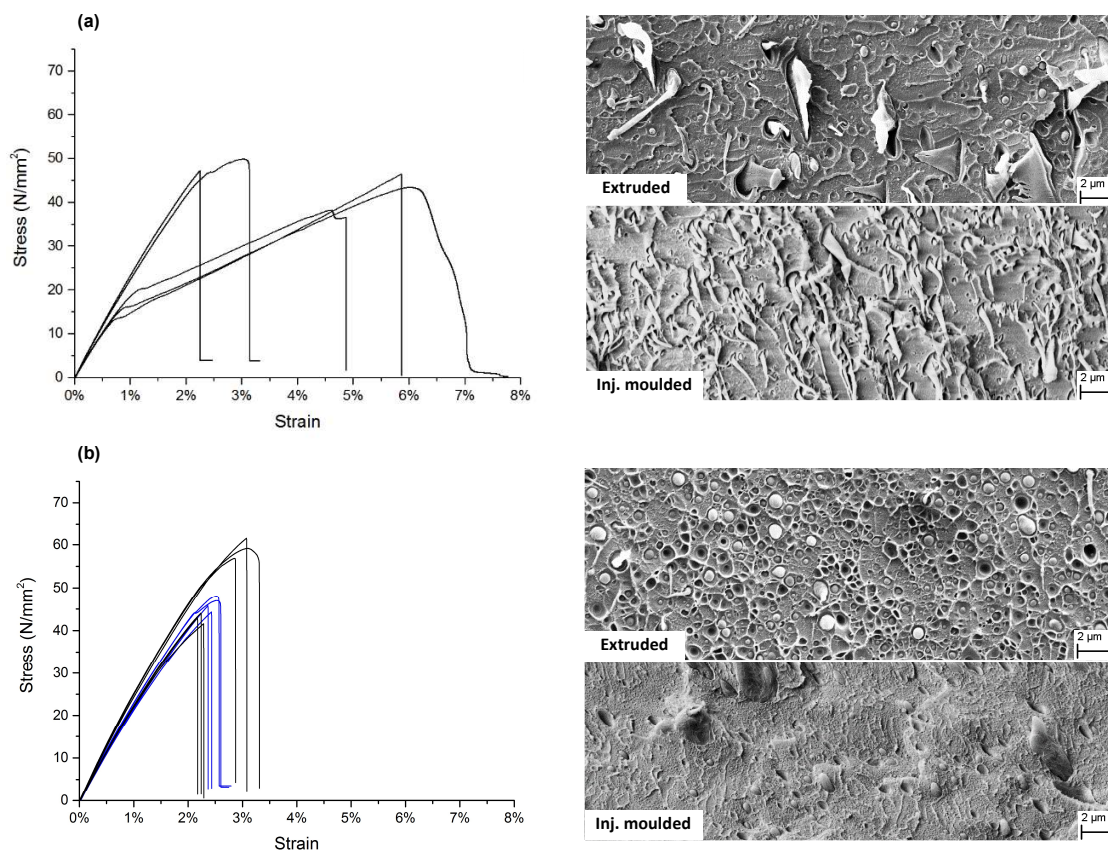
The mechanical properties of recycled polystyrene (PS) are affected dramatically by contamination with other immiscible polymers such as PE. In a preliminary study, samples of commercial PS contaminated with 10% HDPE were prepared using a twin screw extruder, and test specimens were injection-moulded into test bars. Figure 10(a) shows that under tensile deformation this PS/PE blend fails erratically. Scanning electron microscopy (SEM) of cryofractured samples provides an explanation in that the extruded material has poorly distributed PE in a PS matrix as a result of the incompatibility of these polymers, and further that fibrils of PE are drawn out of the injection-moulded material on fracture. When the same blend was extruded with 1% w/w of the PE-PS copolymer of Run 23 (Table 2), clear changes were observed in the stress-strain curves [Figure 10(b) – blue lines] and the blend behaves very similarly to virgin PS samples (black lines). SEM analysis [Figure 10(b)] correspondingly shows a uniform distribution of small, spherical PE domains in the extruded material. This is consistent with reduction of the interfacial tension between the immiscible PS and PE. Further SEM images are presented in SI.

### CONCLUSIONS

The Chung mechanism for copolymerization of ethylene and styrene in the presence of dihydrogen [Figure 2(a)] was extended by a newly discovered aspect – the catalytic hydride insertion depicted in Figure 2(b) – which accounts for the production of some double-capped polymer under these conditions. This led us to design a new and efficient synthesis of end-functionalized polyolefins [Figure 2(c)] which was implemented *via* a highly productive metallocene polymerization. We find that since  $\alpha$ -methylstyrenes do not copolymerize with ethylene, they do not impede zirconocene catalysis, but nevertheless in the presence of dihydrogen they form an initiating unit for each polymer chain.

The new polyolefin macromonomer PE-*i*-DIB and the ethylene/hexene (LLDPE) copolymer EH-*i*-DIB formed in this way *via* use of 1,3-diisopropenylbenzene differ substantially from *e.g.* vinyl termination-rich PEs in that they are readily incorporated into polar polymers *via* simple radical polymerizations. Further, while the  $\alpha$ -methylstyreny end-groups undergo radical addition readily, they propagate slowly thereafter, leading – we propose – to block copolymer architectures. While this might be expected on the basis of the behavior of AMS itself in CCTP-mediated radical copolymerization<sup>54</sup> it is nevertheless unexpectedly simple and efficient. Given the notorious difficulty in convincingly characterizing new classes of block copolymer we have attempted to assemble a body of evidence for the polyolefin polar polymer diblock structures PE-*b*-PX.

The solubility of the copolymers is such that while they are in some instances dissolved or dispersed at room temperature in various solvents, the presence of the PE



**Figure 10. Tensile testing and SEM images of fractured samples.** (a) Five injection moulded test samples of a PS:HDPE 90:10 w/w blend undergo a range of failure types. SEM images of cryofractured samples show poor distribution of PE in the PS matrix; (b) On addition of 1% PE-PS (run 23, Table 2) the tensile properties of the PS/PE blend (blue lines) are similar to those of the returned as a result of substantially improved distribution of PE in the sample.

chain allows their ready isolation by precipitation. The GPC data and DOSY spectra are consistent with the presence of single distributions of MW rather than physical mixtures of polymers with different identities. Further, comparison of molecular weight data and the integrals of high temperature NMR spectra indicate that *ca* one PE block is present in each chain for all systems studied. Indeed, the molecular weights for some of the copolymers synthesized are sufficiently low that only one PE block may be present. This, along with the absence of the conventional radical polymerization end-groups in the samples, essentially excludes all reasonable structures except PO-*b*-PX [Figure 4(c)]. Also, in some instances correlation NMR spectra give direct evidence for the diblock structure.

The new polymers have thermal properties also consistent with these structures and phase separation in the solid – modest changes in  $T_m$  but significant impedance of crystallization ( $T_c$ ) – and undergo micellization in suitable solvents as evidenced by DLS and NMR spectroscopy. Further, evidence for the compatibilization of an immiscible blend of PE and PS using PE-PS is presented from mechanical testing and microscopy.

Noting the extensive use of macromonomers in free-radical copolymerizations,<sup>79</sup> and some relevant insight from Davis and Barner-Kowollik,<sup>68</sup> we searched for published results that might be reinterpreted in the context of our work. The copolymerization of isopropenylbenzyl-terminated poly(ethylene oxide) macromonomers with styrene gave unexpectedly high conversion, particularly when higher molecular weight macromonomer was used.<sup>80</sup> Similarly, copolymerization of isopropenylbenzyl-terminated poly(2-vinylpyridine) with styrene gave apparently only one “graft” per polymer.<sup>81</sup> We suggest that these materials may also be principally block copolymers.

The new polymers PO-*b*-PX (X = styrene, acrylate, methacrylate, vinyl ester) represent classes of materials hitherto unknown, rare, or only available *via* circuitous or expensive routes. The new approach is efficient and versatile, and will we hope allow industrial manufacture of polyolefin block copolymers. Further, the characteristic amphiphilic behavior indicates that a wealth of future applications are now feasible based on modification of the interfacial properties of polyolefins.

## EXPERIMENTAL

### General considerations

Where necessary work was carried out under an inert atmosphere of argon, using standard Schlenk techniques. All

glassware and cannulae were dried at 125°C for at least 24 h prior to use.

Toluene for metallocene polymerizations was dried by reflux over sodium for 3 d prior to distillation, then degassed using three freeze-pump-thaw cycles before use. Styrene ( $\geq 99\%$ , Aldrich),  $\alpha$ -methylstyrene (99%, Aldrich) and 1,3-diisopropenylbenzene (97%, Aldrich) for the same were vacuum distilled from CaH<sub>2</sub> and stored under argon at 5°C.

Research grade ethylene and high purity (99.995%) hydrogen were purchased from BOC. Methylaluminoxane (AXION CA 1310) was purchased from Chemtura as a 10 wt% solution in toluene and used as received. Monomers for the radical polymerizations: *n*-butyl acrylate ( $\geq 99\%$ , Aldrich), vinyl acetate (99+%, Acros Organics), methyl methacrylate (99+%, Acros Organics) and styrene ( $\geq 99\%$ , Aldrich) were passed through a column of alumina to remove inhibitors before use. Dibenzoyl peroxide (75% in H<sub>2</sub>O, Aldrich), di-*tert*-butyl peroxide (98%, Aldrich) and 2,2'-azobis(2-methylpropionitrile) (98%, Aldrich) were used as received.

<sup>1</sup>H NMR spectra of PE samples were recorded on a Bruker AV-400 spectrometer in 1,1,2,2-tetrachloroethane-*d*<sup>2</sup> at 100°C. Residual protio-solvent was used as an internal reference.<sup>82, 83</sup> <sup>13</sup>C NMR spectra of PE samples were recorded on a Bruker DRX-500 spectrometer at 125 MHz in 1,1,2,2-tetrachloroethane-*d*<sup>2</sup> (>10,000 scans, 4 s relaxation time, 100°C) ensuring that the sample was fully dissolved. NMR assignments were confirmed by <sup>1</sup>H-<sup>1</sup>H (COSY), <sup>13</sup>C-<sup>1</sup>H (HMQC) and <sup>13</sup>C-<sup>1</sup>H (HMBC) correlation experiments where necessary (see SI).

Catalysts and air-sensitive reagents were stored in an MBraun glovebox at >5 ppm O<sub>2</sub>.

High temperature GPC was performed in 1,2,4-trichlorobenzene ( $\geq 99\%$ , Aldrich) containing 0.0125 wt% 2,6-di-*tert*-butyl-4-methylphenol (BHT) (Aldrich) at 160°C, flow rate 1 ml/min on a Agilent PL220 equipped with differential refractive index, viscometry and dual angle light scatter detectors. The system was fitted with a 5 cm PLgel guard column (5  $\mu$ M), and two PLgel 30 cm mixed-D columns (5  $\mu$ M). The molecular weight data reported were determined by universal calibration. Agilent PS-H Easivial standards were used to calibrate the system and a standard was run with each set of samples to assess the error of the calibration. The peak average molecular weight ( $M_p$ ) of the standard never differed more than 5% from the stated value. Ambient temperature GPC was performed on soluble homopolymer samples in chloroform containing 2% trimethylamine at 30°C, flow rate 1 ml/min on a Agilent 390-LC-MDS equipped with differential refractive index, viscometry, dual angle light scatter and two wavelength UV detectors. The system was fitted with 5  $\mu$ M and 10  $\mu$ M guard columns and two PLgel 30 cm mixed-C columns. Agilent P(MMA)-H and PS-H Easivial standards were used to calibrate the system (specified where appropriate) and the molecular weight data reported were determined by conventional calibration.

Thermal analyses were carried out on a Mettler Toledo DSC1-400 system. Under an atmosphere of dinitrogen, the samples were heated to 160°C at 10°C/min, and cooled to -160/160°C at 10°C/min for recrystallization. This cycle was

repeated three times in total and after the first melt to erase thermal history, all subsequent thermograms were identical. The melting temperature ( $T_m$ ), crystallization temperature ( $T_c$ ) and glass transition temperature ( $T_g$ ) data reported were taken from the third heating run.

Particle size distributions were measured by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS. To prepare samples for DLS measurements, 10 mg of each polymer were weighed into a vial and made up to concentrations of 1 mg/ml with THF which had been filtered using a 0.22  $\mu$ m filter to remove dust. To aid dissolution, the solutions were stirred using a vortex mixer for at least 5 min. Quartz cuvettes with two clear faces were used and filled with a suitable amount (1 cm depth) for ideal temperature control and two min were allowed for the sample the temperature to stabilize at 25°C. Each solution underwent three measurements of 15 scans each and the average of each set of measurements was reported.

### Metallocene polymerization

This was carried out in a 250 ml stainless steel Parr reactor with internal cooling coil equipped with a thermocouple and a pressure burette system (see SI) for the quantitative monitoring of gas delivery at a fixed pressure. The reactor was dried under vacuum at 100°C for 1 h before addition of a 90 ml solution consisting of toluene, Comonomer and MAO solution *via* cannula, with the reactor initially heated to 50°C for a desired reaction temperature of 60°C. The reactor was purged for 10 min with dihydrogen before the addition of ethylene. Once ethylene uptake had stabilized, a toluene solution of catalyst prepared in the glovebox was injected using an overpressure of argon (partial pressure compensations made). After catalyst addition, the temperature and gas uptake were continuously monitored. The reaction temperature was maintained at the desired temperature (typically 60°C). At the appropriate time, the reaction was stopped by careful addition of methanol (2  $\times$  10 ml) to the vented reactor. The polymer product was precipitated by pouring into a solution of 5% HCl in methanol (600 ml) with stirring for 1 h. The product was recovered by filtration and washed with THF. The polymer product was dried by heating to 70°C *in vacuo* overnight.

### Batch radical polymerization

In a typical small scale radical polymerization example, a 10 ml ampoule equipped with a stirrerbar was charged in air with PE-*i*-DIB (0.2 g,  $9.5 \times 10^{-5}$  mol), *n*-butyl acrylate (2.7 ml,  $1.9 \times 10^{-2}$  mol) (*n*-BA), dibenzoyl peroxide (75% in H<sub>2</sub>O) ( $3.7 \times 10^{-2}$  g,  $9.5 \times 10^{-5}$  mol) (BP), and made up to 8.2 ml with toluene. The ampoule was then sealed and freeze-pump-thaw degassed three times before it was stirred and heated to 125°C in an aluminium heating block. At the appropriate time, the reaction mixture was opened and poured into methanol (100 ml) with stirring to precipitate the product. The precipitate was allowed to settle and the solid recovered by filtration. If required, the crude product may be purified by reprecipitation from toluene/methanol. Samples were dried *in vacuo* at 50-70°C.

### Semi-batch radical polymerizations

Using Run 24 as an example, a 250 ml 3-neck RBF equipped with a stirrer bar, condenser (with bubbler) and two rubber septa was charged in air with PE-*i*-DIB macromonomer (2.4 g,  $1.1 \times 10^{-3}$  mol) and toluene (60 ml). The system was purged by bubbling argon through the reaction mixture with stirring for 15 min at room temperature. After purging, the inert atmosphere was maintained by turning on the di-nitrogen supply as the argon supply was removed and the mixture was heated to 110°C with stirring to dissolve the macromonomer. Separate flasks were charged with a toluene solution of dibenzoyl peroxide (0.37 g,  $1.1 \times 10^{-3}$  mol) and *n*-butyl acrylate (16 ml, 0.114 mol, 100 equivalents) respectively and purged with argon for 15 min with stirring. Syringes were purged with argon three times and then used to draw up the required initiator and monomer feeds, which were then set into syringe pumps. The initiator solution and monomer were continuously fed into the reaction mixture at fixed rates and the total amounts of monomer added and the feed rates were adjusted depending on the required rate to deliver the feeds over the desired reaction time. At appropriate intervals, sampling of the polymerization was achieved by withdrawing a 2.5 ml aliquot from the reaction mixture with a syringe and the contents transferred into stirring methanol (30 ml) to isolate the PE-containing species. At the appropriate time, the 3-neck RBF was opened and the remaining reaction mixture poured into stirring methanol (400 ml) with stirring. The precipitate was allowed to settle before recovery by filtration, reprecipitation from toluene/methanol and drying overnight *in vacuo*. The combined filtrates from precipitation were dried *in vacuo* to isolate the homopolymer by-products.

### Polymer blending and testing

HDPE ( $M_n$  17,000 g/mol,  $M_n$  149,000 g/mol) and polystyrene ( $M_n$  90,000 g/mol,  $M_n$  333,000 g/mol) were sourced commercially. The PE-PS copolymer used was from Run 23 (table 2). Extrusion was performed using a Thermo Scientific HAAKE Minilab II Twin Screw system (160°C, 80 rpm). HDPE, PS and PE-PS were added simultaneously, cycled for 5 min, extruded, recycled again for 5 min, and finally extruded. Mechanical test specimens conforming to the ASTM D638 – 10 using a Thermo Scientific HAAKE Minijet Pro Piston Injection Moulding system at 160°C. Tensile testing was performed using a Shimadzu Autograph AGS-X Universal Tester. Non-injection moulded blends for SEM analysis were made as above in the extruder with the exception that rather than extruding the sample the shear force was stopped, and the system was cooled to 130°C to allow for removal of the polymer without distorting the sample. The blend was then cooled in liquid nitrogen for 5 min before shattering with a hammer.

### ASSOCIATED CONTENT

Further details of polymer synthesis, NMR spectra, thermal data, dynamic light scattering and microscopy. This material is available free of charge via the Internet at <http://pubs.acs.org>. Data created during this study are openly

available from the University of Warwick Research Archive Portal (WRAP) (<http://wrap.warwick.ac.uk>)

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## REFERENCES

1. Franssen, N. M. G.; Reek, J. N. H.; de Bruin, B., Synthesis of functional 'polyolefins': state of the art and remaining challenges. *Chem. Soc. Rev.* **2013**, *42* (13), 5809-5832.
2. Chung, T. C. M., Functional Polyolefins for Energy Applications. *Macromolecules* **2013**, *46* (17), 6671-6698.
3. R., F.; R., J.; Ph., T., Molecular design of multicomponent polymer systems. XIV. Control of the mechanical properties of polyethylene-polystyrene blends by block copolymers. *Journal of Polymer Science Part B: Polymer Physics* **1989**, *27* (4), 775-793.
4. Koning, C.; Van Duin, M.; Pagnouille, C.; Jerome, R., Strategies for compatibilization of polymer blends. *Progress in Polymer Science* **1998**, *23* (4), 707-757.
5. Chung, T. C. M., *Functionalization of Polyolefins*. Elsevier Science: 2002.
6. Busch, M.; Roth, M.; Stenzel, M. H.; Davis, T. P.; Barner-Kowollik, C., The Use of Novel F-RAFT Agents in High Temperature and High Pressure Ethene Polymerization: Can Control be Achieved? *Australian Journal of Chemistry* **2007**, *60* (10), 788-793.
7. Dommanget, C.; Boisson, C.; Charleux, B.; D'Agosto, F.; Monteil, V.; Boisson, F.; Junkers, T.; Barner-Kowollik, C.; Guillaneuf, Y.; Gimes, D., Enhanced Spin Capturing Polymerization of Ethylene. *Macromolecules* **2013**, *46* (1), 29-36.
8. Dommanget, C.; D'Agosto, F.; Monteil, V., Polymerization of Ethylene through Reversible Addition-Fragmentation Chain Transfer (RAFT). *Angew. Chem. Int. Ed.* **2014**, *53* (26), 6683-6686.
9. Ciftci, M.; Norsic, S.; Boisson, C.; D'Agosto, F.; Yagci, Y., Synthesis of Block Copolymers Based on Polyethylene by Thermally Induced Controlled Radical Polymerization Using Mn<sub>2</sub>(CO)<sub>10</sub>. *Macromol. Chem. Phys.* **2015**, *216* (9), 958-963.
10. Boffa, L. S.; Novak, B. M., Copolymerization of Polar Monomers with Olefins Using Transition-Metal Complexes. *Chem. Rev.* **2000**, *100* (4), 1479-1494.
11. Nakamura, A.; Ito, S.; Nozaki, K., Coordination-Insertion Copolymerization of Fundamental Polar Monomers. *Chemical Reviews* **2009**, *109* (11), 5215-5244.
12. Carrow, B. P.; Nozaki, K., Transition-Metal-Catalyzed Functional Polyolefin Synthesis: Effecting Control through Chelating Ancillary Ligand Design and Mechanistic Insights. *Macromolecules* **2014**, *47* (8), 2541-2555.
13. Chum, P. S.; Swogger, K. W., Olefin polymer technologies—History and recent progress at The Dow Chemical Company. *Progress in Polymer Science* **2008**, *33* (8), 797-819.
14. Hustad, P. D., Frontiers in Olefin Polymerization: Reinventing the World's Most Common Synthetic Polymers. *Science* **2009**, *325* (5941), 704-707.
15. Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M., Living alkene polymerization: New methods for the precision synthesis of polyolefins. *Prog. Polym. Sci.* **2007**, *32* (1), 30-92.
16. Yasuda, H.; Furo, M.; Yamamoto, H.; Nakamura, A.; Miyake, S.; Kibino, N., New approach to block copolymerizations of ethylene with alkyl methacrylates and lactones by unique catalysis with organolanthanide complexes. *Macromolecules* **1992**, *25* (19), 5115-5116.
17. Kermagoret, A.; Debuigne, A.; Jérôme, C.; Detrembleur, C., Precision design of ethylene- and polar-monomer-based copolymers by organometallic-mediated radical polymerization. *Nat. Chem.* **2014**, *6* (3), 179-187.
18. Amin, S. B.; Marks, T. J., Versatile Pathways for In Situ Polyolefin Functionalization with Heteroatoms: Catalytic Chain Transfer. *Angew. Chem. Int. Ed.* **2008**, *47* (11), 2006-2025.
19. Yagci, Y.; Atilla Tasdelen, M., Mechanistic transformations involving living and controlled/living polymerization methods. *Progress in Polymer Science* **2006**, *31* (12), 1133-1170.
20. Godoy Lopez, R.; D'Agosto, F.; Boisson, C., Synthesis of well-defined polymer architectures by successive catalytic olefin polymerization and living/controlled polymerization reactions. *Prog. Polym. Sci.* **2007**, *32* (4), 419-454.
21. Zhao, Y.; Wang, L.; Xiao, A.; Yu, H., The synthesis of modified polyethylene via coordination polymerization followed by ATRP, RAFT, NMRP or ROP. *Prog. Polym. Sci.* **2010**, *35* (10), 1195-1216.
22. Kaneyoshi, H.; Inoue, Y.; Matyjaszewski, K., Synthesis of Block and Graft Copolymers with Linear Polyethylene Segments by Combination of Degenerative Transfer Coordination Polymerization and Atom Transfer Radical Polymerization. *Macromolecules* **2005**, *38* (13), 5425-5435.
23. Sugimoto, R.; Kaneko, H.; Saito, J.; Kawahara, N.; Matsuo, S.; Matsugi, T., Controlled radical polymerization with polyolefin macroinitiator: a convenient and versatile approach to polyolefin-based block and graft copolymers. *Polym. Bull.* **2014**, *71* (6), 1421-1431.
24. Godoy Lopez, R.; Boisson, C.; D'Agosto, F.; Spitz, R.; Boisson, F.; Gimes, D.; Bertin, D., Catalyzed chain growth of polyethylene on magnesium for the synthesis of macroalkoxyamines: Application to the production of block copolymers using controlled radical polymerization. *J. Polym. Sci. A: Polym. Chem.* **2007**, *45* (13), 2705-2718.
25. Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J., Development of a Universal Alkoxyamine for "Living" Free Radical Polymerizations. *J. Am. Chem. Soc.* **1999**, *121* (16), 3904-3920.
26. Ring, J. O.; Thomann, R.; Mülhaupt, R.; Raquez, J.-M.; Degée, P.; Dubois, P., Controlled Synthesis and Characterization of Poly[ethylene-block-(L,L-lactide)]s by Combining Catalytic Ethylene Oligomerization with "Coordination-Insertion" Ring-Opening Polymerization. *Macromol. Chem. Phys.* **2007**, *208* (8), 896-902.
27. Li, Q.-Z.; Zhang, G.-Y.; Chen, J.-Z.; Zhao, Q.-L.; Lu, H.-C.; Huang, J.; Wei, L.-H.; D'Agosto, F.; Boisson, C.; Ma, Z., Well-defined polyolefin/poly( $\epsilon$ -caprolactone) diblock copolymers: New synthetic strategy and application. *Journal of Polymer Science Part A: Polymer Chemistry* **2011**, *49* (2), 511-517.
28. Godoy Lopez, R.; Boisson, C.; D'Agosto, F.; Spitz, R.; Boisson, F.; Gimes, D.; Bertin, D., New Functional Polyolefins: Towards a Bridge Between Catalytic and RAFT Polymerizations? *Macromol. Rapid Commun.* **2006**, *27* (3), 173-181.
29. Briquel, R.; Mazzolini, J.; Le Bris, T.; Boyron, O.; Boisson, F.; Delolme, F.; D'Agosto, F.; Boisson, C.; Spitz, R., Polyethylene Building Blocks by Catalyzed Chain Growth and Efficient End Functionalization Strategies, Including Click Chemistry. *Angew. Chem. Int. Ed.* **2008**, *47* (48), 9311-9313.
30. Chung, T. C., Synthesis of functional polyolefin copolymers with graft and block structures. *Prog. Polym. Sci.* **2002**, *27* (1), 39-85.
31. Chung, T. C., 6 - Functionalization via Reactive Polyolefins Containing Borane Groups. In *Functionalization of Polyolefins*, Academic Press: London, 2002; pp 81-104.
32. Chung, T. C., 7 - Functionalization via Reactive Polyolefins Containing p-Methylstyrene Groups. In *Functionalization of Polyolefins*, Academic Press: London, 2002; pp 105-133.
33. Chung, T. C., 10 - Synthesis of Functional Polyolefin Diblock Copolymers. In *Functionalization of Polyolefins*, Academic Press: London, 2002; pp 179-195.

34. Chung, T. C., 11 - Synthesis of Functional Polyolefin Graft Copolymers. In *Functionalization of Polyolefins*, Academic Press: London, 2002; pp 197-226.
35. Dong, J. Y.; Chung, T. C., Synthesis of Polyethylene Containing a Terminal p-Methylstyrene Group: Metallocene-Mediated Ethylene Polymerization with a Consecutive Chain Transfer Reaction to p-Methylstyrene and Hydrogen. *Macromolecules* **2002**, *35* (5), 1622-1631.
36. Coca, S.; Paik, H.-j.; Matyjaszewski, K., Block Copolymers by Transformation of Living Ring-Opening Metathesis Polymerization into Controlled/"Living" Atom Transfer Radical Polymerization. *Macromolecules* **1997**, *30* (21), 6513-6516.
37. Bielawski, C. W.; Morita, T.; Grubbs, R. H., Synthesis of ABA Triblock Copolymers via a Tandem Ring-Opening Metathesis Polymerization: Atom Transfer Radical Polymerization Approach. *Macromolecules* **2000**, *33* (3), 678-680.
38. Mahanthappa, M. K.; Bates, F. S.; Hillmyer, M. A., Synthesis of ABA Triblock Copolymers by a Tandem ROMP-RAFT Strategy. *Macromolecules* **2005**, *38* (19), 7890-7894.
39. Zhang, H.; Alkayal, N.; Gnanou, Y.; Hadjichristidis, N., Anionic polymerization and polyhomologation: an ideal combination to synthesize polyethylene-based block copolymers. *Chem. Comm.* **2013**, *49* (79), 8952-8954.
40. Zhang, H.; Banerjee, S.; Faust, R.; Hadjichristidis, N., Living cationic polymerization and polyhomologation: an ideal combination to synthesize functionalized polyethylene-polyisobutylene block copolymers. *Polym. Chem.* **2016**, *7* (6), 1217-1220.
41. Kaminsky, W., Discovery of Methylaluminoxane as Cocatalyst for Olefin Polymerization. *Macromolecules* **2012**, *45* (8), 3289-3297.
42. Cheng-Gen, Z.; Shu-Yuan, Y.; Liaoyun, Z.; Huayi, L.; Zhi-Xiang, W., DFT mechanistic study of the H<sub>2</sub>-assisted chain transfer copolymerization of propylene and p-methylstyrene catalyzed by zirconocene complex. *Journal of Polymer Science Part A: Polymer Chemistry* **2015**, *53* (4), 576-585.
43. Doherty, N. M.; Bercaw, J. E., Kinetics and mechanism of the insertion of olefins into transition metal-hydride bonds. *Journal of the American Chemical Society* **1985**, *107* (9), 2670-2682.
44. Galdi, N.; Izzo, L.; Oliva, L., Comparison of the Regiochemical Behavior of Zirconium and Hafnium in the Polyinsertion of Styrenes. *Organometallics* **2010**, *29* (20), 4434-4439.
45. Chirik, P. J.; Bercaw, J. E., Cyclopentadienyl and Olefin Substituent Effects on Insertion and  $\beta$ -Hydrogen Elimination with Group 4 Metallocenes. Kinetics, Mechanism, and Thermodynamics for Zirconocene and Hafnocene Alkyl Hydride Derivatives. *Organometallics* **2005**, *24* (22), 5407-5423.
46. Theaker, G. W.; Morton, C.; Scott, P., Awakening a dormant catalyst: salicylaldimine systems for ethene/tert-butylstyrene copolymerization. *Dalton Transactions* **2008**, (48), 6883-6885.
47. W., T. G.; Colin, M.; Peter, S., Substituent effects in ethene/styrene copolymerization: Dormant state destabilization? *Journal of Polymer Science Part A: Polymer Chemistry* **2009**, *47* (12), 3111-3117.
48. Moad, G.; Rizzardo, E.; Moad, C. L.; Ittel, S. D.; Wilczek, L.; Gridnev, A. A. Catalytic Polymerization Process. WO1997031030A1, 1997.
49. Kukulj, D.; Heuts, J. P. A.; Davis, T. P., Copolymerization of Styrene and  $\alpha$ -Methylstyrene in the Presence of a Catalytic Chain Transfer Agent. *Macromolecules* **1998**, *31* (18), 6034-6041.
50. Chiu, T. Y. J.; Heuts, J. P. A.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C., Synthesis of Macromonomers via Catalytic Chain Transfer (CCT) Polymerization and their Characterization via NMR Spectroscopy and Electrospray Ionization Mass Spectrometry (ESI-MS). *Macromol. Chem. Phys.* **2004**, *205* (6), 752-761.
51. Chiefari, J.; Jeffery, J.; Mayadunne, R. T. A.; Moad, G.; Rizzardo, E.; Thang, S. H., Chain Transfer to Polymer: A Convenient Route to Macromonomers. *Macromolecules* **1999**, *32* (22), 7700-7702.
52. John, C.; Justine, J.; Roshan, T. A. M.; Graeme, M.; Ezio, R.; San, H. T., Preparation of Macromonomers via Chain Transfer with and without Added Chain Transfer Agent. In *Controlled/Living Radical Polymerization*, American Chemical Society: 2000; Vol. 768, pp 297-312.
53. Gridnev, A. A.; Ittel, S. D., Catalytic Chain Transfer in Free-Radical Polymerizations. *Chem. Rev.* **2001**, *101* (12), 3611-3660.
54. MOAD, G.; RIZZARDO, E.; MOAD, C., Louise; ITTEL, S., Dale; WILCZEK, L.; GRIDNEV, A., A. CATALYTIC POLYMERIZATION PROCESS. WO/031030, 1997.
55. Morris, K. F.; Johnson, C. S., Diffusion-ordered two-dimensional nuclear magnetic resonance spectroscopy. *J. Am. Chem. Soc.* **1992**, *114* (8), 3139-3141.
56. Johnson Jr, C. S., Diffusion ordered nuclear magnetic resonance spectroscopy: principles and applications. *Prog. Nucl. Magn. Reson. Spectrosc.* **1999**, *34* (3-4), 203-256.
57. Li, W.; Chung, H.; Daefler, C.; Johnson, J. A.; Grubbs, R. H., Application of <sup>1</sup>H DOSY for Facile Measurement of Polymer Molecular Weights. *Macromolecules* **2012**, *45* (24), 9595-9603.
58. Thania S. Jiminez-Martinez, S. R.-M., Nuria Esturau-Escofet, Manuel Briseno-Teran, DOSY Experiments to Monitor Block Copolymer Polymerization. *J. Mex. Chem. Soc.* **2011**, *55* (2), 101-104.
59. Viel, S.; Mazarin, M.; Giordanengo, R.; Phan, T. N. T.; Charles, L.; Caldarelli, S.; Bertin, D., Improved compositional analysis of block copolymers using Diffusion Ordered NMR Spectroscopy. *Anal. Chim. Acta* **2009**, *654* (1), 45-48.
60. Monroy-Barreto, M.; Pérez-Vázquez, M. d. C.; Briseño-Terán, M.; Esturau-Escofet, N., Microstructural Characterization of Diblock Copolymers Formed by Styrene and Different Methacrylic Units. *Int. J. Polym. Anal. Char.* **2014**, *19* (1), 22-30.
61. Debuigne, A.; Caille, J.-R.; Jérôme, R., Synthesis of End-Functional Poly(vinyl acetate) by Cobalt-Mediated Radical Polymerization. *Macromolecules* **2005**, *38* (13), 5452-5458.
62. Britton, D.; Heatley, F.; Lovell, P. A., Chain Transfer to Polymer in Free-Radical Bulk and Emulsion Polymerization of Vinyl Acetate Studied by NMR Spectroscopy. *Macromolecules* **1998**, *31* (9), 2828-2837.
63. Kukulj, D.; Davis, T. P., Mechanism of catalytic chain transfer in the free-radical polymerisation of methyl methacrylate and styrene. *Macromol. Chem. Phys.* **1998**, *199* (8), 1697-1708.
64. Moad, G.; Solomon, D. H., *The Chemistry of Free Radical Polymerization*. 1st ed.; Elsevier Science Ltd: Oxford, 1995.
65. Wang, T. J.; Leamen, M. J.; McManus, N. T.; Penlidis, A., Copolymerization of Alpha-Methyl Styrene with Butyl Acrylate: Parameter Estimation Considerations. *J. Macromol. Sci. Part A Pure Appl. Chem.* **2004**, *41* (11), 1205-1220.
66. Moad, G.; Anderson Albert, G.; Ercole, F.; Johnson Charles, H. J.; Krstina, J.; Moad Catherine, L.; Rizzardo, E.; Spurling Thomas, H.; Thang San, H., Controlled-Growth Free-Radical Polymerization of Methacrylate Esters: Reversible Chain Transfer versus Reversible Termination. In *Controlled Radical Polymerization*, American Chemical Society: 1998; Vol. 685, pp 332-360.



67. Kukulj, D.; Davis, T. P., Average Propagation Rate Coefficients in the Free-Radical Copolymerization of Styrene and  $\alpha$ -Methylstyrene Measured by Pulsed-Laser Polymerization. *Macromolecules* **1998**, *31* (17), 5668-5680.
68. Barner-Kowollik, C.; Davis, T. P., Using Kinetics and Thermodynamics in the Controlled Synthesis of Low Molecular Weight Polymers in Free-Radical Polymerization. *macromol. theory simul.* **2001**, *10* (4), 255-261.
69. Chiefari, J.; Jeffery, J.; Krstina, J.; Moad, C. L.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H., Binary Copolymerization with Catalytic Chain Transfer. A Method for Synthesizing Macromonomers Based on Monosubstituted Monomers. *Macromolecules* **2005**, *38* (22), 9037-9054.
70. Sanders, G. C.; Duchateau, R.; Lin, C. Y.; Coote, M. L.; Heuts, J. P. A., End-Functional Styrene-Maleic Anhydride Copolymers via Catalytic Chain Transfer Polymerization. *Macromolecules* **2012**, *45* (15), 5923-5933.
71. Barner-Kowollik, C.; Junkers, T., Kinetic and mechanistic similarities between reversible addition fragmentation chain transfer intermediate and acrylate midchain radicals. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49* (5), 1293-1297.
72. Peck, A. N. F.; Hutchinson, R. A., Secondary Reactions in the High-Temperature Free Radical Polymerization of Butyl Acrylate. *Macromolecules* **2004**, *37* (16), 5944-5951.
73. Vandenberg, J.; Junkers, T., Macromonomers from AGET Activation of Poly(n-butyl acrylate) Precursors: Radical Transfer Pathways and Midchain Radical Migration. *Macromolecules* **2012**, *45* (17), 6850-6856.
74. Junkers, T.; Barner-Kowollik, C., The role of mid-chain radicals in acrylate free radical polymerization: Branching and scission. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46* (23), 7585-7605.
75. Mandelkern, L., *Crystallization of Polymers*. Cambridge University Press: 2002; Vol. 1: Equilibrium Concepts.
76. Wunderlich, B., *Thermal Analysis*. Academic Press, Inc.: London, 1990.
77. Wunderlich, B., Multiple Component Materials. In *Thermal Analysis of Polymeric Materials*, Springer: Berlin, 2005; pp 705-776.
78. Hamley, I. W., Crystallization in Block Copolymers. In *Interfaces Crystallization Viscoelasticity*, Springer Berlin Heidelberg: 1999; Vol. 148, pp 113-137.
79. Meijs, G. F.; Rizzardo, E., REACTIVITY OF MACROMONOMERS IN FREE RADICAL POLYMERIZATION. *J. Macromol. Sci. Part C: Polym. Rev.* **1990**, *30* (3-4), 305-377.
80. Rempp, P.; Lutz, P.; Masson, P.; Chaumont, P., Macromonomers: A new class of polymeric intermediates in macromolecular synthesis - II - homo- and copolymerization. *Makromol. Chem., Suppl.* **1985**, *13* (S19851), 47-66.
81. Ragnath Rao, P.; Lutz, P.; Lamps, J. P.; Masson, P.; Rempp, P., Copolymerization of polyvinylpyridine macromonomers with styrene. *Polymer Bulletin* **1986**, *15* (1), 69-75.
82. Gottlieb, H. E.; Kotlyar, V.; Nudelman, A., NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities. *J. Org. Chem.* **1997**, *62* (21), 7512-7515.
83. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29* (9), 2176-2179.