1,2-Polybutadiene Latices by Catalytic Polymerization in Aqueous Emulsion

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ABSTRACT: Catalytic aqueous polymerization of butadiene by the cobalt catalyst system [$Co(C_8H_{13})(C_4H_6)$]/CS_2 affords colloidally stable latices of highly crystalline syndiotactic 1,2-polybutadiene (T_m = 190 °C, ΔH_c = 60 J/g, $M_w \sim 10^5$ g/mol, 97% 1,2, 3% 1,4-cis). Catalyst modification with reagents containing electrophilic carbon atoms (e.g., aromatic formamides) strongly decreases polymer crystallinity (T_m = 60−100 °C, ΔH_c = 11 J/g, $M_w \sim 8 \times 10^4$ g/mol for 85% 1,2). Latices of typically 150−200 nm particles are prepared. During polymerization affording low crystalline polymers the number of particles stays constant. Microstructures were analyzed by ^{13}C NMR of hydrogenated polymers. In all polymers the 1,4-units are largely isolated. Crystallinity decrease results from an increase of 1,4-insertion frequency and the resulting decrease of 1,2-block length. Considerations on the nature of the active species are discussed. Copolymerization of butadiene with isoprene by [$Co(C_8H_{13})(C_4H_6)$]/CS_2 affords low crystalline copolymers; styrene is not incorporated as a comonomer.

Introduction

Emulsion polymerization is among the most important polymerization processes.[1] About 10 million tons annually of polymer latices are used for a variety of applications, such as coatings and paints. The use of water as dispersing medium has many advantages, such as environmental friendliness, moderate viscosity of latices even at high solids content, and convenient formulation.

To date, polymer latices are produced industrially by free-radical polymerization exclusively. Styrene−butadiene copolymers, acrylate homo- and copolymers, and vinyl acetate polymers are the major industrial products.[1] However, the range of polymer microstructures and corresponding materials properties accessible by free-radical polymerization are limited. As an approach to the synthesis of polymer dispersions with controlled microstructures, catalytic polymerization in aqueous emulsion, using late transition metal catalysts, is receiving increasing attention.[2] It can be noted that other non-free-radical routes such as polycondensation or ionic polymerization have also been developed in aqueous emulsion.[3]

In the field of catalytic aqueous polymerization we[2,4] and others[5] have recently reported on catalytic homo- and copolymerization of ethylene. This has offered access to latices of linear or highly branched polyethylene inaccessible by other techniques.[4]

In this work we investigate the catalytic polymerization of butadiene in aqueous emulsion. The versatility of butadiene insertion (1,2, 1,4-trans, or 1,4-cis) allows for the synthesis of polymers with various and controlled microstructures and therefore very different materials properties.[6] The free radical polymerization of butadiene and the copolymerization with styrene (styrene butadiene rubber, SBR) in emulsion are well-known processes performed on a large scale. However, only polymer latices with a limited range of properties in terms of microstructure and thermal behavior (typical microstructure of butadiene homopolymer: 60−80% 1,4-trans, 5−20% 1,4-cis, 15−20% 1,2; $T_g \sim -80$ °C; no T_m) are accessible.[1a] The synthesis of polybutadiene latices with a controlled microstructure, and the related control of crystallinity and T_g, is therefore a challenge. The ready availability of butadiene from cracking of hydrocarbon feedstocks in comparison to classical monomers of radical emulsion polymerization (such as styrene, acrylates, vinyl acetate) contributes to the attractivity of this topic.

Examples of catalytic polymerization of dienes in water have been reported. In the 1960s, the use of a rhodium catalyst precursor for producing *trans*-1,4-polybutadiene selectively in aqueous emulsion was reported, but the activity was rather low and data on polymer and latex properties are scarce.[7] Later on, Goodyear[8] and Japan Synthetic Rubber (JSR)[9] reported the synthesis of syndiotactic 1,2-polybutadiene by cobalt-catalyzed suspension or emulsion polymerization of butadiene in water. The catalytic system, based on an in situ prepared cobalt catalyst modified with CS_2 as a ligand, was previously developed for the 1,2-polymerization of butadiene in solution.[10] However, very little is known about latices synthesis, their properties, and particularly their colloidal properties (e.g., polymer microstructure, thermal behavior, colloidal stability, particle size distribution). Much more, the limited data available are restricted to highly crystalline polymers which are not convenient materials for classical latex applications involving film formation, such as coatings or paints. In view of such applications, the control of polymer crystallinity is decisive.

Here we report our investigation on the catalytic polymerization of butadiene to obtain stable 1,2-polybutadiene latices with various controlled microstructures and thermal properties ranging from highly crystalline to amorphous material.

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Table 1. Emulsion Polymerization of butadiene with $[Co(C_8H_{13})(C_4H_6)]/CS_2$[a]

entry no.	T (°C)	yield (g)	sol. content (%)	coag (g)	ϕ^e (nm)
1	40	8.7	7.7	1.0	190
2	10	6.0	5.8	0.2	211
3[b]	40	8.3	1.3	7.0	
4[c]	40	5.5		5.5	
5[d]	40	0.9	0.4	0.5	

[a] Reaction conditions: 320 μmol of $Co(COOC_7H_{15})_2$; 92 mL of water; 7.5 g/L SDS; 5 mL of toluene; 3 mL of EtOH; 25 mL of butadiene (15 g, 0.28 mol); 740 μmol of $NaBH_4$; 320 μmol of CS_2; 0.3 mL of hexadecane; reaction time = 2 h. [b] No organic water immiscible solvent used: 92 mL of water; 7.5 g/L SDS; 8 mL of EtOH. [c] Surfactant: 7 g/L of Triton X-100. [d] Surfactant: 10 g/L of DTAB (dodecyltrimethylammonium bromide). [e] Volume average particle size determined by DLS.

Results and Discussion

1. Synthesis of Latices of Highly Crystalline Syndiotactic 1,2-Polybutadiene. We used the cobalt(I) allyl complex $[Co(C_8H_{13})(C_4H_6)]$[11] as a catalyst precursor for the catalytic polymerization of butadiene in aqueous emulsion. This complex was synthesized in situ by reduction of a cobalt(II) salt by $NaBH_4$ in the presence of a small amount of butadiene, as reported by Natta.[11] It has been reported to catalyze the dimerization of butadiene.[11] Addition of CS_2 to the catalytic system results in formation of an active catalyst for the polymerization of butadiene with a very high 1,2-insertion selectivity.[10]

A solution of the catalyst precursor in a small volume of water-immiscible organic solvent (toluene) is dispersed in water with surfactant (SDS) and a hydrophobic agent (hexadecane) by means of ultrasound to generate a stable miniemulsion of the catalyst precursor solution. Table 1 shows the results after exposure of this miniemulsion to an aqueous emulsion of butadiene containing an equimolar amount of CS_2.

Stable 1,2-polybutadiene dispersions with solids content of ca. 8% are obtained at 40 °C in 2 h (Table 1, entry 1), corresponding to 58% conversion of monomer (51% as latex and 7% as coagulated polymer). Following the solids content with time by periodic withdrawing of samples from the reactor, we observed that the reaction occurs for the larger part (90% of the polymer formed) within the first hour. The rate of polymerization is dependent on temperature; at 10 °C a decrease of productivity is observed (entries 1 and 2).

To investigate the effect of the organic phase in the catalytic emulsion polymerization of butadiene, the organic phase was omitted: the catalyst precursor was directly prepared in a small amount of ethanol and added to the aqueous emulsion of butadiene (entry 3). Interestingly, polymer yield is almost identical to that obtained in the presence of toluene with the miniemulsion technique. This reveals that no need of a previous polyene encapsulation of the catalyst is necessary to avoid interaction of the metal center with the aqueous phase,[8,9] demonstrating a high tolerance of the catalytically active species to water. However, as expected in the absence of any water-immiscible solvent most of the polymer (85%) is formed as large particles of polybutadiene suspended in water, and only a small part is obtained as a colloidal stable latex (solids content: 1.3%). Upon adding the ethanol solution of the catalyst precursor to the water, the catalyst precipitates (the catalyst precursor is not soluble in water). The suspension of relatively large catalyst particles results in the formation of large colloidally unstable polymer particles.

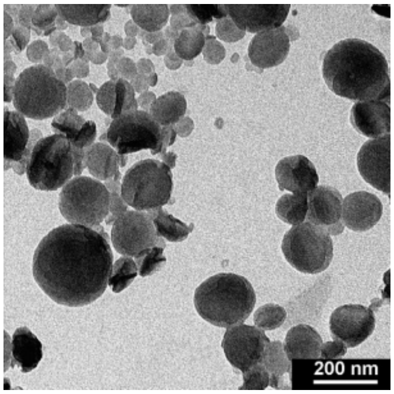


Figure 1. TEM micrograph of 1,2-polybutadiene latex particles (97% 1,2-butadiene units) (Table 1, entry 1).

While the use of the anionic surfactant SDS results in stable 1,2-PBD latices, no colloidal stability was observed with a nonionic surfactant (Triton X-100) under otherwise identical conditions (Table 1, entry 1 vs 4). With a cationic surfactant (DTAB: dodecyltrimethylammonium bromide) the productivity was very low, possibly due to the deactivation of the catalyst by interaction of the cobalt complex with bromide counterions from the surfactant (Table 1, entry 5).

The analysis of the polymer particle size by dynamic light scattering (DLS) shows volume average sizes in the range 190−210 nm. Transmission electronic microscopy (TEM) reveals the presence of hard crystalline particles of 1,2-polybutadiene (Figure 1).

Differential scanning calorimetry (DSC) measurements were performed on the isolated polymers obtained by precipitation from the latices. As expected, high melting points (T_m = 190 °C, T_c = 160 °C, ΔH_c = 60 J/g) are observed, corresponding to a highly crystalline polymer. GPC analysis shows relatively high molecular weights ($M_w \sim 10^5$ g mol^{-1}, M_w/M_n = 3, vs linear polyethylene standards).

Microstructure Analysis. Analysis of the polymer microstructure by IR spectroscopy and ^{1}H NMR shows a very high 1,2-content: 98% (Figure S2a in Supporting Information) and 97%, respectively. To determine the tacticity of the 1,2-polybutadiene polymer, the quality of ^{13}C NMR spectra at 130°C was not satisfactory due to a limited solubility of the samples. A solution to this problem was found by hydrogenating the polymer dispersions.[12] The resulting polybutenes are much more soluble. For these polybutenes, no signals for stereoerrors are observed by ^{13}C NMR spectroscopy, indicating virtually complete syndiotactic arrangement of the 1,2-units (Figure S1 in Supporting Information). Small additional signals can be assigned completely to $-(CH_2)_4-$ units, originating from 1,4-incorporated butadiene units (ca. 3%). An analysis of block length reveals an average block length of 25 for 1,2-blocks and of 1.3 for 1,4-blocks (vide infra, Figure 3).[13] The regioerrors (1,4) largely occur in the form of isolated 1,4-units. This demonstrates a well-behaved nature of the catalytically active species in terms of selectivity: no longer blocks or indications of polymers with different compositions (1,2 vs 1,4) are observed, which would result from more than one type of active species differing in selectivity.

Butadiene Copolymerization. Copolymerization of butadiene with an appropriate comonomer could enable a variation and reduction of crystallinity. The versatility

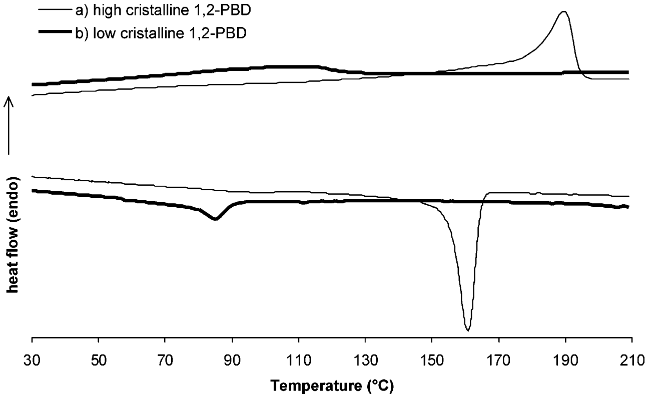


Figure 2. DSC analysis of polymers obtained with (a) [Co(C_8H_{13})(C_4H_6)]/CS_2 catalyst (Table 1, entry 1) and (b) [Co(C_8H_{13})(C_4H_6)]/CS_2/DPF (Table 2, entry 9).

of the catalytic system was investigated in this respect. In the presence of butadiene/styrene mixtures only 1,2-polybutadiene was obtained without decrease of activity by comparison to the absence of styrene and without any insertion of styrene. On the other hand, butadiene/isoprene copolymers were prepared in the form of colloidally stable dispersions. A drop of activity is observed in the presence of isoprene (9 mol %) under otherwise identical conditions as for butadiene homopolymerization (conversion: 13%).[14] A decrease in the melting point of the polymer was observed (T_m = 157 °C, T_c = 127 °C) in comparison with homopolybutadiene (T_m = 190 °C, T_c = 160 °C) due to the insertion of isoprene (7 mol %).[15] By increasing isoprene concentration in the monomer mixture (17 mol %), isoprene insertion increased (30 mol %) and an amorphous copolymer is obtained, which demonstrates the efficiency of copolymerization to reduce polymer crystallinity.

2. Synthesis of Latices of Low Crystalline Polybutadiene with a High 1,2 Content. As stated above, the catalyst system [Co(C_8H_{13})(C_4H_6)]/CS_2 displays a very high selectivity for the 1,2-insertion of butadiene (>97%) and a high stereoselectivity (syndiotactic 1,2-polybutadiene is obtained) in the emulsion polymerization of butadiene. This results in highly crystalline polybutadiene (T_m ~ 190 °C). Patent literature[8,9] indicated that polymer melting points can be reduced by adding to the catalytic system various compounds such as alcohol, aldehyde, ketones, or ester without further data. We have investigated the effect of different additives on polymer microstructure and crystallinity and rationalized it (Table 2). For the emulsion polymerization an important parameter to obviously consider is the solubility or miscibility of additives with water. Indeed, the additives have to interact with the lipophilic cobalt catalyst in organic droplets and not in water. For this purpose we used additives with rather low water solubility or miscibility and in a high ratio to cobalt ([additives]/[Co] = 25).

With alcohols only a slight decrease of melting point (ΔT_m ~ 10 °C) is observed in comparison with the [Co(C_8H_{13})(C_4H_6)]/CS_2 catalyst system (Table 2, entry 1). With valeraldehyde the effect on melting temperature was more significant (ΔT_m ~ 30 °C) (entry 2). Employing an aromatic aldehyde (benzaldehyde), a low crystalline polybutadiene latex (broad T_m between 100 and 140 °C, T_c = 112 °C, and ΔH_c = 12.7 J/g; for comparison, T_m = 190 °C, T_c = 160 °C, and ΔH_c = 60 J/g for highly crystalline 1,2-polybutadiene) was synthesized (entry 3), and a very low crystalline polybutadiene was obtained in lower yield (27% conversion) with 4-(diethylamino)-benzaldehyde (entry 4). By contrast, with *N*,*N*-diethylaniline no effect on crystallinity was observed (entry 5).

A common feature in all the additives that exert an effect on polymer crystallinity seems to be the presence of an electrophilic carbon atom (compare entries 3−5). To further verify this hypothesis, we investigated a range of compounds such as ketones, formamides, nitriles, or ureas. Addition of aromatic or aliphatic ketones resulted in a limited decrease of polymer crystallinity (entries 6 and 7). With formamides, especially with *N*,*N*-dibutylformamide (DBF) and *N*,*N*-diphenylformamide (DPF), very low crystalline polybutadiene latices (broad T_m between 60 and 110 °C, low

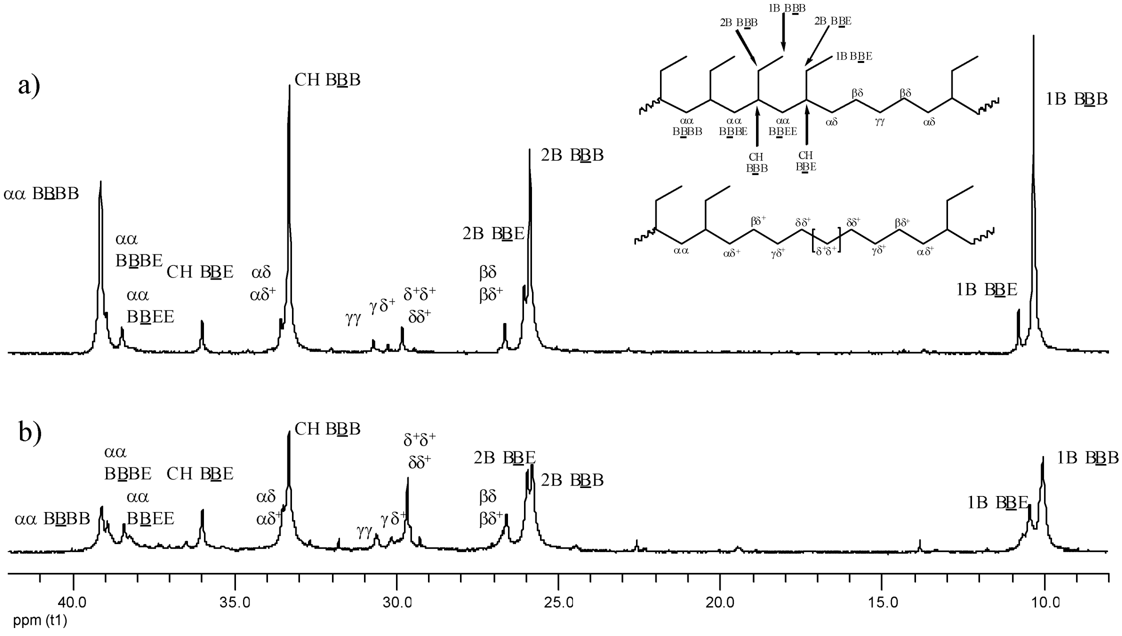


Figure 3. Comparison of ^{13}C NMR spectra of hydrogenated polybutadienes with different portions of 1,2-butadiene units: (a) 97% (Table 1, entry 1), (b) 85% (Table 2, entry 9).

Table 2. Emulsion Polymerization of Butadiene with $[Co(C_8H_{13})(C_4H_6)]/CS_2$/Additive[a]

entry no.	additive[b]	sol. cont (%)	coag polymer (g)	conv (%)	T_m (°C)	T_c (°C)	ΔH_c (J/g)	1,2-content[c]
1	dodecanol	4.1	0.3	30	181	151	47.9	n.d.
2	valeraldehyde	8.0	0.75	58	158	130	37.0	92 (94*)
3	benzaldehyde	7.1	0.8	53	100−140	112	12.7	88
4	4-DEAB	4.0	0.1	27	60−110	69	9.0	80
5	*N*,*N*-diethylaniline	3.7	0.3	27	187	157	51.6	97
6	benzophenone	8.7	1.8	70	160	135	n.d.	93
7	5-nonanone	5.1	1.2	42	160	132	39.2	95
8	DBF	3.2		21	60−100	62	9.2	82 (77*)
9	DPF	7.8	0.4	54	60−110	85	10.8	84 (85*)
10	DMF	4.2	0.1	29	179	147	44.7	98
11	TMU	5.2	0.3	38	182	150	48.8	98
12	DPU	4.3	1.0	35	189	160	53.8	99
13	benzonitrile	0.8		5				(76*)

[a] Polymerization conditions: 91 mL of water, 6 mL of toluene, 7.5 g/L SDS, 0.3 mL of hexadecane, catalyst = 320 μmol of $Co(COOC_7H_{15})_2$ + 710 μmol of $NaBH_4$ (in 3 mL of ethanol) + 1 mL of butadiene, ligand: CS_2 (320 μmol), additives = [additives]/[Co] = 25, monomer = butadiene (25 mL, 0.28 mol), T = 40 °C, reaction time = 2 h. [b] DMF: *N*,*N*-dimethylformamide; DBF: *N*,*N*-dibutylformamide; DPF: *N*,*N*-diphenylformamide; 4-DEAB: 4-(diethylamino)benzaldehyde; TMU: *N*,*N*,*N*′,*N*′-tetramethylurea; DPU: *N*,*N*′-diphenylurea. [c] Determined by IR (and ^{1}H NMR*). n.d.: not determined.

ΔH_c) were produced (entries 8 and 9; Figure 2). Significantly, no decrease of solids content (ca. 8%, 54% conversion) in the case of DPF was observed. The ineffectiveness of DMF (*N*,*N*-dimethylformamide) can be rationalized in terms of its high water miscibility (entry 10). No influence on polymer melting point was observed with ureas (entries 11 and 12). The clearest effect was observed when benzonitrile was used as an additive. A completely amorphous polybutadiene was produced, albeit a latex with a low solids content (ca. 1%, 5% conversion) was obtained (entry 13).

GPC analysis of these lower crystalline polybutadienes shows molecular weights between 5×10^4 and 8×10^4 g mol^{-1} (M_w/M_n = 3−6, vs linear polyethylene standards).

Microstructure Analysis. The analysis of the polymer microstructure by IR spectroscopy (or ^{1}H NMR) shows a clear correlation between the decrease of crystallinity (T_c, ΔH_c) of polymers and the decrease of 1,2-selectivity (Table 2) and the corresponding increase toward the 1,4-cis insertion of butadiene (see Figure S2 in Supporting Information for comparison of IR spectra of polymers obtained with $[Co(C_8H_{13})(C_4H_6)]/CS_2$ and $[Co(C_8H_{13})(C_4H_6)]/CS_2$/DPF). A decrease from 97% 1,2-selectivity obtained with $[Co(C_8H_{13})(C_4H_6)]/CS_2$ catalyst to 76% 1,2-selectivity is observed when benzonitrile is added to the emulsion polymerization. This modification of the polybutadiene microstructure entirely suppresses crystallization of the polymer.

The microstructure of the polymer obtained with $[Co(C_8H_{13})(C_4H_6)]/CS_2$/DPF was further investigated by ^{13}C NMR after hydrogenation of polymer dispersion (Figure 3 and Figure S1 in Supporting Information). Concerning the stereoregularity of the hydrogenated polybutadiene, the absence of the signals of isotactic poly(1-butene) and the relative similarity to that of the syndiotactic poly(1-butene) indicate that the syndiotacticity of the 1,2-blocks of polybutadiene is conserved irrespective of the increase of regioselectivity for 1,4-insertion (Figure S1). From ^{13}C NMR analysis of hydrogenated samples an average block length of 7 for 1,2-blocks and of 1.7 for 1,4-blocks was calculated.[13] The majority (70%) of 1,4-units are isolated. In the presence of additives the event of 1,4-insertion (and to a lesser extent the length of 1,4-units sequences) is increasing, which results in the decrease of 1,2-block length.

The syndiotactic 1,2-blocks are responsible for the crystallinity of polybutadiene. The decrease of average 1,2-block length from 25 (polymer obtained with $[Co(C_8H_{13})(C_4H_6)]/CS_2$) to 7 (polymer obtained with $[Co(C_8H_{13})(C_4H_6)]/CS_2$/DPF) apparently largely prevents crystallization.

Table 3. Emulsion Polymerization of Butadiene at Various DPF Concentrations[a]

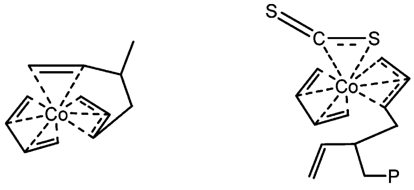
entry no.	[DPF]/[Co]	T_m/°C	1,2-structure[b]
1	25	60−110	84
2	12.5	100−120	85
3	5	100−140	93

[a] Polymerization conditions: 91 mL of water, 6 mL of toluene, 7.5 g/L SDS, 0.3 mL of hexadecane, catalyst = 320 μmol of $Co(COOC_7H_{15})_2$ + 710 μmol of $NaBH_4$ (in 3 mL of ethanol) + 1 mL of butadiene, ligand: CS_2 (320 μmol), monomer = butadiene (25 mL), T = 40 °C, reaction time = 2 h. [b] Determined by IR.

Influence of Additive Concentration. In the case of the most active catalytic system $[Co(C_8H_{13})(C_4H_6)]/CS_2$/DPF, we investigated the influence of the additive concentration. A slight increase of 1,2-insertion selectivity and the related increase of the melting point were observed by decreasing the ratio [DPF]/[Co] (Table 3). Apparently, interaction of the additive with the active species is not so strong in the (multiphase) system investigated that an excess of additive would not be required.

Interaction of Additives with Catalyst. The $[Co(C_8H_{13})(C_4H_6)]/CS_2$ catalyst shows a high activity for the emulsion 1,2-polymerization of butadiene. Our investigations to replace CS_2 by other ligands such as phosphine, phosphine oxides, thioisocyanates, or other organic sulfur compounds always lead to inactive systems. This points to a unique nature of CS_2 as ligand in the emulsion polymerization investigated. However, the nature of the active species for the $[Co(C_8H_{13})(C_4H_6)]/CS_2$ catalyst is not well-known. The structure shown in Figure 4B has been proposed as the active species for butadiene 1,2-polymerization, but this suggestion is not based on experimental or theoretical evidence.[10d] It is considered to result from the addition of CS_2 to the precursor $[Co(C_8H_{13})(C_4H_6)]$ (Figure 4A), which is a dimerization catalyst for butadiene to 5-methyl-1,3,6-heptatriene,[11] affording a polymerization catalyst with a very high regioselectivity for the 1,2-insertion of butadiene. It has been proposed that CS_2 coordinates as a κ^2-ligand and replaces the coordinated pendant vinyl group in $[Co(C_8H_{13})(C_4H_6)]$.

We have shown that by adding additives containing an electrophilic carbon atom to the aforementioned



(A) (B)

Figure 4. Possible active species of syndiotactic 1,2-polymerization of butadiene (B) according to literature[10d] and catalyst precursor (A).

catalyst system a significant decrease of 1,2-selectivity of butadiene insertion was observed. We assume that the active species is based on the structure shown in Figure 4B or a similar structure. To explain the observed effect of additives on polymerization selectivities, a conceivable mechanism could be the additional coordination of additive on the metal by donor atoms such as O or N, inducing a change of reactivity and of selectivity of the catalyst. But this does not account for the observed differences between the various additives. In particular, it does not explain the low effect on polymer crystallinity of alcohols or of *N,N*-diethylaniline, in contrast with additives containing electrophilic carbons atom, albeit the latter should be less strongly coordinating to the metal center. For these reasons we propose a different mechanism based on a modification of CS_2 ligand properties by an interaction of the additives via their electrophilic carbon atom with a nucleophilic sulfur atom of the coordinated CS_2 ligand. Indeed, it is known from investigations of the reactivity of κ^2-CS_2 complexes that the uncoordinated sulfur atom has an enhanced nucleophilic character.[16] In addition, we verified experimentally that no reaction occurs between CS_2 and the additives in the absence of cobalt complexes under our polymerization conditions to form a new potential ligand. This indicates that the interaction of additives with the cobalt catalyst occurs in the coordination sphere of the metal center.

3. Latex Properties and Particle Formation Mechanism for Low Crystalline Polybutadiene Latices. All aforementioned catalyst systems (Table 2) afforded colloidally stable polybutadiene latices. Dynamic light scattering (DLS) reveals volume average particle sizes in the range 120−180 nm. Transmission electron microscopy (TEM) of a latex produced with the $[Co(C_8H_{13})(C_4H_6)]/CS_2/DPF$ catalytic system reveals the presence of low crystalline particles of 1,2-PBD with an increased softness in comparison with defined hard crystalline particles obtained with $[Co(C_8H_{13})(C_4H_6)]/CS_2$ (compare Figures 1 and 5).

The evolution of average particle size over time was investigated by periodically drawing samples from the reactor (Figure 6). For the particular system investigated, this presents technical difficulties in the drawing of noncoagulated samples from the running reaction in a reactor under pressure. For these investigations the concentration of cobalt was decreased in order to decrease reaction rate. The catalyst miniemulsion droplets possess a volume average droplet size of 70 nm according to DLS.[17] Particles sizes and solids contents increase rapidly to 155 nm and 3%, respectively, after which the reaction stalls. A consideration of the evolution of the number of latex particles over time is of interest. Assuming spherical particles of density 0.96 g mL^{-1},[18] from the particle sizes determined by DLS and the solids content of each sample a relatively constant number of latex particles results over time (Figure 6).

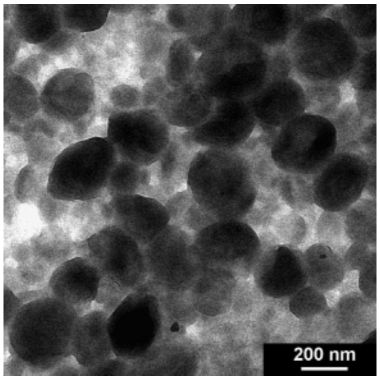


Figure 5. TEM micrograph of low crystalline latex particles (85% 1,2-butadiene units) (Table 2, entry 9).

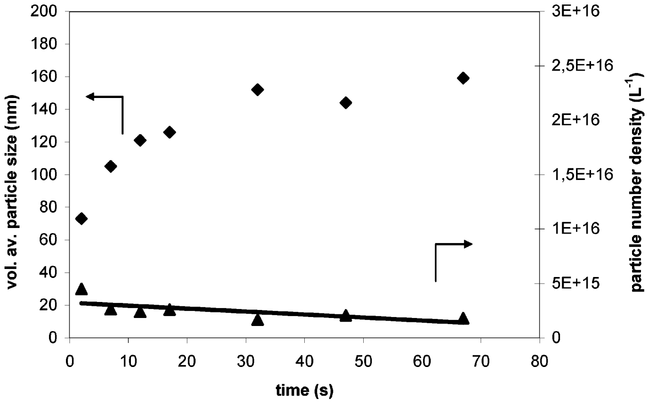


Figure 6. Evolution of average particle size and number of particles over time with $[Co(C_8H_{13})(C_4H_6)]/CS_2/DPF$ catalyst (conditions of entry 9, Table 2 with $n(Co) = 32$ μmol).

No indication of substantial nucleation of new particles during the polymerization is observed. These results are in agreement with Claverie's observations for polyolefin latices.[5c] For latices of crystalline polymers (polyethylene), a large increase in the number of particles in the course of polymerization was observed. This is explained by the growing polymer chains precipitating from the organic droplets (miniemulsified toluene, benzene), generating a crystalline polymer particle and leaving a liquid droplet which can generate a new polymer particle. On the other hand, in the case of low crystalline polymers (ethylene copolymers) a constant number of particles was observed. This was related to the good swelling of polymer by the organic phase, such that it does not precipitate.

As an overall mechanism of particle formation, we can assume that at the beginning of the polymerization miniemulsion droplets of catalyst solution in toluene (~100 nm) and emulsified liquid butadiene droplets (>1 μm) in equilibrium with butadiene in the gas phase are present. Polymerization occurs in toluene droplets, in which butadiene is dissolved and to which butadiene diffuses from butadiene droplets (which serve as a reservoir for the monomer) through the aqueous phase. The low crystalline polybutadiene (85% 1,2; 15% 1,4-cis) is swollen by toluene and does not precipitate, which results in particle growth without nucleation of new particles. Note that this differs from classical "free-radical miniemulsion polymerization", for which polymerization of preformed miniemulsion droplets of monomer results in the formation of polymer particles of the same size.

Summary and Conclusion

Stable latices of polybutadienes with a variable 1,2-content (75 to >97%) and corresponding different materials properties ranging from highly crystalline to amorphous polymers have been synthesized.

Latices of highly crystalline polymer ($T_m \sim 190$ °C, $\Delta H_c = 60$ J/g) are obtained by polymerizing butadiene with the $[Co(C_8H_{13})(C_4H_6)]/CS_2$ catalyst system. A convenient method was developed to determine the microstructure of polybutadienes. By ^{13}C NMR analysis of hydrogenated polymers, we show that the polymer consists of 1,2-syndiotactic block separated by mostly isolated 1,4-cis units, resulting from regioerrors of the catalyst.

Butadiene copolymerization was investigated. No styrene insertion has been observed while low crystalline butadiene–isoprene copolymers have been synthesized in low yield.

On the other hand, a control of polymer crystallinity has been achieved by catalyst modification with organic compounds containing electrophilic carbon atoms, especially with aromatic formamides, aldehydes, or nitriles. Latices of very low crystalline ($T_m < 100$ °C, $\Delta H_c \leq 10$ J/g) or of amorphous polybutadiene are obtained. The decrease of crystallinity was correlated with the decrease of catalyst selectivity for butadiene 1,2-insertion. ^{13}C NMR analysis of hydrogenated polymers shows that 1,4-insertion frequency increases in the presence of additives, which disturbs polymer crystallization by decrease of the syndiotactic 1,2-block length. While polymers with an average block length of the 1,2-block of 25 are higly crystalline, with an average block length of 7 crystallinity is very low. The influence of additives can be rationalized in terms of an interaction between electrophilic carbon atoms of the additives and a nucleophilic uncoordinated sulfur atom of the CS_2 ligand.

In all cases, investigations of latices properties have shown the formation of 150–200 nm particles with shapes depending on polymer crystallinity. For low crystalline polybutadiene latices the particles formation is controlled as no additional particles are generated during the polymerization.

Experimental Section

General Considerations. All manipulations (catalyst preparation and polymerizations) were performed using standard Schlenk techniques under an argon atmosphere.

NMR spectra were recorded with either a Bruker ARX 300, a Bruker Avance DRX 600, or a Varian Inova 400 spectrometer. ^1H and ^{13}C chemical shifts were referenced to ^1H and ^{13}C signals of the deuterated solvents, respectively. High-temperature NMR measurements were performed in 1,1,2,2-tetrachloroethane-d_2 at 100 or 130 °C. IR spectra were recorded on a FT-IR Bruker Vector 22 spectrometer using KBr pellets. The 1,2-content of polybutadiene was determined by IR[19] and NMR[10c] spectroscopy according to the literature. The detailed microstructure of polybutadiene was determined by NMR after hydrogenation of samples.[12] Dynamic light scattering (DLS) on diluted latex samples was performed on a Malvern Nano-ZS ZEN 3600 particle sizer (173° backscattering). Miniemulsion droplets sizes were measured on undiluted samples. Differential scanning calorimetry (DSC) was performed on a Netzsch DSC 204 F1 at a heating rate of 10 K/min. The polymers were investigated in the temperature range 25–230 °C. DSC data reported are second heats. Transmission electron microscopy (TEM) was carried out on a LEO 912 Omega apparatus using an acceleration voltage of 120 kV. Samples were prepared by applying a drop of the dispersion to a carbon-coated grid.

Materials. 1,3-Butadiene (99.5% purity) supplied by Messer-Griesheim GmbH was used without further purification. Isoprene was dried over CaH_2 and distilled under argon. Styrene was purified by passing through an alumina column and distilled under argon. Toluene was dried over Na and distilled under argon. Hexadecane and ethanol were degassed by repeated freeze–pump–thaw cycles. Deionized water was degassed by distillation under nitrogen prior to use. Sodium dodecyl sulfate (SDS), dodecyltrimethylamonium bromide (DTAB), and poly(ethylene glycol) *tert*-octylphenyl ether (Triton X-100) were purchased from Fluka and degassed under argon prior to use. Cobalt(II) 2-ethylhexanoate, sodium borohydride, carbon disulfide, 1-dodecanol, valeraldehyde, benzaldehyde, 4-(diethylamino)benzaldehyde, *N,N*-diethylaniline, benzophenone, 5-nonanone, *N,N,N′,N′*-tetramethylurea, *N,N′*-diphenylurea, benzonitrile, and *N,N*-diphenylformamide were purchased from Aldrich and degassed under argon prior to use. *N,N*-Dimethylformamide and *N,N*-dibutylformamide (Fluka) were distilled under argon prior to use.

Polymerization Procedure. The precatalyst solution was prepared under argon by adding at −30 °C to a toluene solution (2–3 mL) of cobalt(II) 2-ethylhexanoate an ethanol solution (3 mL) of sodium borohydride in the presence of a small amount of butadiene (1 mL, $[NaBH_4]/[Co] = 2.2$).

Polymerization was carried out in a mechanically stirred 250 mL pressure glass reactor equipped with a heating/cooling jacket, the temperature being controlled by means of a sensor dipping into the reaction mixture.

For the polymerization in miniemulsion the main part of an aqueous solution of surfactant (SDS, DTAB, or Triton X-100) was transferred to the reactor while the other was added to the precatalyst solution. In the reactor was first condensed the desired amount of butadiene at −5 °C. Then the main part of the aqueous solution of surfactant and a toluene solution (3 mL) of carbon disulfide ($[CS_2]/[Co] = 1$) (and of the desired additive if required) was transferred under argon into the reactor by means of a pump. For copolymerization, the desired amount of styrene or isoprene was used instead of toluene.

To the precatalyst solution were added under argon at low temperature (<0 °C) hexadecane (0,3 mL) and the remaining part of the aqueous solution of surfactant. The resulting biphasic mixture was ultrasonified (Bandelin HD 2200 with a KE76 tip, operated at 120 W) to afford the precatalyst miniemulsion, which was then pumped into the reactor. The reactor was then rapidly heated to the desired temperature under vigorous stirring (1000 rpm). After the desired reaction time the reaction was stopped by releasing the gas pressure. The obtained latex was then filtered through a funnel with glass wool prior to further work-up and analysis. For determination of solids content the latex was added to an excess of methanol after adding octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate to the latex for preventing cross-linking. The precipitated polymers were isolated by filtration, washed with methanol, and dried at 50 °C under vacuum overnight.

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Supporting Information Available: ^{13}C NMR of hydrogenated poly(butadiene)s and IR spectra of poly(butadiene)s. This material is available free of charge via the Internet at http://pubs.acs.org.

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