220 *Macromolecules* **2005,** *38,* 220−222

Synthesis of Submicrometer Particles of a Stereoregular Polyolefin by Catalysis in Aqueous Dispersion

Amaia Bastero and Stefan Mecking*

Universität Konstanz, Fachbereich Chemie,
Universitätsstrasse 10, D-78457 Konstanz, Germany

Received November 15, 2004
Revised Manuscript Received November 24, 2004

Stereoregular polyolefins are of vast academic and industrial interest.[1] A multitude of polymer microstructures are accessible today via catalyst design. A control of polymer morphology is equally important. Polyolefin particle sizes and structures have been studied intensively in the context of traditional olefin polymerization processes. However, a synthesis of defined *submicrometer* particles of stereoregular polyolefins remains a challenge, despite the increasing general interest in the preparation of particles and other structures on the length scale of 1 nm to 1 μm (i.e., the colloidal range). Such defined particles, that is individual nonaggregated and thus easy to handle particles could be possible by preparing them in an aqueous dispersion, that is a polymer latex. Beyond the aforementioned fundamental interest in the synthesis of small particles, it can be noted that polymer dispersions are also of practical interest, e.g. for environmentally friendly coatings and paints.[2]

The early transition metal Ziegler or metallocene catalysts used traditionally for stereospecific olefin polymerization are very sensitive to water.[3,4] Late transition metal catalysts are much more water-stable, and they enable the synthesis of polyolefin dispersions by ethylene polymerization in aqueous systems.[5,6] However, transition metal catalysts most often polymerize 1-olefins in a nonstereospecific fashion.[7]

As an approach to the preparation of dispersions of submicrometer particles of stereoregular polyolefins, we have investigated catalytic polymerization in emulsion proceeded by polymer-analogous modification in the dispersed particles. Catalytic polymerization of butadiene with a CS_2-modified cobalt catalyst yields latices of syndiotactic 1,2-polybutadiene (1,2-PBD).[8] Catalytic hydrogenation[9] of such latices seemed a possible route to stereoregular poly(1-butene) dispersions (Scheme 1).

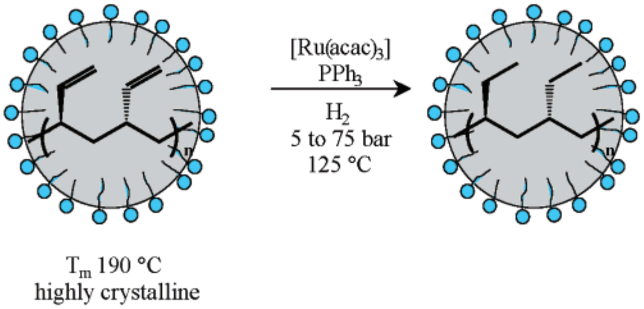
To the aqueous 1,2-PBD dispersion, ruthenium(III) tris(2,4-pentanedionate) and triphenylphosphine were added, and the emulsion was submitted to hydrogen pressure. Colloidal stability is fully retained despite the high reaction temperature (vide infra). The ^{1}H NMR spectra of the polymer (Supporting Information, Figure S1) reveals the disappearance of the olefinic protons (5.0−5.5 ppm range), demonstrating complete hydrogenation (> 99%) of the double bonds present in the starting polymer (Table 1, entry 4, 75 bar H_2).[10] No metathesis, which could be conceivable,[11] is observed.

Table 1. Hydrogenation Results[a]

entry	hydrogen pressure (bar)	degree of hydrogenation[b] (%)	$Ø_{final}/Ø_{starting}$[c] (nm)	T_m[d] (°C)
1	5	65	242/260	147
2	50	91	221/228	*e*
3	75	95	173/177	*e*
4[f]	75	>99	169/177	*e*
5[g]	70	<5[h]	n.d.	177

[a] Reaction conditions: 40 mL of 1,2-PBD dispersion (4−6% solids content); catalyst prepared in 2 mL toluene; [C=C]/[Ru] = 10^3, $[PPh_3]/[Ru] = 4$; time: 14 h; $T = 125$ °C. [b] Determined by ^{1}H NMR. [c] Volume average particle sizes determined by DLS. [d] Determined by DSC (10 °C min^{-1}). Starting 1,2-PBD has $T_m = 190$ °C. [e] No clear thermal transition observed. [f] [C=C]/[Ru] = 500. [g] $T = 100$ °C. [h] Determined by IR.

Scheme 1. Catalytic Hydrogenation Affording Poly(1-butene) Dispersions



Remarkably already low hydrogen pressures (5 bar) are sufficient to hydrogenate a substantial part of the double bonds of the polymer as seen by NMR and IR (65%, entry 1). At higher pressures an increase of the degree of hydrogenation is observed (entries 2−4) under otherwise identical conditions. Reasonable conversions are only observed at temperatures greater than 100 °C (entry 5). Most likely, this effect relates to the necessity of some softening of the crystalline dispersed particles to facilitate diffusion of the hydrogen substrate and possibly also the catalyst in the initially highly crystalline latex particles. At 150 °C substantial coagulation was observed.

Differential scanning calorimetry (DSC) measurements were performed on the isolated polymers obtained by precipitation from the dispersions (cf. Supporting Information, Figure S4). As expected, the high T_m of the 1,2-PBD (190 °C) is reduced by hydrogenation of part of the vinyl groups (65%, entry 1). Complete hydrogenation affords a rubbery, noncrystalline polymer. No thermal transitions are observed, in accordance with the properties expected for syndiotactic poly(1-butene).[12]

Transmission electronic microscopy (TEM) reveals how the increase of the degree of hydrogenation of the polymer dispersion results in soft particles, by comparison to the hard crystalline particles of the starting 1,2-PBD dispersion (Figure 1).

Chain scission resulting in substantial molecular weight decrease is a crucial issue for any polymer-analogous modification, albeit it appears unlikely for the reaction studied. GPC reveals no evidence for chain ruptures, e.g. for a >99% hydrogenated polymer (Table 1, entry 4) $M_w = 1.2 \times 10^5$ g mol^{-1} was determined vs $M_w = 1.1 \times 10^5$ g mol^{-1} for the 1,2-PBD starting material (Figure S6). This difference is within experimental error, given that these are apparent molecular weights (determined vs polyethylene standards).

One of the remarkable attributes of this catalytic polymer-analogous modification is that it proceeds in

---

* Corresponding author. E-mail: stefan.mecking@uni-konstanz.de.

10.1021/ma047649z CCC: $30.25

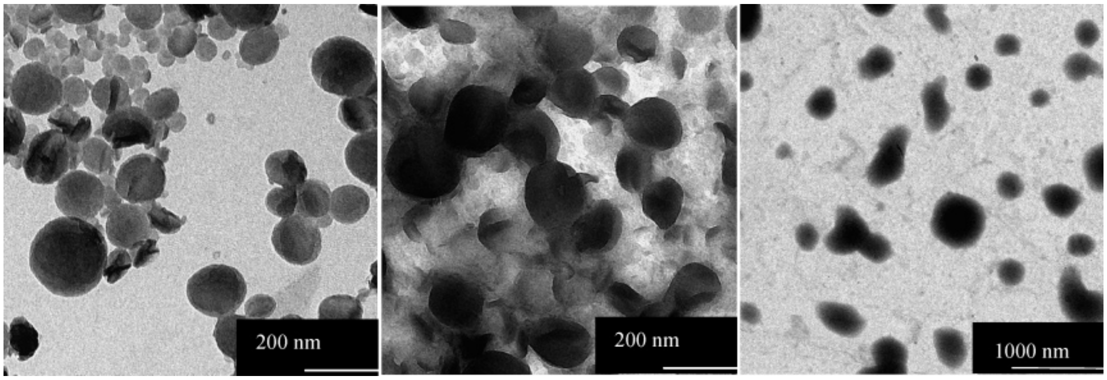


Figure 1. TEM micrographs of a 1,2-PBD dispersion (left); 26% hydrogenated (middle); syndiotactic poly(1-butene) dispersion (>99% degree of hydrogenation; right).

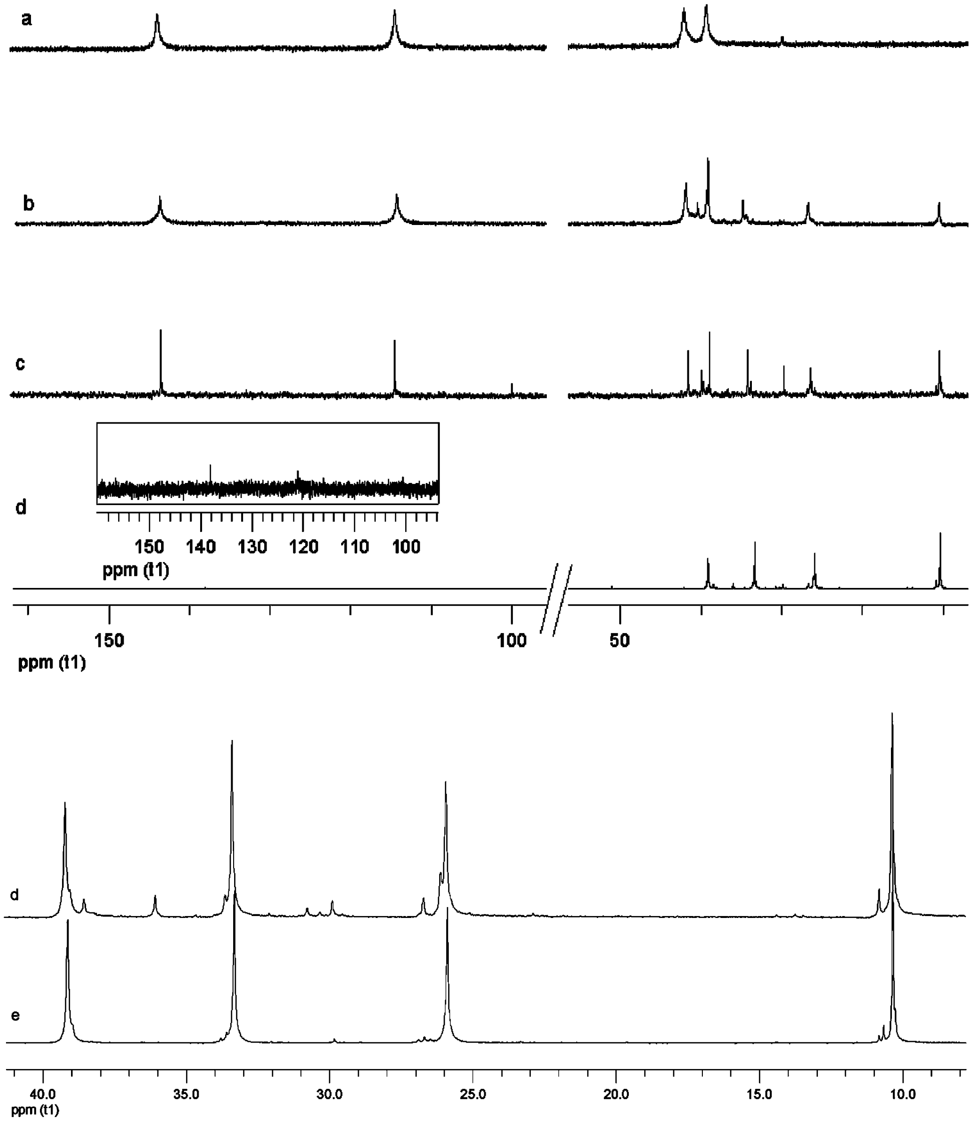


Figure 2. ^{13}C NMR spectra for polybutadienes with different degrees of hydrogenation: (a) 1,2-polybutadiene; (b) 26% hydrogenated; (c) 60% hydrogenated; (d) >99% hydrogenated; (e) genuine sample of syndiotactic poly(1-butene) prepared according to ref 13.

the polymer particles, which can be considered as nanoreactors. Measurement of the volume average particle size by dynamic light scattering (DLS) of the starting 1,2-PBD dispersion and the final hydrogenated dispersion (Table 1) confirms that the catalytic reaction is performed without modification of the particle size within experimental error, that is the individual particles retain their identity.

The microstructure of the polymer was investigated by ^{13}C NMR spectroscopy (Figure 2). Comparison of the ^{13}C NMR spectrum with that of genuine samples of isotactic poly(1-butene) (iPB) and syndiotactic poly(1-butene) (sPB)[12] confirm that indeed our polymer is syndiotactic. Small additional signals can be assigned completely to $-(CH_2)_4-$ units, originating from 1,4-incorporated butadiene units (ca. 3%, largely isolated units. Supporting Information, Figure S2).[13] As for stereoregularity, comparison with the aforementioned spectra of iPB and sPB gives no indication of any stereoerrors (Figure S3). A very small amount of stereoerrors cannot be absolutely excluded, as the key signals would coincidentally be obscured by those arising from the aforementioned $-(CH_2)_4-$ units.[14] Although the retention of stereoregularity could be expected, both maintenance of particle and polymer structure are here first shown in dispersion.

In summary, a controlled synthesis of submicrometer particles of a stereoregular polyolefin, in the form of an aqueous dispersion, is reported for the first time. Syndiotactic poly(1-butene) latices are prepared by a convenient 2-step procedure, involving a highly efficient hydrogenation in the submicrometer particles.

Acknowledgment. The Alexander von Humboldt Foundation is acknowledged for a fellowship (A.B). S.M. is indebted to the Fonds der Chemischen Industrie and the Hermann Schnell foundation for financial support. We thank Ralf Thomann for TEM analyses and Peter Wehrmann and Lars Bolk for assistance with GPC analyses.

Supporting Information Available: Text giving synthesis procedures and figures showing ^1H, ^{13}C NMR, and IR spectra, DSC, and GPC of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223−1252.

(2) (a) *Wässrige Polymerdispersionen*; Distler, D., Ed.; VCH: Weinheim, Germany, 1999. (b) *Polymer Dispersions and Their Industrial Applications*; Urban, D., Takamura, K., Eds.; Wiley-VCH: Weinheim, 2002. (c) *Emulsion Polymerization and Emulsion Polymers*; Lovell, P. A.; El-Aasser, M. S., Eds.; Wiley: Chichester, U.K., 1997.

(3) (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170. (b) Kaminsky, W.; Arndt, W. *Adv. Polym. Sci.* **1997**, *127*, 143.

(4) Syndiospecific suspension-type polymerization of styrene by a titanocene: Manders, B.; Sciandrone, L.; Hauck, G.; Kristen, M. O. *Angew. Chem., Int. Ed.* **2001**, *40*, 4006−4007.

(5) (a) Bauers, F. M.; Mecking, S. *Macromolecules* **2001**, *34*, 1165−1171. (b) Bauers, F.; Mecking, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 3020−3022. (c) Bauers, F. M.; Chowdhry, M. M.; Mecking, S. *Macromolecules* **2003**, *36*, 6711−6715. (d) Bauers, F. M.; Thomann, R.; Mecking, S. *J. Am. Chem. Soc.* **2003**, *125*, 8838−8840. (e) Zuideveld, M. A.; Wehrmann, P.; Röhr, C.; Mecking, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 869−873. (f) Kolb, L.; Thomann, R.; Mecking, S. *Macromol. Rapid. Commun.* **2004**, *25*, 1824−1828. (g) Kolb, L.; Monteil, V.; Thomann, R.; Mecking, S. *Angew. Chem., Ind. Ed.*, in press. (h) Reviews: Mecking, S.; Held, A.; Bauers, F. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 544−561. Mecking, S.; Claverie, J. P. In *Late Transition Metal Polymerization Catalysis*; Riger, B. Baugh, L. S.; Kacker, S.; Striegler, S., Eds. Wiley-VCH: Weinheim, 2003, pp 231.

(6) (a) Tomov, A.; Broyer, J.-P.; Spitz, R. *Macromol. Symp.* **2000**, *150*, 53−58. (b) Soula, R.; Novat, C.; Tomov, A.; Spitz, R.; Claverie, J.; Drujon, X. *Macromolecules* **2001**, *34*, 2022−2026. (c) Soula, R.; Saillard, B.; Spitz, R.; Claverie, J.; Llaurro, M. F.; Monnet, C. *Macromolecules* **2002**, *35*, 1513−1523.

(7) In some cases, moderate stereoregularities have been achieved at low temperatures: (a) Pellecchia, C.; Zambelli, A. *Macromol. Rapid Commun.* **1996**, *17*, 333−338. (b) Small, B. L.; Brookhart, M. *Macromolecules* **1999**, *32*, 2120−2130.

(8) (a) Henderson, J. N.; Donbar, K. W.; Barbour, J. J.; Bell, A. J. (Goodyear) US Patent 4,429,085, 1984. (b) Ono, H.; Matsumura, Y.; Okuya, E. (JSR) EP Patent 0152175, 1985.

(9) (a) Stefan Meier, PhD. Thesis Freiburg University, 2003. (b) Meier, S. M.; Scheuermann, G.; Thomann, R.; Mecking, S.; Mülhaupt, R. unpublished results. (c) Leube, H. F.; Schmidt-Thümmes, J.; Zeller, E.; Maas, H. (BASF) US Patent 6,403,727, 2002. (d) Reviews on catalytic modification of polymers: McManus, N. T.; Rempel, G. L. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1995**, *35*, 239−285. McGrath, M. P.; Sall, E. D.; Tremont, S. J. *Chem. Rev.* **1995**, *95*, 381−389.

(10) Weak resonances at 5.2 ppm (^1H NMR) and 138 and 121 ppm (^{13}C) are found in highly hydrogenated samples, correlating with a trisubstituted double bond, see blow-up in Figure 2. For Ru-catalyzed isomerization at high temperatures, cf., e.g.: Schmidt, B. *Chem. Commun.* **2004**, 742−743.

(11) Coates, G. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 229−230.

(12) For this comparison syndiotactic poly(1-butene) was prepared in solution with $[\{(Flu)CMe_2(Cp)\}ZrCl_2]/MAO$ (Zr, 6 μmol; Al/Zr, 500; 30 °C; 2 h) according to: Asanuma, T.; Nishimori, Y.; Ito, M.; Uchikawa, N.; Shiomura, T. *Polym. Bull. (Berlin)* **1991**, *25*, 567−570.

(13) Sahoo, S. K.; Zhang, T.; Reddy, D. V.; Rinaldi, P. L.; McIntosh, L. H.; Quirk, R. P. *Macromolecules* **2003**, *36*, 4017−4028.

(14) Rossi, A.; Odian, G.; Zhang, J. *Macromolecules* **1995**, *28*, 1739−1749.

MA047649Z