

Latex-supported catalysts for the autoxidation of thiols. 1. Use of ionene-based macromonomers

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Latex-supported catalysts for the autoxidation of thiols, 1

Use of ionene-based macromonomers

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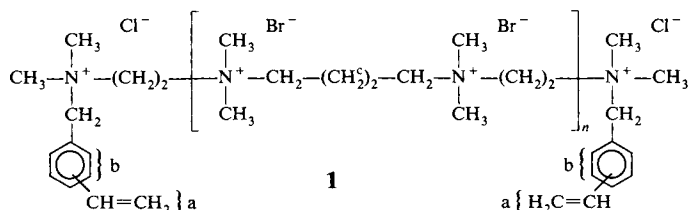
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Introduction

The catalytic activity of cobalt(II)phthalocyanine tetra(sodiumsulfonate) (CoPCTS) in the thiol autoxidation is strongly enhanced by the addition of ionenes, poly(quaternary ammonium salts)¹. Immobilization of these ionenes on latex particles will make separation and reuse of the ionene cocatalyst possible, while mass transfer limitations are prevented by the large surface area and the non-porous character of this type of catalyst support.

In this paper the synthesis of vinylbenzyl-telechelic macromonomers of 2,4-ionene **1** by end capping of tertiary amine-terminated 2,4-ionene with chloromethylstyrene (CMS), the emulsion copolymerization of these macromonomers with styrene, and the cocatalytic activity of the obtained latex particles in the thiol autoxidation will be described.



Experimental part

Tertiary amine-terminated 2,4-ionene was synthesized according to Rembaum et al.². Equimolar amounts of 1,4-dibromobutane (Janssen Chimica 99%) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA; Janssen Chimica 99%) were dissolved in 1:1 (v/v) *N,N*-dimethylformamide (DMF; Janssen Chimica 99,5%)/methanol (Merck 99,8%) (concentration 1,5 M in both starting materials). After a few days of stirring at room temperature under an argon atmosphere, the product was precipitated in a ten-fold volume of acetone (Merck 99%) and filtered. In order to terminate the 2,4-ionene with tertiary amine groups, it was redissolved in 1:1 (v/v) DMF/methanol, TMEDA (0,25 g per g product) was added and the mixture was allowed to react

for one night at room temperature. Precipitation and filtration before adding the fresh amount of TMEDA was necessary, because gelation occurred. The product was again precipitated in acetone, filtered off, and dried at 50 °C and 100 Pa. The number-average molecular weight (\bar{M}_n) of the tertiary amine-terminated 2,4-ionene was determined by potentiometric titration of the tertiary amine end-groups with 0,1 M hydrochloric acid (Merck Titrisol).

The macromonomers were synthesized by reacting the prepared 2,4-ionenes with a 10- to 20-fold excess of chloromethylstyrene (CMS, kindly supplied by Dow Chemical; 96% of CMS isomers, 67% *meta* and 29% *para*; distilled under reduced pressure before use). Mixtures of DMF/methanol and DMF/water (both 1 : 1 v/v) were used as solvent. The CMS concentration was maintained at 1,5 mol · L⁻¹ in all experiments. After stirring for 2 to 4 days under an argon atmosphere, the reaction mixtures were poured in a 10-fold volume of acetone, and the macromonomers were obtained by filtration and were then dried for 24 h at 50 °C and 100 Pa.

The degree of end capping of the 2,4-ionene with CMS was determined with UV-VIS spectroscopy, ¹H NMR spectroscopy and titration. In the UV-VIS spectroscopic determination it was assumed that the molar absorption coefficient at 244 nm of the vinylbenzyl end-group of the macromonomers was the same as that of styrene, i. e., 12000 L · mol⁻¹ · cm⁻¹. If the degree of end capping was below 100%, the product was allowed to react for another 2 to 4 days with a 10 to 20-fold excess of CMS. In order to determine the degree of end capping of the final product by ¹H NMR spectroscopy, the ratio of the vinylic protons ($\delta H_a = 5,4-6,8$), the aromatic protons ($\delta H_b = 7,5-7,8$) and the aliphatic protons ($\delta H_c = 2,0$) was used (see formula 1). Completeness of the conversion of the tertiary amine end-groups of the 2,4-ionene was also determined by titration of the residual tertiary amine end-groups with hydrochloric acid.

Styrene (Merck 99%) was distilled under reduced pressure before use. The emulsion polymerizations were carried out at 70 °C in a double-walled reaction vessel, equipped with a 6-bladed turbine stirrer, in an argon atmosphere. The stirring rate was 200 rpm. In all experiments 50 g of monomers (styrene plus macromonomer), 0,25 g of 2,2'-azobis(2-amidinopropane hydrochloride) (AIBA; Polyscience) and 450 g of water (deionized and ultrafiltered; conductivity $\leq 0,6$ $\mu\text{S} \cdot \text{cm}^{-1}$) were used. Conversions were determined gravimetrically. After 24 h the latex formed was filtered over a paper filter to remove any possible coagulum. Latex particle size and polydispersity were determined by scanning electron microscopy.

The resulting latices were purified by serum replacement with the deionized, ultrafiltered water till no desorbed macromonomer could be detected in the serum. This detection was carried out according to Van Streun et al.³); detection limit: $[\text{N}^+] \approx 10^{-7} \text{ mol} \cdot \text{L}^{-1}$. If no macromonomer could be detected in the serum anymore, silica (Merck Kieselgel 60) was added to the latex, in order to remove the last traces of adsorbed macromonomer from the latex particle surface⁴). After 6 to 8 h of shaking, the silica was filtered off and the procedure was repeated with a fresh batch of silica. Then the latex was further purified by serum replacement.

The N⁺ content of the latex was determined by adsorption of CoPcTS (synthesized according to Zwart⁵). An excess of CoPcTS was added to a known quantity of latex, the serum of the latex was isolated by ultracentrifugation and the CoPcTS concentration in the serum was determined spectrophotometrically³). The N⁺ content was then calculated from the adsorbed quantity of CoPcTS, assuming the formation of a complex with a N⁺/Co ratio of 4.

The catalytic activities of the latices were measured at 25 °C and at an oxygen pressure of 10⁵ Pa, as described by Brouwer et al.⁶). A stirring rate of 2600 rpm was applied to prevent gas-liquid mass transport limitations¹). 2-Mercaptoethanol (Janssen Chimica 98%) was distilled before use.

Results and discussion

Monomer synthesis

By varying the reaction time, 2,4-ionenes with different number-average molecular weights were obtained. In Tab. 1 these results and the results of the reaction of these 2,4-ionenes with CMS (determined by UV-VIS spectroscopy) are shown.

Tab. 1. Synthesis of macromonomers

Macromonomer	Molecular weight of ionene in $10^3 \text{ g} \cdot \text{mol}^{-1}$	Solvent	Solubility	Yield ^{a)} in %
1-1	1,9	DMF/MeOH	moderate	100
1-2	1,9	DMF/water	complete	— ^{b)}
1-3	7,0	DMF/MeOH	low	57 85 ^{c)} 94 ^{d)}
1-4	12,5	DMF/MeOH	low	93 100 ^{c)}

a) Determined by UV-VIS spectroscopy.

b) Product did not redissolve in DMF, water, MeOH or combinations of these solvents after precipitation in acetone and drying.

c) Yield after second reaction period.

d) Yield after third reaction period.

High degrees of end capping were obtained in DMF/methanol 1:1 (v/v) mixtures. When DMF/water 1:1 (v/v) was used, a product was formed that, after precipitation in acetone and drying, became insoluble in water, methanol, DMF or combinations of these solvents.

In Tab. 1 can be seen that the tertiary amine end-groups of the 2,4-ionene with the lowest molecular weight reacted faster with CMS than those of the higher molecular weight 2,4-ionenes. The reaction had to be carried out twice or thrice to obtain complete conversion of these 2,4-ionenes. This was probably necessary because of the lower solubility of the high-molecular-weight ionenes in the reaction mixture.

The results of ^1H NMR and of the titration with hydrochloric acid were in good agreement with those obtained by UV-VIS spectroscopy. ^1H NMR showed that the ratio of the peak areas was in reasonable agreement with the theoretical proton ratio (see Tab. 2), indicating almost complete conversion of the tertiary amine end-groups of the 2,4-ionene and also that the double bonds of the CMS were still intact. The deviations in the peak areas are due to a low signal/noise ratio for the small peaks of the vinylbenzyl end-groups, especially for macromonomers containing 2,4-ionene blocks with a rather high molecular weight (macromonomers 1-3 and 1-4). Titration

Tab. 2. ^1H NMR relative peak areas of macromonomers

Macromonomer	$\text{H}_a : \text{H}_b : \text{H}_c$ ^{a)}	
	theoretical	experimental
1-1	6:8:22	6,0:8:27
1-3	6:8:84	6,3:8:84
1-4	6:8:154	4,0:8:92

a) See formula 1.

of the macromonomers with hydrochloric acid also indicated complete conversion of the tertiary amine end-groups of the 2,4-ionene. The titration curves showed no equivalence point, so no tertiary amine groups were present anymore.

Emulsion polymerization

The macromonomers appeared to be effective stabilizers in the emulsion polymerization of styrene. Without macromonomer a latex yield of only 2,6% was obtained due to excessive coagulation, whereas addition of a small amount of macromonomer increased the latex yield to 95 to 100% (Fig. 1). This stabilizing effect of the macromonomers is also illustrated by a decreasing latex particle size with increasing macromonomer concentration (Fig. 1). The latices were moderately polydisperse, having polydispersities of 1,05 to 1,10. This phenomenon will be discussed in detail later⁷⁾.

Because the macromonomers are derivatives of CMS, they will probably have approximately the same reactivity ratios and can therefore be expected to copolymerize with styrene. This was confirmed by surface charge density measurements after the very extensive cleaning of the latex. A rather high surface charge density ($11,9 \mu\text{C} \cdot \text{cm}^{-2}$) was found, indicating that the macromonomer was not removed from the latex particle surface, as would be the case if it was not covalently bound to the polymer.

Catalytic activity

As is common in the autoxidation of 2-mercaptoethanol, optima in both pH and N^+/Co ratio were observed for the macromonomer on latex cocatalyst. In Tab. 3 the optimal pH, the optimal N^+/Co ratio and the activity under these optimal conditions are shown for several cocatalyst systems.

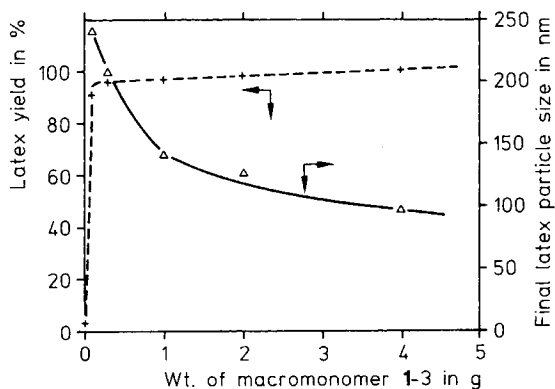


Fig. 1. Effect of macromonomer concentration on latex yield and final latex particle size (see Exptl. part for conditions)

Tab. 3. Optimal pH, optimal N⁺/Co ratio and maximal activity in the autoxidation of 2-mercaptoethanol^{a)}

Cocatalyst	Optimal pH ^{b)}	Optimal N ⁺ /Co ^{c)}	Maximal activity ^{d)} in mol O ₂ · (mol Co) ⁻¹ · s ⁻¹
2,4-Ionene, homogeneous	9	50–100	875
Macromonomer/latex ^{e)}	9	150	650
PMAD/latex ^{f)}	9	9	153
qPVP/latex ^{g)}	9	25	20

a) Conditions; [CoPcTS]: 10⁻⁷ mol · L⁻¹, [2-mercaptoethanol]: 0,071 mol · L⁻¹, temp.: 25,0 ± 0,5 °C, O₂ pressure: 10⁵ Pa.

b) At about the optimal N⁺/Co ratio.

c) At optimal pH.

d) At optimal pH and optimal N⁺/Co ratio.

e) 0,297 g of macromonomer 1-4 copolymerized with 49,7 g of styrene, number-average particle diameter: 209 nm, polydispersity: 1,10; surface charge density: 11,9 μC · cm⁻².

f) 3-(Methacrylamidinopropyl)trimethylammonium chloride copolymerized in emulsion with styrene⁸⁾.

g) Quaternized 4-vinylpyridine copolymerized in emulsion with styrene⁹⁾.

For all cocatalyst systems, the optimal pH was about 9, which indicates that the presence of latex particles has no effect on the dissociation of 2-mercaptoethanol.

However, large differences in optimal N⁺/Co ratios and maximal activities were observed for the various cocatalysts. The optimal N⁺/Co ratio and the maximal activity of the macromonomer on latex cocatalyst were close to those of homogeneous 2,4-ionene, while for the other latex cocatalyst systems mentioned in Tab. 3^{8,9)} much lower values were obtained.

These differences are probably due to the presence of relatively long 2,4-ionene blocks at the surface of the latex particles of the macromonomer on latex cocatalyst as compared with only short polycation blocks at the particle surface of the other latices. The latter cocatalysts can be assumed to have only short polycation blocks on their surface on the grounds of a comparison of the reactivity ratios of the cationic monomers used and that of styrene.

Conclusions

By reacting chloromethylstyrene (CMS) with the amine end-groups of 2,4-ionene, telechelic macromonomers can be prepared that are effective stabilizers in the emulsion polymerization of styrene. The so prepared latices proved to be very active heterogeneous cocatalysts for the autoxidation of thiols. It can be assumed that this high activity is due to the presence of 2,4-ionene *blocks* at the latex particle surface, extending into the water phase.

- 1) W. M. Brouwer, P. Piet, A. L. German, *J. Mol. Catal.* **31**, 169 (1985)
- 2) A. Rembaum, W. Baumgartner, E. Eisenberg, *J. Polym. Sci., Polym. Lett. Ed.* **6**, 159 (1968)
- 3) K. H. van Streun, J. Meuldijk, A. L. German, *Angew. Makromol. Chem.* **173**, 119 (1989)
- 4) K. H. van Streun, W. J. Belt, P. Piet, A. L. German, *Eur. Polym. J.* **27**, 931 (1991)
- 5) J. Zwart, H. C. van der Weide, N. Bröker, C. Rummens, G. C. A. Schuit, A. L. German, *J. Mol. Catal.* **3**, 151 (1977)
- 6) W. M. Brouwer, P. Piet, A. L. German, *J. Mol. Catal.* **22**, 297 (1984)
- 7) H. van Beek, J. W. Leclercq, E. M. Oudenbroek, P. Piet, A. L. German, in preparation
- 8) K. H. van Streun, W. J. Belt, E. T. W. M. Schipper, P. Piet, A. L. German, *J. Mol. Catal.* **71**, 245 (1992)
- 9) F. Twigt, P. Piet, A. L. German, *Eur. Polym. J.* **27**, 939 (1991)