No Polymerization with Metallocenes in Water?—A Prejudice is Refuted**

Bart Manders,* Luigi Sciandrone, Gerhard Hauck, and Marc O. Kristen*

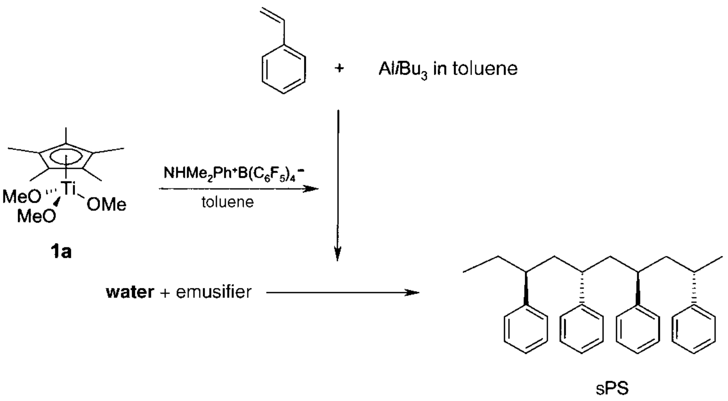
Emulsion polymerization is a process of significant industrial relevance.[1] Especially the use of water as a reaction medium ensures its importance in terms of sustainable development. Important industrial products such as coatings and dye stuffs can be manufactured on a large scale using this polymerization process. Generally radical initiation is used in emulsion polymerization to obtain a polymer dispersion. To get a better control of the properties of the dispersion, controlled radical-polymerization methods have recently attracted attention.[2] However, this method offers only limited control of the polymer structure. A much higher potential for controlling the polymer properties is possible by applying insertion-polymerization techniques, for example, with transition metal complexes.[3]

In the aqueous emulsion polymerization of ethylene, the groups of Mecking,[4] and Spitz and Claverie,[5] introduced neutral nickel complexes as catalysts. These complexes as well as cationic palladium complexes, which are used for olefin polymerization in aqueous media,[6] are much less water sensitive than complexes of the early transition metals. For the emulsion polymerization of butadiene in an aqueous environment cobalt catalysts have also been used.[7]

Metallocene complexes[8] of early transition metals are generally converted into the catalytically active form (the metallocenium cation) by methylalumoxane (MAO) or special boron reagents.[3a,b] The metallocenium cations are very electrophilic and have to be handled under strictly inert conditions avoiding any contact with air or moisture. Therefore, the polymerization of olefinic unsaturated monomers with these catalysts has to be performed under these inert conditions as well.

We report here the first use of metallocene catalysts in aqueous emulsion polymerization. Styrene polymerization was chosen as a model system since it allows the easy differentiation of the two possible polymerization mechanisms (radical or catalytic insertion) by the type of polymer (atactic or syndiotactic,[9] respectively) obtained.

Initially a prepolymerization was performed for 30 s (Scheme 1). A solution of the monocyclopentadienyl complex **1a** and a borate activator ($NHMe_2Ph^+B(C_6F_5)_4^-$)[10] was prepared and then added to a solution of styrene in toluene to which an aluminum alkyl compound was added. This prepolymerization solution was then fed into water with added emulsifier. After the reaction was stopped polystyrene could be isolated (66 % conversion). The analysis of the polymer by means of differential scanning calorimetry (DSC; Figure 1) and NMR spectroscopy demonstrated that exclusively syndiotactic polystyrene (sPS) was formed. This clearly shows that all the polymer was produced by insertion polymerization at the metal center since sPS is only obtainable by this route.[9] We assume the catalyst was encapsulated by the prepolymerization process and its addition to the water/emulsifier mixture resulted in the formation of a type of mini emulsion. The styrene droplets shaped by the emulsifier are then completely polymerized by the catalyst inside the droplets. The crystalline sPS formed inside the droplets provides extra protection for the catalyst against water. Obviously the high degree of crystallinity of sPS is the reason why the dispersions have a poor long-term stability, and why by precipitation of sPS unusually large particles for emulsion polymerization are formed (500 µm).



Scheme 1. Preparation of syndiotactic polystyrene in water.

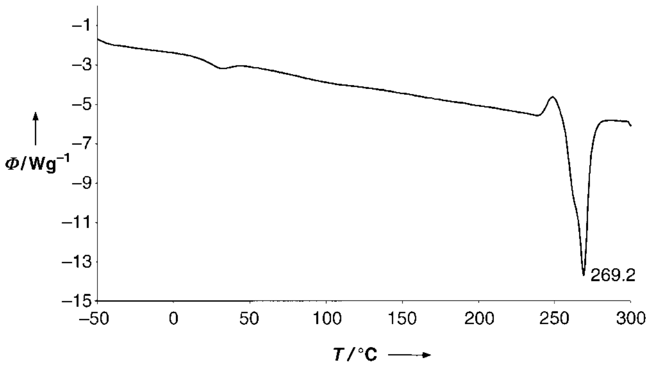


Figure 1. DSC curve of syndiotactic polystyrene.

Further experiments to increase the stability of the dispersions by variation of the emulsifier were performed. The use of cationic (cetyltrimethylammonium chloride) and nonionic (Lutensol AT18) emulsifiers (Figure 2) resulted in the formation of polymer, whereas reactions with anionic emulsifiers were not successful under the conditions examined. A possible explanation is the interaction of the anionic part of the emulsifier with the catalytically active, cationic metal center. On the other hand, the fact that no polymer was formed with the anionic emulsifier shows that the sPS formed

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[*] Dr. B. Manders, Dr. M. O. Kristen, L. Sciandrone, G. Hauck
BASF AG
Polymerforschung
67056 Ludwigshafen (Germany)
Fax: (+49) 621-60-56574
E-mail: marc.kristen@basf-ag.de

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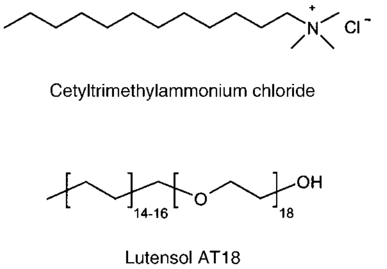

Figure 2. Successfully employed cationic and nonionic emulsifiers.

during the prepolymerization accounts for an insignificant amount of the sPS obtained with cationic and nonionic emulsifiers. Thus, the bulk of the polymer is produced in the aqueous environment in emulsion.

In attempts to further increase the shielding of the catalyst from water, the alkoxide substituent was varied. The original system contained methoxide ligands, which were subsequently replaced by more sterically demanding substituents (Figure 3). However, no improvement in terms of turnover or dispersion stability was observed.

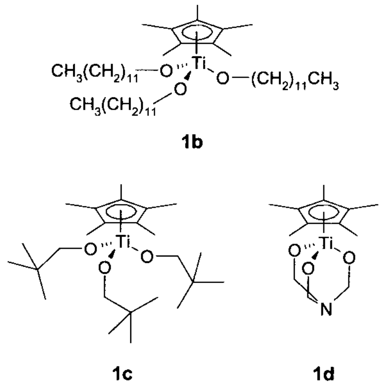

Figure 3. Monocyclopentadienyl complexes for the polymerization of styrene in aqueous emulsion.

The influence of other metal complexes and emulsifiers on the styrene polymerization is part of ongoing investigations as is the transfer to other monomers. In addition, particle size distribution as well as dispersion stability will be further optimized.

Experimental Section

The polymerizations were performed under the exclusion of air. All chemicals were obtained commercially.

Aqueous emulsion polymerization: In a 1 L flask styrene (75 g) was dissolved in toluene (300 g) and heated to 80 °C. Then a 25 % triisobutylaluminium solution in toluene (9.5 g) was added. A solution of of *N,N*-dimethylanilinium tetrakis(pentafluorophenyl) borate (0.385 g) and of pentamethylcyclopentadienyl titanium trimethoxide (**1a**; 0.135 g) in toluene (10 mL) was prepared seperately and added from a feed vessel. After 0.5 min the resulting mixture was added to a solution of 20 % Lutensol AT18 (18.75 g) in deionized water (300 g). The reaction was quenched with ethanol after 1 h. The suspension was dried at 80 °C in vacuo. Conversion: 66 %; tacticity: ^{13}C NMR rr = 99 %, mm = 0 %, rm = 1 % (r = racemic diad (syndotactic); m = meso diad (isotactic)); m. p. (DSC): 269 °C; average particle size (determined from scanning electron microscopy (SEM) pictures): ca. 500 µm.

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α(1-3)-Galactosyltransferase Inhibition Based on a New Type of Disubstrate Analogue[**]

Bernhard Waldscheck, Markus Streiff, Wolfgang Notz, Willy Kinzy, and Richard R. Schmidt[*]

Oligosaccharides play an important role in various cellular recognition and signal transduction processes.[1] Therefore, control of the biosynthesis of the structurally diverse oligosaccharides is of great interest for biological studies. An important control mechanism is the specific inhibition of the various glycosyltransferases.[2] In enzymatic oligosaccharide synthesis, a glycosyl donor (commonly a nucleoside mono- or diphosphate) and an acceptor are generally coupled, with the

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[*] Prof. Dr. R. R. Schmidt, Dr. B. Waldscheck, Dr. W. Notz
Fachbereich Chemie, Universität Konstanz
Fach M725, 78457 Konstanz (Germany)
Fax: (+49) 7531-883135
E-mail: Richard.Schmidt@uni-konstanz.de

Dr. M. Streiff, Dr. W. Kinzy
Novartis Pharma AG
Transplantation Research, WSJ 386.643
4002 Basel (Switzerland)

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