ORIGINAL ARTICLE

Aqueous emulsion homo- and copolymerization of 1,3-dienes and styrene in the presence of Cp_2TiCl_2

Stefania Pragliola, Teresa Acierno and Pasquale Longo

The aqueous emulsion homopolymerizations of 1,3-butadiene and isoprene were investigated using bis-cyclopentadienyl titanium dichloride (Cp_2TiCl_2) as an active initiator. The copolymerizations of the same monomers with styrene were also performed. Cp_2TiCl_2, which has already been used for the production of atactic polystyrene, exhibited low activity in the homopolymerization of conjugated dienes, whereas better performance was obtained in copolymerization reactions. Both of the homopolymers, polybutadiene and polyisoprene, presented similar microstructures. The majority of the polymer chains were formed by 1,4-*trans* units and, to a lesser extent, by 1,4-*cis* and 1,2 (3,4 in the case of isoprene) units. All the copolymers presented a statistical distribution with atactic polystyrene sequences and 1,4-*trans*, 1,4-*cis* and 1,2 (3,4 in the case of isoprene) diene units. The copolymerization activity values and the percentage of inserted diene units were strictly correlated to the composition of the reaction mixture. The molecular weights of the co-polymers were substantially less than those detected for the styrene homopolymer and similar to those detected for polybutadiene and polyisoprene. Depending on the composition of the copolymer, the glass transition temperatures presented values between those of polystyrene and polydienes.
Polymer Journal (2013) 45, 904–908; doi:10.1038/pj.2013.7; published online 20 February 2013

INTRODUCTION

Aqueous emulsion polymerization has become increasingly important since the middle of the past century because this technique can be applied to the production of a wide range of specialty polymers that are used in a variety of applications, such as coatings, paints, adhesives, binders, paper additives and so on.[1–4] The use of water as a polymerization medium, which replaces the majority of the commonly used organic solvent-based systems, ensures considerable economic savings and important attention to the safeguard of the environment.[1–4] In this framework, although free radical-initiated aqueous emulsion polymerization has been widely investigated,[1–4] and is currently applied for the large-scale preparation of polymers, a deeper focus on metal-catalyzed aqueous emulsion polymerization has only recently been developed.

In this regard, late-transition metal-based species such as neutral nickel compounds or cationic palladium complexes have already been investigated in the aqueous emulsion polymerization of olefins because of their low oxophilicity.[5–9] Stereospecific 1,3-butadiene polymerization leading to *trans*-1,4-polybutadiene in aqueous media catalyzed by rhodium salts was also reported as early as the 1960s.[10,11] Complexes of late-transition metals other than rhodium, such as cobalt complexes, are also well known to yield polybutadienes that present different microstructures.[12–20] The best performance for this type of polymerization has been achieved using anionic emulsifiers such as alkylbenzene sulfonates.[12–20] From the microstructural

analysis of the obtained polymers and from comparative experiments with radical inhibitors, a coordination polymerization mechanism was also hypothesized.

Compared with late-transition metal-based species, early-transition metal-based species[21–24] such as Ziegler–Natta or metallocene catalysts, which are well known to be extremely sensitive to moisture, have received less attention. The applications of these early-transition metal-based species were primarily focused in the field of coordination polymerization.[25–27] Recently, the bis-cyclopentadienyl titanium dichloride (Cp_2TiCl_2)-mediated living radical polymerization of styrene and conjugated dienes in nonaqueous media has also been reported.[28–31] Organo-titanium (III) species, which are readily obtained by the reduction of inexpensive Cp_2TiCl_2 with Zn, have been reported to catalyze styrene, substituted styrene or conjugated diene living radical polymerization initiated by epoxides, peroxides or aldehydes.[28–31]

In the literature, a few articles by Bhattacharjee *et al.*[32–36] have described the use of Cp_2MCl_2 (with Cp = cyclopentadienyl and M = Ti, Zr) as an active catalytic precursor for the aqueous emulsion homopolymerization of styrene and methylmethacrylate. This Cp_2MCl_2-catalyzed reaction produced stereoirregular polymers that had high molecular weights.[32–36] Moreover, in these reports, it has been hypothesized that the active catalytic species could be a cation such as $[Cp_2MOH]^+$, which is one of the species formed by the hydrolysis of Cp_2MCl_2,[37] stabilized by the large non-coordinating

Dipartimento di Chimica e Biologia, Università di Salerno, Fisciano, Salerno, Italy
Correspondence: Dr S Pragliola, Dipartimento di Chimica e Biologia, Università di Salerno, Via Ponte don Melillo, Fisciano, Salerno I-84084, Italy.
E-mail: spragliola@unisa.it

anion *n*-dodecylsulfate and utilized as an emulsifier.[32–36] Although the polymerization mechanism has not been definitively determined, the authors suggested that the polymerization reaction start by insertion of a monomer into the 'labile' metal-hydroxyl group bond, which excludes the possibility of free radical or spontaneous polymerization.[32–36]

Herein, we present the first report on the aqueous emulsion homopolymerization of 1,3-butadiene and isoprene catalyzed by Cp_2TiCl_2 with sodium dodecylsulfate as a co-catalyst and the copolymerization of both diene monomers with styrene. The homo- and copolymers were characterized using nuclear magnetic resonance spectroscopy (NMR) and thermal analysis, and their molecular weights and polydispersity index values were also determined using gel permeation chromatography.

EXPERIMENTAL PROCEDURE

General procedure

Styrene, isoprene, 1,3-butadiene, toluene, sodium *n*-dodecylsulfate (SDS) and Cp_2TiCl_2 were purchased from Sigma-Aldrich (Milan, Italy). Styrene and isoprene were purified by distillation over calcium hydride (CaH_2). Toluene was refluxed over sodium for 48 h and distilled before use. 1,3-butadiene, SDS and Cp_2TiCl_2 were used without further purification.

All polymerizations were conducted under a nitrogen atmosphere in degassed water at 50 °C following a procedure that was very similar to that previously described by Bhattacharjee and Patra.[32]

Homopolymerization of isoprene and styrene

A total of 0.05 mol of the monomer was emulsified in 80 ml of an aqueous solution of SDS (1.6×10^{-3} mol), and then 20 ml of a previously aged (1 h at room temperature) aqueous solution of Cp_2TiCl_2 (5.0×10^{-5} mol) was added. After 2 h, the mixture was quenched in acidified methanol. The polymer was recovered by filtration, washed with fresh methanol and dried at 40 °C in a vacuum oven.

Homopolymerization of 1,3-butadiene

A total of 0.05 mol of the monomer was dissolved in 5 ml of toluene and quickly transferred into 80 ml of an aqueous solution of SDS (1.6×10^{-3} mol). The emulsion was thermostated at 50 °C, and then 20 ml of a previously aged (1 h at room temperature) aqueous solution of Cp_2TiCl_2 (5.0×10^{-5} mol) was added. After 2 h, the mixture was quenched in acidified methanol. The polymer was recovered by filtration, washed with fresh methanol and dried at 40 °C in a vacuum oven.

Copolymerization of diene with styrene

The styrene–1,3-butadiene (S/B) and styrene–isoprene (S/I) copolymers were prepared following the same procedure used for the homopolymerization reactions using 0.05 mol of styrene and the appropriate amount of diene, as indicated in Tables 3 and 4.

Polymer analysis

NMR spectra were recorded on an AM 250 Bruker spectrometer (Bruker, Milan, Italy) operating at 62.89 MHz at 298K. The samples were prepared by dissolving 40 mg of polymer in 0.5 ml of deuterated chloroform ($CDCl_3$). Tetramethylsilane was used as an internal reference for the chemical shifts. Calorimetric measurements were conducted on a DSC 2920 instrument manufactured by TA Instruments (Milan, Italy) under a flow of nitrogen (N_2) at a heating rate of 10 °C per min.

The molecular weights and molar mass distributions of the polymers were measured by gel permeation chromatography at 30 °C, in which tetrahydrofurane (THF) was used as a solvent, the eluent flow rate was 1 ml min⁻¹ and narrow polystyrene standards were used as references. The gel permeation chromatography measurements were performed on a Waters 1525 binary system equipped with a Waters 2414 RI detector (Waters, Milan, Italy) using four Styragel columns (range 1000–1 000 000 Å).

RESULTS

Homopolymerization of 1,3-butadiene and isoprene

The polymerizations of both monomers were conducted under a nitrogen atmosphere in degassed water at 50 °C. The polymerization of isoprene was performed using the procedure described by Bhattacharjee and Patra[32] for the polymerization of styrene, whereas in the case of 1,3-butadiene, the monomer was previously dissolved in toluene. All the reaction procedures used in this study are detailed in the Experimental procedure section.

The experimental data related to the homopolymerization of 1,3-butadiene and isoprene are presented in Table 1. For comparison, the data related to the polymerization of styrene are also reported.

Both diene monomers polymerize, although their activities are less than that detected for styrene. The molecular weights of the polydienes are also less than those of polystyrene, whereas the polydispersity index values are comparable to those collected for polystyrene.

The microstructures of the polymers were determined by ¹³C NMR analysis. The NMR spectra of the polybutadiene and polyisoprene samples are presented in Figures 1a and b, respectively. The resonances relative to the carbons of all recognized structural units were assigned on the basis of the data reported in the literature.[38,39]

The obtained polydienes exhibit similar microstructures. The polybutadiene chains are formed from 66%, 21% and 13% of 1,4-*trans* 1,4-*cis* and 1,2 units, respectively. The polyisoprene chains are also composed of 63%, 20% and 17% of 1,4-*trans*, 1,4-*cis* and 3,4 units, respectively. For both polymers, the 1,2 units of polybutadiene and the 3,4 units of polyisoprene are present in the polymer chains as isolated units. In fact, the obtained microstructures of both polybutadiene and polyisoprene are very similar to those of polydienes produced by the widely utilized industrial free radical polymerization.[40]

Table 1 1,3-butadiene, isoprene and styrene homopolymerization data

Monomer	Yield (g)	%Conv.	A^a (g per mol h)	M_w Dalton $\times 10^5$	MWD^b	T_g^c (°C)
1,3-butadiene	0.10	3.7	1000	18.0	2.7	−89.0
Isoprene	0.21	6.2	2100	7.1	3.6	−49.2
Styrene	1.57	30	15 700	54.0	2.4	100

Abbreviations: M_w, molecular weight; MWD, molar mass distribution.
ᵃA (activity): g of polymer per mol of bis-cyclopentadienyl titanium dichloride (Cp_2TiCl_2) × polymerization time (h).
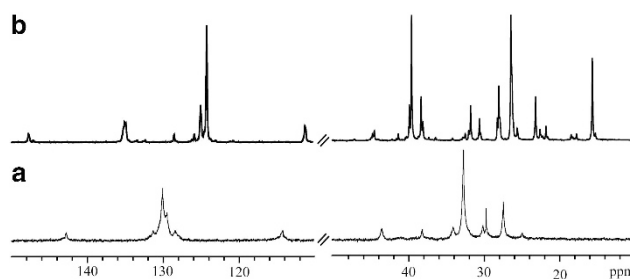ᵇPolydispersity index.
ᶜGlass transition temperature.

Figure 1 The ¹³C nuclear magnetic resonance (NMR) spectra of polybutadiene (**a**) and polyisoprene (**b**) samples of Table 1. Tetramethylsilane scale, deuterated chloroform ($CDCl_3$), room temperature (RT).

Finally, the glass transition temperatures of both the polybutadiene and polyisoprene samples are those expected for polymers that present similar microstructures.[41,42]

Copolymerization of dienes (1,3-butadiene or isoprene) with styrene

The copolymerizations were conducted under a nitrogen atmosphere in degassed water at 50 °C. All the procedures used for the copolymerizations are described in the Experimental procedure section.

The obtained S/B and S/I copolymers were analyzed by ¹³C NMR. The compositions of the copolymers are reported in Table 2.

As an example, the ¹³C NMR spectra of samples 2B and 3I in Table 2 are presented in Figures 2a and b, respectively. The resonances relative to the carbons of all the recognized structural units were assigned on the basis of the data reported in the literature[43–45] and are listed in the Supplementary Information.

All the copolymers present a statistical distribution with atactic polystyrene sequences and *trans*-1,4-, *cis*-1,4- and 1,2- (for S/B copolymers) and 3,4- (for S/I copolymers) diene units. Note that the percent content of different types of diene units in the copolymers are almost the same as that observed in diene homopolymers and

does not substantially depend on the content of styrene. As in the case of diene homopolymerization, these experimental data relative to the obtained copolymer microstructures support the hypothesis that diene homopolymerization and their copolymerization with styrene follow a free radical rather than an insertion mechanism. In fact, for the insertion polymerization mechanism, a strong dependence of the *cis/trans* diene units ratio from the content of copolymer styrene units is usually observed.

In Tables 3 and 4, the experimental data concerning the S/B and S/I copolymers are reported. As expected, the percentage of diene units in copolymer chains, which was evaluated via ¹³C NMR measurements, is closely related to the amount of the diene monomer present in the reaction mixture. In fact, when the amount of diene in the feed is decreased, a decrease in the number of inserted diene units is observed.

The copolymerization activity values can also be correlated to the composition of the reaction mixture. Consistent with the lower homopolymerization activity observed for the dienes compared with styrene (see Table 1), a gradual decrease in the activity values with the increase of copolymer diene unit percentage was detected.

The molecular weights of both the S/B and S/I copolymers are significantly less than those observed for the styrene homopolymer and are comparable to those of polybutadiene and polyisoprene.

Table 2 S/B and S/I copolymer composition data

| | | | | Inserted diene units (%) | | | |
Sample	X_S in the feed[a]	Comonomer	$\%_{comon.}$in the copolymer[b]	1,4-Trans	1,4-Cis	1,2-	3,4-
1B	0.60	1,3-butadiene	22.9	62.3	17.9	19.8	—
2B	0.50	1,3-butadiene	27.1	67.1	20.8	12.1	—
3B	0.40	1,3-butadiene	37.1	60.1	21.7	18.2	—
4B	0.30	1,3-butadiene	41.2	65.6	17.3	17.1	—
5B	0	1,3-butadiene	100	66.0	20.9	13.1	—
1I	0.90	Isoprene	49.1	63.4	28.8	—	7.8
2I	0.50	Isoprene	57.3	61.3	32.6	—	6.1
3I	0.30	Isoprene	71.6	61.1	28.8	—	10.1
4I	0.20	Isoprene	76.5	64.4	31.8	—	3.8
5I	0	Isoprene	100	63.0	20.9	—	17.1

Abbreviations: S/B, styrene–1,3-butadiene; S/I, styrene–isoprene.
[a]Molar fraction of styrene in the reaction mixture.
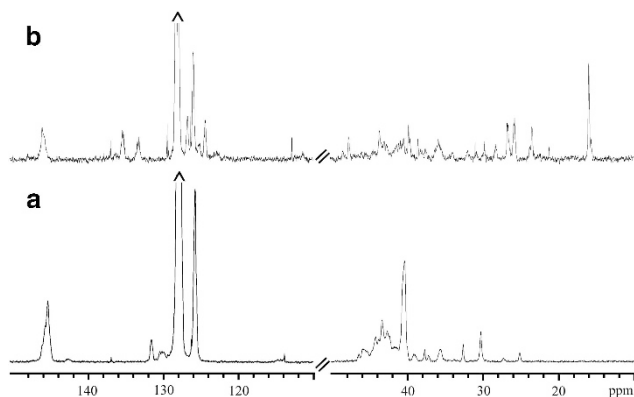[b]Molar percentage of inserted diene units.

Table 3 S/B copolymer experimental data

Sample	X_S in the feed[a]	$\%_B$ in the copolymer[b]	A[c] (g per mol h)	M_w Dalton $\times 10^5$	MWD[d]	T_g[e] (°C)
S[f]	1	—	15 700	54.0	2.4	100
1B	0.60	22.9	5595	21.2	2.1	81.0
2B	0.50	27.1	5851	19.3	2.2	61.6
3B	0.40	37.3	2797	18.4	3.2	56.5
4B	0.30	41.2	2711	17.9	2.6	51.8
5B	0	100	1000	18.0	2.7	−87.0

Abbreviations: M_w, molecular weight; MWD, molar mass distribution; S/B, styrene–1,3-butadiene.
[a]Molar fraction of styrene in the reaction mixture.
[b]Molar percentage of inserted B units.
[c]A (activity): g of polymer per mol of bis-cyclopentadienyl titanium dichloride (Cp₂TiCl₂) × copolymerization time (h).
[d]Polydispersity index.
[e]Glass transition temperature.
[f]Polystyrene sample.

Table 4 S/I copolymer experimental data

Sample	X_S in the feed[a]	$\%_I$ in the copolymer[b]	A[c] (g per mol h)	M_w Dalton $\times 10^5$	MWD[d]	T_g[e] (°C)
S[f]	1	—	15 700	54.0	2.4	100
1I	0.90	49.1	4168	3.9	5.9	16.6
2I	0.50	57.3	3597	13.8	3.0	−0.61
3I	0.30	76.5	3568	1.7	3.4	−23.8
4I	0.20	71.6	3026	6.3	3.1	−11.8
5I	0	100	2100	7.1	3.6	−49.2

Abbreviations: M_w, molecular weight; MWD, molar mass distribution; S/I, styrene–isoprene.
[a]Molar fraction of styrene in the reaction mixture.
[b]Molar percentage of inserted isoprene units.
[c]A (activity): g of polymer per mol of bis-cyclopentadienyl titanium dichloride (Cp₂TiCl₂) × copolymerization time (h).
[d]Polydispersity index.
[e]Glass transition temperature.
[f]Polystyrene sample.

Figure 2 The ¹³C nuclear magnetic resonance (NMR) spectra of samples 2B (**a**) and 3I (**b**) of Table 2. Tetramethylsilane scale, deuterated chloroform (CDCl₃), room temperature (RT).
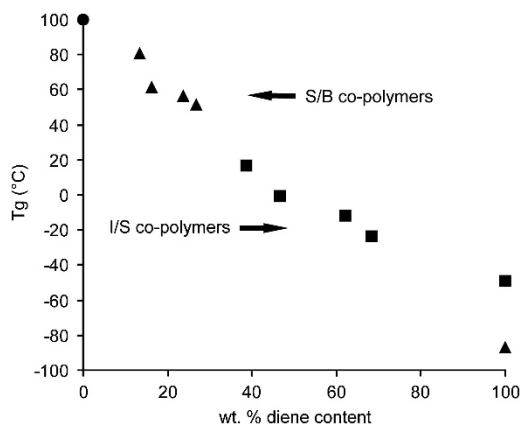
Figure 3 The styrene–1,3-butadiene (S/B; ▲) and styrene–isoprene (S/I; ■) copolymer glass transition temperature values versus composition of the copolymer. Polystyrene (●).

Moreover, a slight decrease in the molecular weights of the S/B copolymer, even if not really significant, was observed as the number of inserted 1,3-butadiene units increased, whereas in the case of the S/I copolymers, no correlation between their composition and molecular weight values was observed. The polydispersity index values of the S/B copolymer do not appear to be affected by the composition of the copolymer. The polydispersity index values of the S/I copolymer are greater than those of S/B copolymers, ranging between 2.5 and 6. These data are consistent with the higher molecular weights detected for the S/I copolymers than those observed for the S/B copolymers.

Finally, a strong dependence of the glass transition temperatures of both the S/B and S/I copolymers on the copolymer composition was also observed. As expected for copolymers of monomers that yield amorphous homopolymers and provide a statistical distribution, the glass transition temperatures of the copolymers are between those observed for styrene and 1,3-butadiene homopolymers and decrease almost linearly with the increasing content of diene units (see Figure 3). In particular, the trend followed by the glass transition temperatures of the S/B copolymer very closely follows that predicted by the Fox equation.[46]

CONCLUSIONS

1,3-Butadiene and isoprene were investigated in aqueous emulsion homopolymerization using Cp_2TiCl_2 as an active catalytic precursor, which has already been used for the production of atactic polystyrene. Copolymerizations of the same monomers with styrene were also performed.

Cp_2TiCl_2 exhibited low activity in the homopolymerization of conjugated dienes, whereas better performance was obtained during copolymerization.

Both of the homopolymers, polybutadiene and polyisoprene, present similar microstructures. The majority of the polymer chains are formed by 1,4-*trans* units and, to a lesser extent, by 1,4-*cis* and 1,2 (3,4 in the case of isoprene) units.

All the copolymers present a statistical distribution with atactic polystyrene sequences and 1,4-*trans*, 1,4-*cis* and 1,2 (3,4 in the case of isoprene) diene units, and the percent content of different types of diene units in the copolymers is almost the same as that detected for homopolymers.

The copolymerization activity values and the percentage of inserted diene units are strictly correlated to the composition of the reaction mixture. When the diene monomer in the feed is decreased, a gradual decrease in the activity values and in the number of inserted diene units is observed.

The molecular weights of the copolymers are substantially less than those detected for the styrene homopolymer and similar to those detected for polybutadiene and polyisoprene.

A strong dependence of the copolymer glass transition temperatures on the compositions of the copolymers was also observed, and as expected for statistical copolymers, their values follow a linear trend and are between those observed for styrene and diene homopolymers.

From the experimental data related to the microstructures of the homo- and copolymers, the hypothesis that in both cases the reaction proceeds following a free radical mechanism, which is likely generated by Ti (III) species derived from the hydrolysis of Cp_2TiCl_2, should be considered, at least, to be an 'educated guess.' At the present, the nature of the titanium species responsible for the polymerization reaction has not yet been clarified, and therefore further experimental studies are in progress.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

1   Lovell, P. A. & El-Aasser, M. S. (eds) *Emulsion Polymerization and Emulsion Polymers* (Wiley, Chicester, England, 1997).
2   Urban, D. & Takamura, K. (eds.) *Polymer Dispersions and Their Industrial Applications* (Wiley-VCH: Weinheim, Germany, 2002).
3   Asua, J. M. Emulsion polymerization: from fundamental mechanisms to process developments. *J. Polym. Sci. A Polym. Chem.* **42**, 1025–1041 (2004).
4   Fitch, R. M. *Polymer Colloids: A Comprehensive Introduction* (Academic Press, San Diego, 1997).
5   Held, A., Bauers, F. M. & Mecking, S. Coordination polymerization of ethylene in water by palladium(II) and nickel(II) catalysts. *Chem. Commun.* 301–302 (2000).
6   Held, A. & Mecking, S. Coordination polymerization in water affording amorphous polyethylenes. *Chem. Eur. J.* **6**, 4623–4629 (2000).
7   Bauers, F. M. & Mecking, S. Aqueous homo- and copolymerization of ethylene by neutral nickel(II) complexes. *Macromolecules* **34**, 1165–1171 (2001).
8   Soula, R., Novat, C., Tomov, A., Spitz, R., Claverie, J., Drujon, X., Malinge, J. & Sudemont, T. Catalytic polymerization of ethylene in emulsion. *Macromolecules* **34**, 2022–2026 (2001).
9   Johnson, L. K., Killian, C. M., Arthur, S. D., Feldman, J., McCord, E., McLain, S. J., Kreutzer, K. A., Bennet, M. A., Coughlin, E. B., Ittel, S., Parthasarathy, A., Tempel, D. J. & Brookhart, M. S. α-Diimine-transition metal complexes, their preparation and use as catalysts for (co)polymerization of (fluoro)olefins and olefinic esters (Du Pont) WO-A-96/23010 (1996). *Chem. Abstr.* **125**, 222773t (1996).
10 Rinehart, R. E., Smith, H. P., Witt, H. S. & Romeyn, H. The preparation of trans 1,4-polybutadiene by rhodium salts in solution. *J. Am. Chem. Soc.* **83**, 4864–4865 (1961).
11 Canale, A. J., Hewett, W. A., Shryne, T. M. & Youngman, E. A. Stereospecific polymerization of butadiene by transition metal salts in polar media. *Chem. Ind.* 1054–1055 (1962).
12 Henderson, J. N., Donbar, K. W., Barbour, J. B. & Bell, A. J. Microencapsulated aqueous polymerization catalyst (Goodyear) US 4429085 (1984). *Chem. Abstr.* **100**, 157154j (1984).
13 Burroway, G. L., Magoun, G. F. & Gujarathi, R. N. Preparation of syndiotactic 1,2-polybutadiene latex in presence of microencapsulated catalysts (Goodyear) US 5278263 (1991). *Chem. Abstr.* **112**, 236729b (1990).
14 Burroway, G. L. Syndiotactic 1,2-polybutadiene synthesis in an aqueous medium utilizing N,N-dibutylformamide as a modifier (Goodyear) US 5278263 (1994). *Chem. Abstr.* **120**, 218842u (1994).
15 Hidetomo, A., Kazuya, J. & Haruo, U. Syndiotactic 1,2 polybutadiene with cobalt-carbon disulfide catalyst system. Catalysts for stereospecific polymerization of butadiene to syndiotactic 1,2-polybutadiene. *J. Polym. Sci. Polym. Chem. Ed.* **21**, 1951–1972 (1983).

16 Hidetomo, A., Kazuya, J. & Haruo, U. Syndiotactic 1,2-polybutadiene with cobalt-carbon disulfide catalyst system. Mechanism of syndiotactic polymerization of butadiene with cobalt compounds-organoaluminum-carbon disulfide. *J. Poym. Sci. Polym. Chem. Ed.* **21,** 1989–1995 (1983).

17 Ono, H., Ito, N., Kasai, K., Sakurai, N. & Okuya, E. Polymer particles. *Eur. Pat. Appl* European patent 170456 (1986).

18 Ono, H. & Kato, T. Stereoregular emulsion polymerization of butadiene. *J. Polym. Sci. A Polym. Chem.* **38,** 1083–1089 (2000).

19 Monteil, V., Bastero, A. & Mecking, S. 1,2-polybutadiene latexes by catalytic polymerization in aqueous emulsion. *Macromolecules* **38,** 5393–5399 (2005).

20 Monteil, V., Wehrmann, P. & Mecking, S. A general route to very small polymer particles with controlled microstructures. *J. Am. Chem. Soc.* **127,** 14568–14569 (2005).

21 Fink, G., Mülhaupt, R. & Brintzinger, H. H. *Ziegler Catalysts* (Springer, Berlin, 1995).

22 Brintzinger, H. H., Fischer, D., Mülhaupt, R., Rieger, B. & Waymouth, R. Stereospecific olefin polymerization with chiral metallocene catalysts. *Angew. Chem. Int. Ed. Engl.* **34,** 1143–1170 (1995).

23 Britovsek, G. J. P., Gibson, V. C. & Wass, D. F. The search for new-generation olefin polymerization catalysts: life beyond metallocenes. *Angew. Chem. Int. Ed. Engl.* **38,** 428–447 (1999).

24 Kaminsky, W. & Arndt, M. Metallocenes for polymer catalysis. *Adv. Polym. Sci.* **127,** 143–187 (1997).

25 Resconi, L., Cavallo, L., Fait, A. & Piemontesi, F. Selectivity in propene polymerization with metallocene catalysts. *Chem. Rev.* **100,** 1253–1346 (2000).

26 Razavi, A. & Thewalt, U. Site selective ligand modification and tactic variation in polypropylene chains produced with metallocene catalysts Coord. *Chem. Rev.* **250,** 155–169 (2006).

27 Delferro, M. & Marks, T. J. Multinuclear olefin polymerization catalysts. *Chem. Rev.* **111,** 2450–2485 (2011).

28 Asandei, A. D., Chen, Y., Saha, G. & Moran, I. W. Cp2TiCl-catalyzed radical chemistry: living styrene polymerizations from epoxides, aldehydes, halides and peroxides. *Tetrahedron* **64,** 11831–11838 (2008).

29 Asandei, A. D., Simpson, C. P., Yu, H. S., Adebolu, O. I., Saha, G. & Chen, Y. Cp2TiCl-catalyzed controlled radical polymerization of isoprene initiated by epoxide radical ring opening. *ACS Symp. Ser. Control./Living Radic. Polym.* **1024,** 149–166 (2009).

30 Asandei, A. D. & Chen, Y. Cp2TiCl-catalyzed SET Reduction of aldehydes: a new initiating protocol for living radical polymerization. *Macromolecules* **39,** 7459–7554 (2006).

31 Asandei, A. D., Moran, I. W., Saha, G. & Chen, Y. Ti-mediated living radical styrene polymerizations. 6. Cp2TiCl-catalyzed initiation by epoxide radical ring opening: effect of reducing agents, temperature, Ti/Epoxide and Ti/Zn ratios. *J. Polym. Sci. A Polym. Chem.* **44,** 2156–2165 (2006).

32 Bhattacharjee, M. & Patra, B. N. [Cp$_2$TiCl$_2$] as polymerization catalyst in aqueous medium: polymerization of styrene in water. *J. Organomet. Chem.* **689,** 1091–1094 (2004).

33 Bhattacharjee, M. & Patra, B. N. [Cp$_2$TiCl$_2$] Catalyzed polymerization in water: polymerization of methyl methacrylate to a high molecular weight polymer. *Polymer* **45,** 3111–3114 (2004).

34 Patra, B. N. & Bhattacharjee, M. Synthesis of high molecular weight polystyrene and poly(methyl methacrylate) with low polydispersity by [Cp2ZrCl2] catalyzed aqueous polymerization. *J. Polym. Sci. A Polym. Chem.* **43,** 3797–3803 (2005).

35 De, S. K. & Bhattacharjee, M. An environmentally benign room temperature aqueous homo- and copolymerization of styrene and methyl methacrylate catalyzed by [Cp2TiCl2]/NaBPh4. *J. Polym. Sci. A Polym. Chem.* **47,** 6496–6503 (2009).

36 De, S. K. & Bhattacharjee, M. Synthesis of high molecular weight polymer nanoparticles by [Cp2ZrCl2] catalyzed emulsion polymerization. *J. Polym. Sci. A Polym. Chem.* **49,** 3920–3927 (2011).

37 Bottrill, M., Gavens, P. D., Kelland, J. W. & McMeeking, J. in *Comprehensive Organometallic ChemistryWilkinson, G. (eds. Vol. 3,* 331–431 (Pergamon Press, Oxford, 1982).

38 Matsuzaki, K., Uryu, T. & Asakura, T. *NMR Spectroscopy and Stereoregularity of Polymers* 41–50 (Japan Scientific Societies Press, 1996).

39 Tanaka, Y. & Sato, H. Sequence distribution of polyisoprenes. *Polymer* **17,** 413–418 (1976).

40 Obrecht, W. *Ullmann's Encyclopedia of Industrial Chemistry.* 6th ednVol. 31, 461–600 (Wiley-VCH, Weinheim, Germany,, 2003).

41 Widmaier, J. M. & Meyer, G. C. Glass transition temperature of anionic polyisoprene. *Macromolecules* **14,** 450–452 (1981).

42 Sircar, A. K. Characterization of isomeric elastomers using thermal analysis. *J. Ther. Anal.* **49,** 293–301 (1997).

43 Zambelli, A., Caprio, M., Grassi, A. & Bowen, D. E. Syndiotactic styrene-butadiene block copolymers synthesized with CpTiX3/MAO (Cp = C5H5, X = Cl, F; Cp = C5Me5, X = Me) and TiXn/MAO (n = 3, X = acac; n = 4, X = O-tert-Bu). *Macromol. Chem. Phys.* **201,** 393–400 (2000).

44 Caprio, M., Serra, M. C., Bowen, E. D. & Grassi, A. Structural characterization of novel styrene-butadiene block copolymers containing syndiotactic styrene homosequences. *Macromolecules* **35,** 9315–9322 (2002).

45 Cuomo, C., Serra, M. C., Gonzalez-Maupoey, M. & Grassi, A. Copolymerization of styrene with butadiene and isoprene catalyzed by the monocyclopentadienyl titanium complex Ti(η5-C5H5)(η2-MBMP)Cl. *Macromolecules* **40,** 7089–7097 (2007).

46 Fox, T. Influence of diluent and of copolymer composition on the glass temperature of a polymer system. *Bull. Am. Phys. Soc.* **123,** 1 (1956).

Supplementary Information accompanies the paper on Polymer Journal website (http://www.nature.com/pj)