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Preparation and co-catalytic properties of amphiphilic diblock copolymers consisting of polystyrene and ionene^{a)}

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SUMMARY:

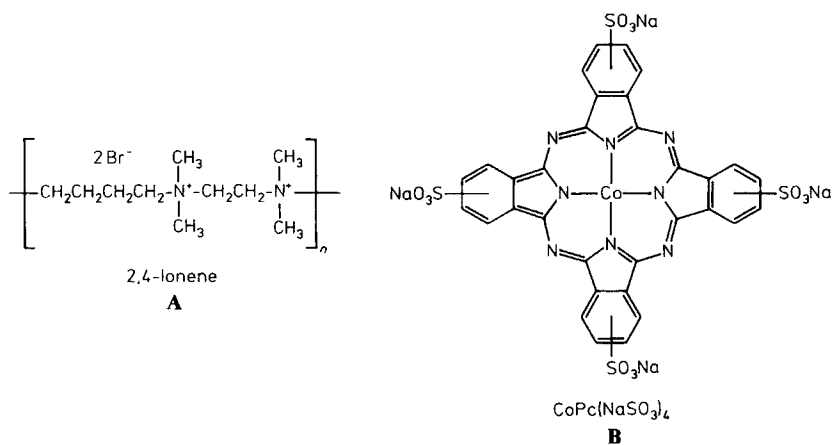
Well defined amphiphilic diblock copolymers, consisting of an oligomeric quaternary ammonium block, a so-called ionene, and a polystyrene block, were synthesized. The route started with the preparation of monofunctionalized polystyrene by anionic polymerization, using 3-(dimethylamino)propyllithium as initiator. The polystyrene was obtained with relatively narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n = 1,2-1,4$). This polystyrene was coupled stepwise with a number of different monodisperse oligomer units of 2,4-ionene, having reactive end-groups, resulting in a monodisperse 2,4-ionene block. End-group titration, size exclusion chromatography, thin-layer chromatography and infrared spectroscopy were utilized to characterize the polymers. Additionally the block copolymer in combination with tetrasodium phthalocyaninatocobalt(II)tetrakisulfonate ($\text{CoPc}(\text{NaSO}_3)_4$) was tested as co-catalyst in the phase-transfer-catalyzed autoxidation of 1-dodecanethiol. Very high catalytic activities (775 mol $\text{O}_2/(\text{mol Co} \cdot \text{s})$) were achieved, 40 times higher as compared with the polymer-free system, due to a combination of the formation of the most active species and hydrophobic interaction with the hydrophobic thiol. This hydrophobic interaction resulted in an enhancement of the autoxidation rate by a factor 2,5, compared with the analogous hydrophilic homopolymer 2,4-ionene.

Introduction

A growing interest exists in the synthesis of tailor-made well defined ionic block copolymers, because they offer a wide variety of practical and potential applications¹⁾. In particular, we are interested in using these ionic block copolymers to study polymeric effects on catalytic reactions, especially when they contain a hydrophilic poly(quaternary ammonium) part, a so-called ionene (**A**), because of their promoting effect on certain catalytic oxidations. Therefore, in our laboratory extensive research has been carried out on the oxidative coupling of 2-mercaptoethanol catalyzed by tetrasodium phthalocyaninatocobalt(II)tetrakisulfonate ($\text{CoPc}(\text{NaSO}_3)_4$) (**B**), both in homogeneous and heterogeneous systems²⁻⁵⁾. The addition of ionenes leads to a fifty-fold rate enhancement as compared with the polymer-free system. This drastic increase in reaction rate can be explained by polymer-induced aggregation of the highly active form of $\text{CoPc}(\text{NaSO}_3)_4$ and substrate enrichment at the catalytic sites⁶⁾.

Recently, the phase-transfer-catalyzed oxidation of the water-insoluble hydrophobic 1-dodecanethiol was investigated, using $\text{CoPc}(\text{NaSO}_3)_4$ in the presence of an ionene as catalyst. It has been shown before that even with hydrophilic ionenes, high catalytic activities are present⁷⁾. Further enhancement of the catalytic reactivity can be achieved by coupling a hydrophobic moiety to the ionene chain. Oleyl-3,3-ionene, an

^{a)} This paper was presented at the fourth International Symposium on Macromolecule-Metal Complexes (Siena, 1991).



ionene end-capped with a hydrophobic alkyl chain, exhibited almost a two-fold higher activity compared with the hydrophilic 2,4-ionene. This effect was ascribed to the probability of hydrophobic interaction between the polymer and the hydrophobic thiol. In order to improve such polymer-substrate interactions, and thus to increase the catalytic activity, block copolymers consisting of a hydrophobic and an ionene part should be preferable.

The general method which is mostly employed for the preparation of ionic block copolymers is a sequential polymerization of different monomers, added successively. An alternative method to synthesize ionic block copolymers is by end-to-end linkage of preformed homopolymers, as it has been used before to obtain ionene-*b*-poly(oxyethylene)-*b*-ionene and ionene-*b*-poly(oxytetramethylene)-*b*-ionene^{8,9}. These triblock polymers were prepared by quaternization of the amine end-group of ionene with poly(oxyethylene) or poly(oxytetramethylene) having a reactive brominated end-group.

In this paper we will present a promising route for the synthesis of a new amphiphilic diblock copolymer by coupling polystyrene and ionene, both having reactive end-groups. Different techniques can be used to prepare monofunctionalized polystyrene. One of the best suited routes for synthesizing predictable monofunctionalized polystyrene with an amine end-group is by living anionic polymerization, especially when the amine group can be introduced by a functional initiator. This approach was first followed and further developed by Eisenbach et al.^{10,11}, who synthesized a tertiary-amine-functionalized polymer, utilizing 3-(dimethylamino)propyllithium as initiator. More recently, Stewart et al.¹² improved this concept and obtained polybutadiene with tertiary amine end-groups.

We will discuss in this article the use of the 3-(dimethylamino)propyllithium initiator to prepare monodisperse polystyrene, monofunctionalized with a reactive tertiary amine end-group. Also the stepwise coupling of the resulting polymer with reactive oligomer units of 2,4-ionene will be described. Additionally the catalytic activity of the ionic block copolymer, in combination with $\text{CoPc}(\text{NaSO}_3)_4$, will be presented, tested in the phase-transfer-catalyzed oxidation of 1-dodecanethiol.

Experimental part

Materials

Styrene (Merck) was distilled under reduced argon atmosphere, after which it was kept in the dark and stored on CaH_2 at 2 °C. Tetrahydrofuran (THF) p. a. (Merck) was collected on CaH_2 after refluxing under argon in the presence of sodium benzophenone (sodium diphenylketyl), generating a permanent violet colour. Lithium metal (Fluka) was supplied and used as a 30% dispersion in mineral oil. 3-(Dimethylamino)propyl chloride (DMAP-Cl) (Janssen Chimica) was isolated from its hydrochloric salt according to a method described elsewhere¹³. Toluene p. a., benzene p. a. and hexane p. a. (Merck) were stored on CaH_2 under argon atmosphere and used without further purification.

1,4-Dibromobutane and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (Janssen Chimica) were distilled and stored under argon before use. 1-Dodecanethiol (Janssen Chimica) was vacuum-distilled and stored under argon. The water used throughout the experiments was doubly distilled. $\text{CoPc}(\text{NaSO}_3)_4$ was synthesized according to an adaption by Zwart¹⁴ of the method described by Weber and Busch¹⁵. All other reagents and solvents were of analytical purity and used without further purification.

General procedure

All reactions were carried out under an anhydrous argon atmosphere. The glassware and equipment were cleaned with acetone. Until needed it was dried and stored in an oven at 200 °C. All additions and transfers were conducted using polyethylene syringes equipped with stainless steel needles or by siphoning with stainless steel capillaries.

Preparation of 3-(dimethylamino)propyllithium

3-(Dimethylamino)propyllithium (DMAP-Li) was prepared according to a route quite similar to that developed by Stewart¹². In a 50-mL crimp top flask (equipped with a septum and a magnetic stirrer) a ten-fold excess of lithium slurry (0,82 mol Li) over DMAP-Cl was placed. The slurry was diluted with 20 mL of hexane over a period of 15 min. After settling for 2 h the hexane was removed with a syringe and replaced by another 20 mL of hexane. The final wash was allowed to stand overnight before removal, after which 20 mL of hexane was introduced, which acted as reaction medium. To start the reaction, about 20% of the total required amount of DMAP-Cl (0,041 mol DMAP-Cl) was added dropwise with a syringe at 15 °C, which resulted in an exotherm of 2 °C. Throughout the whole reaction the reaction mixture was magnetically stirred. Over a period of 2 h the remaining aliquots DMAP-Cl were added dropwise, keeping the temperature below 20 °C. To guarantee complete reaction, the reaction mixture was stirred for a further 3 h. After reaction the hexane was removed with a steel capillary and the mixture was washed with 20 mL of hexane. Finally toluene was added to dissolve the hexane-insoluble DMAP-Li and allowed to stand overnight at 2 °C. Subsequently the toluene solution was removed and maintained in the dark at -15 °C until required.

Preparation of 3-(dimethylamino)propyllithium-initiated polystyrene

In a 50-mL crimp top flask, 25 mL of toluene and 0,5 mL of THF were introduced at 40 °C. In order to remove last traces of water and other impurities, a titration solution (0,8 mL of styrene, 2 mL of 1,6 M butyllithium in hexane (Merck) and 30 mL of toluene) was added until a light yellow solution was obtained. If decolorization resulted, more titration solution was added. When the colour remained constant for at least 30 min, the temperature was lowered to 4 °C, followed by the addition of the required quantity of styrene and again careful titration of the solution. If no decolorization had occurred after 15 min, polymerization was initiated by fast addition of the amount of initiator needed. Then the temperature was raised and maintained at 20 °C for 5 min,

and subsequently increased to 40 °C and kept at that level for 1 h. The polymer was precipitated in 2-propanol, filtered off and dried at 50 °C under reduced pressure (10 mmHg).

Preparation of ionene oligomers

The ionene oligomers were synthesized corresponding to the method of Rembaum¹⁶, with a few modifications. A typical experiment to prepare the N-terminated 2,4-ionene trimer (**1**): 18,2 g of 1,4-dibromobutane and 146,9 g of TMEDA (a fifteen-fold excess over 1,4-dibromobutane) were dissolved in 250 mL of methanol/dimethylformamide (DMF) (1/1, v/v) at 50 °C. After two days the reaction mixture was precipitated in acetone, filtrated and washed with acetone. Then the product was dried at 50 °C (10 mmHg). The Br-terminated 2,4-ionene trimer (**2**) was prepared in a similar way using the same reaction conditions: 11,4 g of TMEDA and 317,5 g of 1,4-dibromobutane (a fifteen-fold excess over TMEDA).

The Br-terminated 2,4-ionene pentamer (**3**) was synthesized by dissolving 10,5 g of N-terminated 2,4-ionene trimer (**1**) and 100,9 g of 1,4-dibromobutane (a twenty-fold excess over **1**) in 40 mL of methanol, 20 mL of DMF and 2 mL of water. After a reaction time of 3 days at 40 °C the product was treated the same way as the other ionenes.

Br-terminated 2,4-ionene was prepared in a quite similar way as described above. All yields were determined by mass and appeared to be approximately 90%. The molecular weights of the ionenes were determined by titration of the dimethylamino end-group with hydrochloric acid and were in agreement with the theoretical values. For this reason the ionene was end-capped with dimethylamino groups by reaction with a large excess of TMEDA in water for one day.

End-coupling of dimethylamino-functionalized polystyrene with ionene oligomers

First the dimethylamino-functionalized polystyrene (**4**) was quaternized with 1,4-dibromobutane (step (1.1), *Scheme 1*): 3,0 g of polystyrene T ($\bar{M}_n = 2700$ g/mol, Tab. 1) and a forty-fold excess of 1,4-dibromobutane were dissolved in 40 mL of DMF. The reaction conditions were chosen in such a way as to accomplish the complete solution of both reactants throughout all the reactions. After reacting one day at 40 °C, the quaternized polystyrene (**5**) was precipitated in 2-propanol, then filtrated and dried under vacuum at 50 °C.

The next step was the coupling of the quaternized polystyrene (**5**) with the N-terminated 2,4-ionene trimer (**1**) (step (1.3)). Again the reaction medium was chosen in such a way that both polymers dissolved easily: 2,08 g of quaternized polystyrene (**5**), which was dissolved in 10 mL of DMF, was added to a solution of a twenty-fold excess (6,40 g) of **1** in 10 mL of DMF and 7 mL of methanol. After two days at 50 °C the reaction was complete. The polymer was obtained by precipitation in water and filtration, followed by washing with water and drying under vacuum.

1,49 g of the resulting polymer (**6**) was dissolved in 15 mL of DMF and added to a solution of a sixteen-fold excess (6,24 g) of Br-terminated 2,4-ionene pentamer (**3**) (step (1.4)) in 7 mL of water, 17 mL of methanol and 5 mL of DMF. In order to obtain a clear solution, an additional 10 mL of DMF was added, followed by reacting 7 days for complete conversion at 50 °C. Furthermore, the polymer was purified according to the procedure mentioned above. The so obtained polystyrene-ionene block copolymer (**7**) included nine quaternary ammonium groups in the backbone.

Characterization

The yield of the initiator preparation was determined by measuring the number-average molecular weight \bar{M}_n of the polystyrene prepared by anionic polymerization with the initiator. The number-average molecular weights of the dimethylamino-functionalized polystyrenes, as well as the block copolymers, were determined by titration of the amine chain ends in a 1/1 (v/v) mixture of glacial acetic acid and chloroform, using perchloric acid in glacial acetic acid (0,1001 N, Aldrich) as the titrant and methyl violet as the indicator¹⁷. Molecular weight distributions were determined by gel permeation chromatography (GPC) on a linear μ -Styragel HT column

(Waters) (THF as eluent, flow rate 1 mL/min, 30 °C) equipped with an UV (254 nm) and a refractive index detector. The conditions using a linear Shodex and a linear ultra-Styrigel column (both Waters) were the same. Thin-layer chromatography (TLC) was carried out in SiO₂ plates (Merck Art. 5554). Fourier-transformed infrared spectra of quaternized polystyrene (KBr, film technique) were recorded with a PolarisTM (Mattson) spectrometer.

Catalytic activity measurements

Thiol oxidations were carried out batchwise, as reported previously¹⁸⁾, in an all-glass double-walled Warburg apparatus, equipped with a powerful mechanical glass stirrer (the stirring speed was 2600 r.p.m.) and thermostated at 25,0 ± 0,5 °C. During the reaction the pressure was maintained constant at 10⁵ ± 50 Pa. Reaction rate was measured by monitoring the oxygen uptake rate with a digital flow meter (Inacom Instruments, Veenendaal), keeping the pressure constant. During reaction, the pH was monitored with a GK 2401 pH-electrode connected to a pHM 82 pH-meter (Radiometer).

A modification of the reaction procedure⁷⁾ was the introduction of the block copolymer as a solution in 2 mL of DMF. The reactions were started by addition of CoPc(NaSO₃)₄ to the oxygen-saturated mixture of polystyrene-ionene block copolymer, 0,1 mol of NaOH and 1-dodecanethiol in water⁶⁾. The reaction volume was always 100 mL.

Results and discussion

Preparation of 3-(dimethylamino)propyllithium-initiated polystyrene

The anionic functional initiator 3-(dimethylamino)propyllithium, which has been used before for the anionic polymerization of butadiene^{12,19)}, also proved to be successful in synthesizing polystyrenes with relatively narrow molecular weight distributions, as can be seen in Tab. 1. Several observations are important in evaluating the presented results. First of all, the use of solvent in which DMAP-Li is stored, has a strong influence on the initiator stability. Comparison of the different solvents showed

Tab. 1. Characterization data of aminated polystyrene

Sample number	End-group titration	Size exclusion chromatography	
		$10^{-3} \cdot \bar{M}_n$	\bar{M}_w/\bar{M}_n
	g/mol	g/mol	
A	—	15,1	1,3
B	14,4	18,9	1,4
K	4,3	5,8	1,2
Q	9,2	9,3	1,4
T ^{a)}	2,7	2,1	1,4
V ^{b)}	5,2	2,6	1,3

a) Initiator stored in benzene instead of toluene.

b) Initiator prepared and stored in benzene.

us the remarkable decomposition behaviour of the initiator in toluene. After one day, 90% of the initiator had been decomposed, even under an inert argon atmosphere at -15°C . This behaviour was not observed when the initiator was stored in benzene before use; then even after 2 days no decomposition occurred. The decomposition could be caused by reaction of DMAP-Li with the methyl group of toluene. Thus it can be assumed that just after preparation the initiator yield should be much higher. The low initial yields (maximal 50%) obtained, in contrast to results reported by Stewart¹²⁾, are probably caused by impurities in the hexane.

Also one initiator preparation was carried out in benzene instead of hexane, but a low yield was obtained, probably due to the fact that more Wurtz-coupling occurs between DMAP-Li and DMAP-Cl when both reactants dissolve. These results were in good agreement with those of Ikker²⁰⁾, who prepared DMAP-Li in benzene by a sonochemical reaction and achieved maximal yields of 40%. He also showed that solutions of DMAP-Li did not degenerate over several months. Therefore, it can be concluded that the best solvent to prepare DMAP-Li in high yields is hexane and that the initiator should be stored in benzene.

Comparing the number-average molecular weights of the aminated polystyrenes determined by titration (Tab. 1), with those obtained by size exclusion chromatography, no large differences were found. The range of molecular weight distributions that could be obtained lies between 1,2 and 1,4, values similar to those reported by Ikker²⁰⁾. The distributions are relatively broad for anionic polymerizations, which implies that the initiation is not as fast as when using other anionic alkyllithium initiators.

A typical chromatogram of a dimethylamino-functionalized polystyrene, prepared with DMAP-Li, is given in Fig. 1. It can be seen that the peak is symmetrical. This phenomenon was not only observed for polystyrene K, but also for all the other polystyrenes. Apparently, polystyrenes with tertiary amine end-groups are giving less problems in GPC analysis than those with primary amine end-groups. Ueda et al.²¹⁾ encountered problems in characterizing their amine-functionalized polystyrenes, which, in contrast to our polymers, were equipped with a primary amine group. Their chromatograms always showed broad molecular weight distributions with low-molecular-weight tails, prohibiting the determination of the number-average molecular weight. Quirk and Cheng²²⁾ suggested that physical adsorption effects are complica-

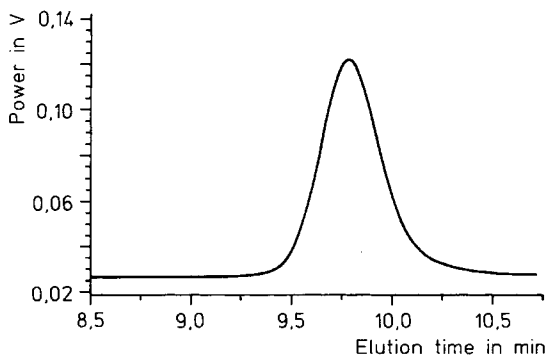


Fig. 1. Size exclusion chromatogram of the dimethylamino-functionalized polystyrene K

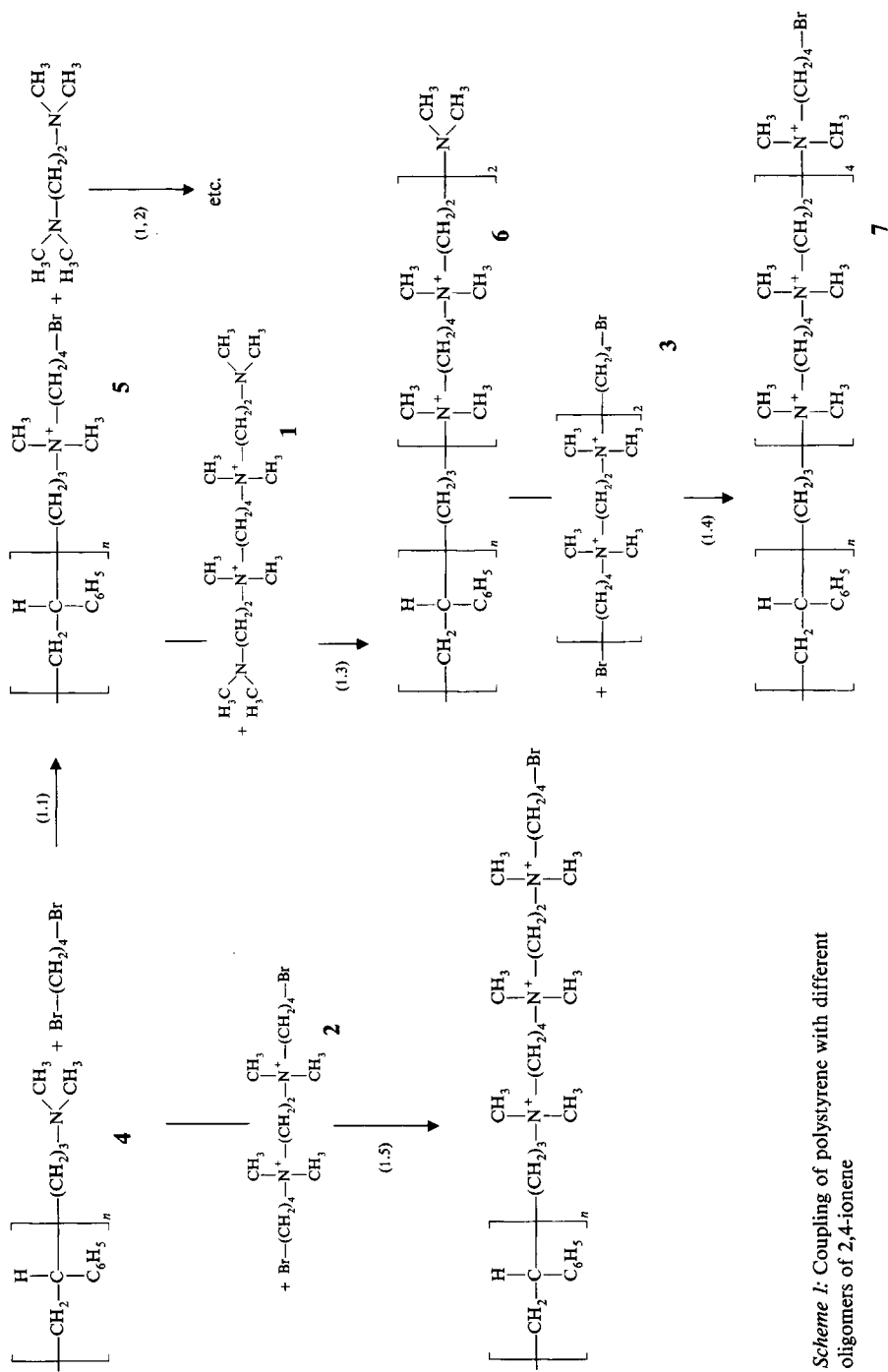
ting the size exclusion process for this type of amine-functionalized polymer. After benzylation of the aminated polymers, Ueda and Quirk managed to perfectly characterize their polymers by GPC.

Aminated polystyrenes with tertiary amine end-groups attached to a phenyl group were analyzed by Quirk²³, and none of the above mentioned problems were observed. Probably steric hindrance of the bulky phenyl groups near the nitrogen prevents interaction with the column packing. Because of the difficulties in analyzing the amine-functionalized polystyrenes, we investigated the effects of different types of columns on the interaction between polymer and column material. Replacing the linear μ -Styragel HT column by a linear Shodex column or a linear ultra-Styragel column turned out not to affect the chromatograms at all. So we may conclude that polystyrenes carrying a dimethylamino end-group exhibit no adsorption or repulsion characteristics towards the packing material in GPC analysis.

End-coupling of dimethylamino-functionalized polystyrene with ionene oligomers

The complete synthesis of ionic diblock copolymers consisting of polystyrene and ionene by anionic polymerization is not possible, since ionene can only be prepared by step reaction polymerization, therefore other techniques have to be applied. Earlier attempts to prepare these types of block copolymers were made by van Streun²⁴, who synthesized low-molar-mass functionalized polystyrene by anionic polymerization, followed by termination with 1,4-dibromobutane. After purification, the product was reacted with aminated 2,4-ionenes in various solvent combinations and at various temperatures. One of the major problems encountered was the insolubility of the hydrophobic polystyrene in polar solvents, and the opposite for 2,4-ionene. Not the lack of reactivity of the hydrophobic polystyrene, but its insolubility, and therefore the lower concentrations of reactive end-groups, turned out to be the major problem. Another approach followed was the polymerization of DMAP-Cl (a monomer for 3,3-ionene) in the presence of functionalized polystyrene under different experimental conditions. No coupling between DMAP-Cl and the polystyrene could be detected, due to the high homopolymerization rate of DMAP-Cl as compared with the low reactivity of the polystyrene end-group. Since none of the outlined routes above turned out to be successful, a new strategy had to be developed.

Our idea was that if a monomer or an oligomeric ionene is soluble in the same solvent as the polystyrene, good solubilities of both reactants, and thus high concentrations of reactive end-groups, will be achieved. In the step-growth process, each extension of the polymer chain with a neutral monomer molecule or a charged oligomer of 2,4-ionene occurs via a quaternization reaction and leads to a substituted ammonium ionic site in the polymer backbone. Eventually one obtains a diblock copolymer consisting of an ionene and a polystyrene block. The different approaches to synthesize these ionic diblock copolymers are outlined in Scheme 1. Theoretically it is possible to obtain the block copolymer by reacting the polystyrene first with 1,4-dibromobutane (step (1.1) in Scheme 1), then with TMEDA (step (1.2)), again with 1,4-dibromobutane, and so further on. Unfortunately, this route is impractical because of the large number of reaction steps.



Scheme 1: Coupling of polystyrene with different oligomers of 2,4-ionene

The reason why we have chosen to treat the polystyrene first with 1,4-dibromobutane and subsequently with an N-terminated trimer of 2,4-ionene (**1**) (step (1.3)) is the difference in solubility between the N- and the Br-terminated trimer. The N-terminated trimer, in contrast with the Br-terminated trimer (**2**), dissolves rapidly in CH₃OH or a combination of CH₃OH and DMF, which is also a good solvent for polystyrene. Dissolving the Br-terminated trimer, where the distance between the separated charges is shorter, gives more problems. But nevertheless the Br-terminated trimer dissolves to much higher concentrations than high-molecular-weight 2,4-ionene.

The quaternization of aminated polystyrene (**4**) with 1,4-dibromobutane (step (1.1)) in a proper solvent like DMF occurs quantitatively in one day. Different techniques can be applied to characterize the quaternized polystyrene. FT-IR turned out to be a suitable technique, because the quaternized polystyrene (**5**) has a characteristic absorption²⁵ at 1260 cm⁻¹ (Fig. 2), which is absent in regular polystyrene.

Another method of determining the extent of coupling 1,4-dibromobutane to the aminated polystyrene proved to be thin-layer chromatography. It has been reported before that aminated polystyrene can be readily observed and separated from unfunctionalized polystyrene by thin-layer chromatography with different eluents using SiO₂ or Al₂O₃ as solid phase²¹). When a proper solvent system (CHCl₃/CH₃OH = 9/1, v/v) is selected, well-separated spots can be obtained, because the amino group has a strong interaction with Al₂O₃ or SiO₂.

These TLC experiments showed that the quaternization of the polystyrene with 1,4-dibromobutane was quantitative, because of the differences in *R_f*-values between non-quaternized and quaternized polystyrene. Furthermore, it can also be concluded that we succeeded in successfully preparing polystyrene with DMAP-Li, because only one spot could be detected. It also became clear that polystyrenes with more than two positive charges, obtained by reacting **5** with an excess of TMEDA (step (1.2)), cannot be separated by TLC. Even when varying the eluent composition, the separation between polystyrenes with more than two quaternized nitrogens could not be established.

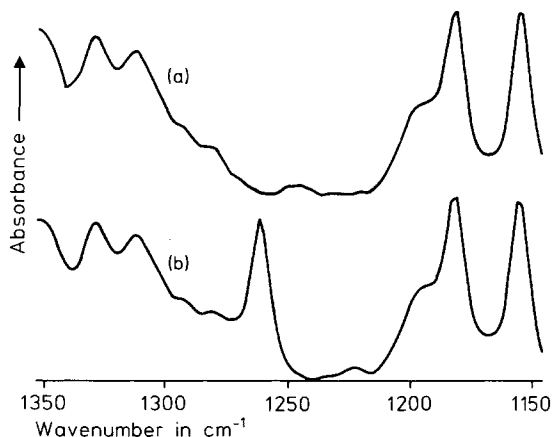


Fig. 2. FT-IR spectrum of polystyrene A before (a) and after (b) reaction with 1,4-dibromobutane

TLC was also applied in the analysis of the coupling between the quaternized polystyrene (**5**) with the N-terminated trimer (**1**) (step (1.3)). Quantitative quaternization was observed after two days. The obtained ionic block copolymer (**6**) was also analyzed by end-group titration, confirming that coupling between **5** and **1** was successful, because the corresponding number-average molecular weight of 1600 g/mol was found.

Via step (1.4) it was possible to extend the ionene chain, by coupling **3** with **6**. Therefore it was important to dissolve both reactants very thoroughly. It appeared that a mixture of DMF/CH₃OH/water was the most effective solvent. During the reaction, gelation of the mixture was observed, indicating that conversion had taken place. Because of the fact that TLC could not be used anymore, other techniques had to be applied to analyze the block copolymers formed. Titration of block copolymer (**7**) instantly gave a change in colour, showing the absence of amino end-groups, and indicating that coupling had been completed.

Besides we also succeeded in reacting aminated polystyrene (**4**) with the Br-terminated trimer (**2**) (step (1.5)) in a CH₃OH/DMF mixture within three days. Additionally, a direct coupling between the Br-terminated pentamer (**3**) and the amino-functionalized polystyrene (**4**) (step (1.6)) was accomplished within twelve days. The conversions could be followed perfectly well with TLC and by titration of the block copolymer formed. Thus this extra information is another verification that we are able to prepare an ionic diblock copolymer with nine positive charges.

Variations in reaction periods, noticed between step (1.6) and the corresponding step (1.4), are due to the better solubility of the polystyrene with 4 positive charges and consequently an improved accessibility for the ionene pentamer (**3**) to react. Based on these findings we tried to couple a polystyrene which already possessed two quaternary ammonium groups, with 2,4-ionene with bromo end-groups. Despite the better solubility and accessibility no block copolymer could be detected.

No problems showed up during the coupling of polystyrenes of higher molecular weights, with small units of 2,4-ionene. Hence, we were also capable of preparing ionic diblock copolymers with an ionene block length of seven units, starting, for example, from polystyrene Q ($\bar{M}_n = 9300$ g/mol) according to quite similar reaction procedures. Therefore, it can be concluded that we have succeeded in synthesizing block copolymers consisting of polystyrene with different monodisperse ionene blocks, having different numbers of quaternary ammonium groups (between 1 and 9).

Catalytic activity measurements

Catalytic autoxidation experiments of 1-dodecanethiol so far always were performed in water⁷⁾. Using the normal procedure, only very low catalytic activities were achieved, due to the low solubility of the block copolymer (**7**), a behaviour characteristic of block copolymers having hydrophobic sequences. Selb et al. observed that a polystyrene-poly(vinylpyridinium) block copolymer was completely insoluble in water, despite its very high vinylpyridinium content (94%)²⁶⁾. These results emphasize that the poor solubility arises from a hindering of the penetration of water into the

hydrophobic domains of the polystyrene, and therefore cannot sufficiently swell and break-up the structure of the solid particles.

Several authors have reported before that the dissolution of copolymers apparently insoluble in water can be achieved by first dissolving the copolymer in a better solvent. Selb was able to dissolve the block copolymer in a water-methanol mixture (1 vol.-% methanol). Schwab dissolved polystyrene-*b*-quaternized poly(2-vinylpyridine) in a THF-water mixture and then stripped the THF off under vacuum²⁷.

A modification of the dissolving procedure of **7** had to be developed, which would first destroy the packing of the macromolecules, after which the copolymer can exhibit its real micellar properties. First of all we tried to swell and dissolve the block copolymer (**7**) in 1-dodecanethiol, but only a low solubility and consequently a low activity was realized. However, it appeared that the block copolymer could be dissolved in 2 mL of DMF, after which it was introduced in the reactor.

It should be mentioned here that the phthalocyanine aggregates, the most catalytically active species, are known to dissociate into monomeric species upon addition of DMF in an aqueous polymer-free system, but if the mixture of DMF and water also contained ionene, then the aggregates will remain²⁸). The addition of DMF will not affect the catalytically active aggregates, but only enhance the solubility of the ionic block copolymer (**7**). Nevertheless, it is possible that the solubility of 1-dodecanethiol increases and therefore higher catalytic activities could be observed than in a DMF-free reaction mixture. In order to check these considerations, the catalytic activities of the CoPc(NaSO₃)₄/(water-soluble 2,4-ionene) complex for the autoxidation of 1-dodecanethiol in a DMF/H₂O mixture were compared with those achieved in water. In Fig. 3 the optimal ionene/CoPc(NaSO₃)₄ ratio, expressed as N⁺/Co ratio, is depicted as a function of the oxidation rate of 1-dodecanethiol in a DMF/water (2/98, v/v) mixture. Comparing the optimal N⁺/Co ratio, the corresponding optimal activity and the shape of the curve, with the properties of the aqueous systems⁷), no differences were found. Thus the modification of the reaction procedure assures that the entire block copolymer is dissolved and available to interact with the catalyst and substrates. So we may conclude that DMF does not affect the catalytic experiments at all.

The effect of the hydrophobic block on the catalytic activity, investigated using block copolymer (**7**) (\bar{M}_n (polystyrene) = 2700 g/mol and \bar{M}_n (2,4-ionene) = 1544 g/mol) is presented in Fig. 3. The maxima in both curves occur because the ionene interacts electrostatically with the thiolate anions present at the thiol-water interface⁷). At low ionene concentrations, where the oxidation rate is low, only a small part of CoPc(NaSO₃)₄ is in the highly active aggregated form. Upon increasing the ionene concentration, catalytically active aggregates are formed and the ionene-thiol contact surface is enhanced, both resulting in an increased activity. After reaching an optimum, further addition of ionene leads to an increase of the ionene concentration in the water phase, which will probably bind a part of the cobalt complex.

Comparing the block copolymer (**7**) with 2,4-ionene, no differences can be determined between the optimal N⁺/Co ratios. The optimal catalytic activity of the block copolymer is 2,5-fold higher than that of 2,4-ionene, most probably due to the hydrophobic interaction of the polystyrene block with the hydrophobic thiol. It is interesting that even higher activities were measured when compared with the

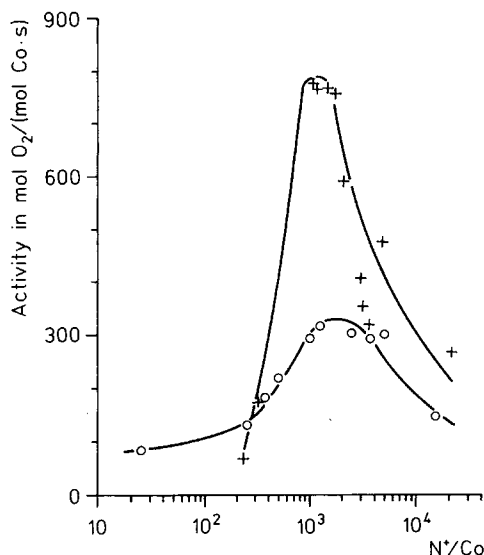


Fig. 3. Catalytic activity as function of the N^+/Co ratio. Conditions: pH = 13, [1-dodecanethiol] = 0,021 mol/L, $[\text{CoPc}(\text{NaSO}_3)_4] = 2 \cdot 10^{-7}$ mol/L, DMF/ H_2O = 2/98 (v/v). (○): 2,4-Ionene; (+): polystyrene-2,4-ionene block copolymer (7)

analogous block copolymer oleyl-ionene⁷⁾ (Tab. 2). Apparently, a more effective hydrophobic interaction with the thiol, as result of the longer hydrophobic blocks, gives better co-catalytic properties.

Since such high oxidation rates were reached, even 40 times higher than in the polymer-free system, we also tried to study the influence of the length of the ionene block on the activity. After testing block copolymer (6) with only 4 N^+ as co-catalyst, it turned out that under the same conditions similar reaction rates (600 mol O_2 / (mol Co · s)) were achieved. It is surprising that such high activities were realized with only four quaternary ammonium groups, while it is known that long and flexible chains are necessary to stabilize the most active aggregated form of the catalyst⁶⁾. Probably, in contrast to the homogeneous systems⁶⁾, here the quaternary ammonium groups of the ionene are concentrated at the thiol-water interface and various ionene chains collectively contribute to the stabilization of dimers of $\text{CoPc}(\text{NaSO}_3)_4$. It can be concluded that very high catalytic activities can be achieved when using ionic diblock copolymers, containing a relatively short ionene block needed for interaction with the catalyst, and a hydrophobic polystyrene block providing enhanced substrate enrichment by hydrophobic interactions.

Immobilization of this highly active catalytic system is one of our goals in the near future. This might be accomplished by utilizing the polystyrene-ionene block copolymer as surfactant in emulsion polymerization and by using the resulting active latices as cocatalysts in the oxidation of thiols. Furthermore, we also intend to equip the block copolymer with a polymerizable end-group, leading to a polymerizable, i. e. chemically bonded, emulsifier. Additionally it would be interesting to determine the

Tab. 2. Catalytic activities of several CoPc(NaSO₃)₄-containing systems^{a)}

	Maximal rate (mol O ₂ /(mol Co · s)) at optimal N ⁺ /Co ratio
OH ⁻	20
2,4-Ionene	310
6	600
7	775
Oleyl-ionene ⁷⁾	410 ^{b)}

^{a)} Conditions: pH = 13, [1-dodecanethiol] = 0,021 mol/L, [CoPc(NaSO₃)₄] = 2 · 10⁻⁷ mol/L, N⁺/Co = 1250, DMF/H₂O = 2/98 (v/v).

^{b)} N⁺/Co = 2500, 100 vol.-% H₂O.

minimum amount of quaternary ammonium groups necessary to stabilize the highly active aggregated form of CoPc(NaSO₃)₄ at the thiol-water interface.

Conclusions

Dimethylamino-functionalized polystyrene synthesized by anionic polymerization using a functional initiator can be obtained in high yields and with fairly narrow molecular weight distributions. The preparation of well defined block copolymers by reactive endcoupling of the polystyrene with ionene oligomers proved to be a successful new route. The catalytic system CoPc(NaSO₃)₄ (ionene-containing block copolymer) shows high reaction rates in the phase-transfer-catalyzed autoxidation of hydrophobic thiols. Higher catalytic activities, compared with the analogous hydrophilic homopolymer 2,4-ionene, can be achieved, as a result of hydrophobic interaction with the hydrophobic substrate 1-dodecanethiol.

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