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Laboratory of Polymer Chemistry, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Autoxidation of Thiols with Cobalt(II)Phthalocyanine-Tetra-Sodium Sulfonate Attached to Poly(Vinylamine), 6

Immobilized Catalysts by Crosslinking of Poly(vinylamine)

Wilfried M. Brouwer, Piet A. M. Traa, Teun J. W. de Weerd, Pieter Piet, and
Anton L. German

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SUMMARY:

Poly(vinylamine), being both carrier and promotor of the thiol oxidation catalyst cobalt(II)phthalocyanine-tetra-sodium sulfonate ($\text{CoPc}(\text{NaSO}_3)_4$), was crosslinked with α, α' -dichloro-p-xylene, thus yielding porous hydrophilic networks. The effects of experimental parameters such as stirring speed, particle size, degree of crosslinking, distribution of catalytic sites ($\text{CoPc}(\text{NaSO}_3)_4$) in the catalyst particles, pH, temperature, and thiol concentration were investigated. Reaction rates observed for the immobilized catalyst systems appeared to be 4 – 30 times lower as compared with the water soluble polymeric catalyst system but still higher than those of the polymer free $\text{CoPc}(\text{NaSO}_3)_4$ catalyst.

At a stirring speed around $3 \cdot 10^3$ rpm not the mass transfer from the bulk to the catalyst particles but intra-particle diffusion limits the reaction rate. Accordingly, an uncrosslinked polymeric catalyst anchored to silica, with catalytic sites situated close to the particle surface, exhibited comparatively high activity, i.e. only four times lower than the soluble polymeric catalyst.

In addition, the heterogeneous catalyst systems showed resemblance in kinetic behaviour with the soluble polymeric thiol oxidation catalyst.

ZUSAMMENFASSUNG:

Poly(vinylamin), gleichzeitig Träger und Promotor des Thiol-Oxidations-Katalysators Kobalt(II)phthalocyanin-tetra-natriumsulfonat ($\text{CoPc}(\text{NaSO}_3)_4$) wurde mit α, α' -Dichlor-p-xyloil vernetzt und ergab so poröse hydrophile Netzwerke. Die Effekte von experimentellen Parametern wie Rührgeschwindigkeit, Korngröße, Vernetzungsgrad, Verteilung der katalytischen Zentren ($\text{CoPc}(\text{NaSO}_3)_4$) innerhalb der Katalysatorkörner, pH, Temperatur und Thiolkonzentration wurden untersucht.

Die an den immobilisierten Systemen beobachteten Reaktionsgeschwindigkeiten waren etwa 4–30mal kleiner im Vergleich mit dem wasserlöslichen polymeren Katalysatorsystem, aber immer noch höher als diejenigen vom polymerfreien $\text{CoPc}(\text{NaSO}_3)_4$ -Katalysator. Bei einer Geschwindigkeit von ungefähr $3 \cdot 10^3$ rpm beschränkt nicht der Massentransport von den sog. ‚bulks‘ zu den Katalysatorteilchen sondern intragranulare Diffusion die Reaktionsgeschwindigkeit. Übereinstimmend zeigt ein auf Silica verankerter nicht vernetzter polymerer Katalysator mit katalytischen Zentren nahe bei der Kornoberfläche eine vergleichsweise hohe Aktivität, d.h. eine nur vier mal kleinere als diejenige beim löslichen polymeren Katalysator. Außerdem zeigen die heterogenen Katalysatorsysteme Ähnlichkeiten in ihrem kinetischen Verhalten mit dem löslichen polymeren Thiol-Oxidations-Katalysator.

Introduction

Immobilization of active soluble macromolecular catalysts is an important topic in the field of polymeric catalysis, as it offers the possibility of easy separation of the catalyst from the reaction products.

Many reviews on heterogeneous polymer supported catalyses have been published recently^{1–4}.

In general the apparent catalytic activity diminished tremendously after immobilization. In many cases this decrease in rate was ascribed to the occurrence of a rate limitation by matrix diffusion or to specific effects of the carrier itself, e.g. steric hindrance, microenvironmental effects etc.

In this paper the effect of immobilization of the very active polymeric thiol oxidation catalyst cobalt(II)phthalocyanine-tetra-sodium sulfonate ($\text{CoPc}(\text{NaSO}_3)_4$; **1**), bound to poly(vinylamine) (PVAm), has been examined for its catalytic activity. Immobilization was achieved by crosslinking of the functional polymeric promotor, PVAm, thus serving as both insoluble support and catalyst promotor.

When immobilizing in this manner, specific rate retarding effects originating from a 'foreign' carrier surface were thought to be reduced or absent.

The effects of several experimental parameters on the reaction rate have been investigated and from these results conditions have been formulated to obtain optimal activities of immobilized thiol oxidation catalysts.

Experimental

Crosslinking of Poly(vinylamine)

All reagents were obtained commercially and used as supplied. Crosslinking reactions of poly(vinylamine) (PVAmHCl, Polysciences; $\bar{M}_n = 5 \cdot 10^{-4} \text{ g} \cdot \text{mol}^{-1}$) and α, α' -dichloro-*p*-xylene (Fluka) were carried out in a 1 : 1 v/v mixture of methanol and water at 60°C during 5 h (see following scheme). Polymer concentration (repeating units) was $1 \text{ mol} \cdot \text{kg}^{-1}$, reaction volume 8 ml.

The crude resin so obtained was washed with 100 ml NaOH_{aq} ($5 \cdot 10^{-3} \text{ M}$) and a large excess of distilled water in order to remove chloride and caustic soda, respectively. Hereafter, the highly swollen resin was washed with acetone, pulverized, and dried at 40°C/10 Pa. The degree of crosslinking was in the range of 1–20%, as determined by potentiometric titration.

Swelling Behaviour

The degree of swelling of the resin was determined after equilibration of the resin particles with distilled water. The samples were isolated by filtration under suction, until separation of water had ceased. Immediately afterwards, the weight of the highly swollen samples was determined.

Titration Experiments

The basicity of the amine groups was determined by potentiometric titration of the dried resins with HCl (0.01 M) in 2 M NaCl. A PHM 62 pH meter (Radiometer Copenhagen) fitted with a GK 2401 B electrode was used. In order to prevent absorption of atmospheric CO₂ the titration vessel was carefully kept under a stream of nitrogen. The titrant was added in small portions (1 ml) and the pH was measured 25 min after each addition, when constant pH levels were attained.

Degree of Crosslinking

The degree of crosslinking (DC) is defined as the molar ratio of crosslinking agent (c) to polymeric repeating units (p)*:

$$DC = \frac{c}{p} \cdot 100 (\%) \quad (1)$$

For the experimental determination of the degree of crosslinking, potentiometric titrations with 0.1 M HCl on freshly prepared, crude resins were performed directly in the reaction vessel.

Anchorage of Poly(vinylamine) to Silica

Macroporous silica (Merckogel 1000) was used; particle size: 63 – 125 µm; specific surface by BET absorption: 17.3 m²/g; average pore radius: 55 nm.

The functional silane (γ-glycidyloxy-n-propyl trimethoxy-silane; Union Carbide Silane A-187) was kindly supplied by Mr. A. Graal, Contivema BV.

At first the silica was treated with the functional silane in water at room temperature for 6 h (silane/silica = 1:20 w/w). Unreacted silane was removed by washing with water and acetone successively. One gram of pretreated silica was added to 4.5 mmol of aqueous PVAm. After standing for 24 h at room temperature, the particles were washed thoroughly with water and acetone, and dried at reduced pressure (10 Pa). Elemental analysis of the PVAm coated silica: 0.21% N; 0.63% C, which means that the ratio of polymer repeating units:silane was 4:1.

The CoPc(NaSO₃)₄ solution was added to the PVAm coated silica particles in the reaction vessel just before the kinetic measurements.

Catalyst Preparation

Active thiol oxidation catalysts could be obtained by adding a very dilute blue solution of CoPc(NaSO₃)₄ to the polymeric functional carriers, causing the latter to

* If all amine groups of **2** are crosslinked by **3**, the percentage of crosslinking is 50.

take on a deep blue colour. The bonding of $\text{CoPc}(\text{SO}_3)_4^{4-}$ to the polymer has been studied earlier and appeared to be caused by Coulombic and coordinative interaction⁵.

In the case of crosslinked PVAm particles, two types of catalysts were used. Type A was obtained by adding the $\text{CoPc}(\text{NaSO}_3)_4$ solution *after* crosslinking of PVAm; in the preparation of type B, $\text{CoPc}(\text{NaSO}_3)_4$ was added to PVAm *before* the crosslinking took place. It is expected that the former procedure (Type A) leads to the occurrence of $\text{CoPc}(\text{NaSO}_3)_4$ sites on the particle surface, whereas the latter procedure (Type B) yields a homogeneous distribution of $\text{CoPc}(\text{NaSO}_3)_4$ sites within the catalyst particles.

$\text{CoPc}(\text{NaSO}_3)_4$ appeared to be tightly bound and could not be rinsed out. The ratio Co/N in the resins was in the range 0.001–0.002.

Catalytic Activity Measurements

Catalytic measurements were carried out in a double-walled thermostated Warburg apparatus, equipped with an all-glass mechanical stirrer (maximum speed 4000 rpm). Initial reaction rates were determined by measuring the oxygen uptake during the first minute of reaction. Rates were expressed either in $\text{ml O}_2/\mu\text{mol Co} \cdot \text{min}$ or in $\text{mole RSH}/\text{dm}^3 \cdot \text{s}$. In the latter case a stoichiometry was assumed according to the reaction:

Unless otherwise stated, the initial thiol concentration was 0.19 M and the temperature 25 °C. Oxygen pressure was 0.1 MPa. The pH was adjusted with NaOH (1 M) or HCl (0.1 M). Measurements were carried out as described elsewhere in detail⁶.

Results and Discussion

Catalyst Preparation

In order to get insight into the effectiveness of the crosslinking reaction, potentiometric titration experiments with HCl were performed. Under a few assumptions the (experimental) degree of crosslinking (DC) could be obtained from these data. From the molar amount of HCl (t), required to reach the equivalence point and from the molar amount of polymer repeating units (p), the DC was calculated by Eq. (2):

$$\text{DC} = \frac{p - t}{4p} \cdot 100 (\%) \quad (2)$$

Here the following assumptions were made:

- (1) Only primary amines can be titrated, as the basicity of the secondary amine groups, formed in the crosslink reaction will be strongly reduced due to the electron withdrawing character of the aromatic moiety of the crosslinker^{7,8}.
- (2) No further reaction of secondary amine groups to tertiary or quaternary amines is taking place.

Thus, addition of c moles of crosslinker will cause a decrease of $4c$ of titratable primary amine groups according to Eq. (1). In Tab. 1 the titration results and the theoretical and observed DC, calculated according to Eq. (1) and (2), respectively, are shown. The DC values obtained from the titration

Tab. 1. Comparison of theoretical and observed degrees of crosslinking.

$10^4 \cdot c$ (mol)	$10^3 \cdot p$ (mol)	$10^3 \cdot t$ (mol)	Theoretical degree of crosslinking ^a	Observed degree of crosslinking ^b
0.234	1.97	1.88	1.2	1.1 ± 0.2^c
1.24	1.81	1.35	6.8	6.4 ± 0.4^c
2.66	2.52	1.51	10.5	10.0 ± 1.0^c

^a According to Eq. (1).

^b According to Eq. (2).

^c Interval error based on the uncertainty in the determination of the equivalence point.

experiments are in very good agreement with the theoretical values, which indicates that the crosslink reaction proceeds quantitatively within 5 h and justifies the assumptions made in the calculation of the experimental DC according to Eq. (2).

Basicity of Amine Groups in Crosslinked Resins

In Fig. 1 the titration diagrams (pH vs. degree of protonation of the titratable groups) are shown of a monomeric amine: 1,3 propanediamine

Fig. 1. Titration plots (pH versus degree of protonation of titratable base groups) of polyamines in 2 M NaCl.

(■) 1,3-propanediamine; (○) PVAm; crosslinked PVAm, (▲) DC = 2.5%, (□) DC = 10%, (●) DC = 20%.

(1,3PDA), poly(vinylamine) (PVAm), and crosslinked PVAm (DC: 2.5, 10, and 20%). From the figure it appears that the basicity of the amine groups is reduced in PVAm and even more in crosslinked PVAm, with respect to the monomeric analog 1,3PDA. This effect may be explained by taking into account neighbour interactions between adjacent amine groups, causing a lower pH dependent basicity of the amine groups⁹. The electron withdrawing properties of the crosslinker will contribute to this lower basicity level as well. A similar decrease of basicity as the DC of the networks increases was observed by Bolto et al. for poly(diallylamine) networks⁸.

pH Dependence of Reaction Rate

In Fig. 2 the pH dependence of the oxidation rate of RSH with catalyst type B (homogeneously distributed $\text{CoPc}(\text{NaSO}_3)_4$ in the crosslinked PVAm matrix) is shown. An optimal reaction rate is observed at pH = 7.5. In the polymer free systems $\text{CoPc}(\text{NaSO}_3)_4/1,3\text{PDA}/\text{OH}^-$ and $\text{CoPc}(\text{NaSO}_3)_4/\text{OH}^-$ an optimal

Fig. 2. pH dependence of catalytic activity.

(■) CoPc(NaSO₃)₄/crosslinked PVAm (type B, DC = 4%); (★) CoPc(NaSO₃)₄/1,3-propanediamine/OH⁻; (●) CoPc(NaSO₃)₄/OH⁻.

catalytic activity is found at pH = 10. The CoPc(NaSO₃)₄/1,3PDA/OH⁻ system is about 3 times as active as the CoPc(NaSO₃)₄/OH⁻ system which is in agreement with previous findings¹⁰.

A similar shift in the pH optimum as compared with the polymer free systems was earlier observed for the CoPc(NaSO₃)₄/PVAm (DC = 0) system with an optimal activity at pH = 8¹¹. This phenomenon was discussed in terms of changes in chain charge and local substrate concentrations, caused by the pH dependent basicity of the amine groups.

Accessibility of CoPc(NaSO₃)₄ Sites and Degree of Crosslinking of the Particles

As described in the Experimental section, two types of crosslinked particles were investigated. Type A was prepared by adding CoPc(NaSO₃)₄ *after* crosslinking of PVAm, in contrast with type B, where CoPc(NaSO₃)₄ was added *before* crosslinking of PVAm. The apparent catalytic activity of the sites in both catalyst types and the effect of the degree of crosslinking on the water swelling and on the activity of catalysts A and B was investigated. The results are shown in Fig. 3. System A appears to be at least three times more active than system B, measured at the same DC. From this result it may be inferred that in system A most of the large, square planar, rigid

Fig. 3. Effect of the degree of crosslinking of PVAm on its swelling (●) and on the catalytic activity V of catalyst type A (□) and B (■).

$\text{CoPc}(\text{NaSO}_3)_4^-$ moieties are attached to the polymer matrix close to the particle surface while in system B the $\text{CoPc}(\text{SO}_3)_4^-$ will be homogeneously distributed in the crosslinked particle. This is shown schematically in Fig. 4. The rate difference between A and B may then be explained by the occurrence of a rate limiting intra-particle diffusion, which should be more pronounced in system B than in system A.

As expected, the degree of swelling increases as the degree of crosslinking decreases (see Fig. 3). The water swelling is very high due to the presence of polar charged groups in the polymeric matrix.

The catalytic activity follows curves of similar shape. This behaviour is also indicative of a rate limiting matrix diffusion process, although the lower basicity (see Fig. 1) and thus the network charge at higher DC may also contribute to the rate retardation¹².

Stirring Speed and Particle Size

Variation around the high stirring rate applied ($3 \cdot 10^3$ rpm) caused no significant change in reaction rate for both systems A and B. This indicates that the reaction rate is not limited by mass transfer to or from the catalyst particles.

The effect of the particle size of catalysts A and B was also measured. Two particle sizes, about 60 and 10 μm (obtained from scanning electron micro-

graphs), were investigated. When using the small particles, no significant change could be observed in system A, but for system B the rate increased over 35%, indicating that the rate limiting effect of matrix diffusion in system B will be larger than in system A, which is consistent with the schematic representation in Fig. 4.

Fig. 4. Schematic representation of a cross-section of crosslinked PVAm. A: $\text{CoPc}(\text{NaSO}_3)_4$ added *after* crosslinking; B: $\text{CoPc}(\text{NaSO}_3)_4$ added *before* crosslinking.

The observed effects of experimental parameters on the reaction rate have been summarized in Tab. 2. The effects expected when mass transfer, intrinsic reactivity, or both intrinsic reactivity and matrix diffusion limit the rate, are shown in Tab. 3¹³⁻¹⁵. It becomes evident that all experimental observations indicate that reaction rate is limited by both matrix diffusion and intrinsic reactivity.

Tab. 2. Effect of experimental parameters on reaction rate in crosslinked PVAm catalyst systems.

Stirring speed	Particle size	Degree of cross-linking	Distribution of catalytic sites
independent	dependent ^a	dependent	dependent

^a For catalyst type A this dependency was very small.

Activation Energy

The importance of intra-particle diffusion in these crosslinked systems may also appear from an analysis of the apparent activation energies. If matrix diffusion is rate limiting, the observed activation energy will be lower

Tab. 3. Effect of experimental parameters on rate-limiting processes.

Process	Stirring speed	Particle-size	Degree of crosslinking	Distribution of catalytic sites
mass transfer	dependent	dependent	independent	independent
intrinsic reactivity	independent	independent	uncertain	independent
matrix diffusion and intrinsic reactivity	independent	dependent	dependent	dependent

than the true activation energy¹³⁻¹⁵. The latter will be observed when the intrinsic reaction rate is low as compared with the matrix diffusion rate. Tab. 4 shows the observed activation energies at pH = 8 in the soluble polymeric catalyst system and in the crosslinked systems A and B (DC = 4.9%). The table shows that rate limitation by matrix diffusion is more pronounced in system B than in system A, suggesting a larger diffusion path in the case of catalyst B. These findings support our explanation of the other phenomena observed.

Tab. 4. Apparent activation energies for several catalyst systems^a.

Catalyst support for CoPc(NaSO ₃) ₄	Degree of crosslinking	Apparent activation energy E_{app}^* (kJ · mol ⁻¹)
Soluble PVAm	0	40 ± 4
Catalyst type A	4.9	33 ± 4
Catalyst type B	4.9	24 ± 2

^a At pH = 8.

Thiol Concentration

Initial reaction rates were determined for different initial thiol concentrations ranging from 0.04–0.7 M. Fig. 5 shows the results. The Michaelis-

Fig. 5. Effect of 2-mercaptoethanol concentration C_{RSH} on reaction rate V .

Menten kinetic concept¹⁶ appears to be applicable to these data, implying a rate law of the type

$$v = \frac{k_2 \cdot E_0}{1 + \frac{K_m}{S}} \quad (3)$$

where E_0 is the total catalyst concentration ($\text{CoPc}(\text{NaSO}_3)_4$), S is the initial substrate concentration, k_2 is the rate determining reaction constant and K_m is the Michaelis constant. From the Lineweaver-Burk plot in Fig. 6, the apparent values of k_2 and K_m have been derived and are listed in Tab. 5, together with the parameters for the soluble polymeric catalyst system, found previously⁶. The significantly larger value of K_m as well as the lower value of k_2 in the immobilized system B may be due to diffusional resistance, causing a lower local substrate concentration in the vicinity of the catalytic sites as compared with the soluble polymeric catalyst system.

Fig. 6. Lineweaver-Burk plot. Data from Fig. 5.

Tab. 5. Kinetic parameters for soluble and crosslinked $\text{CoPc}(\text{NaSO}_3)_4/\text{PVAm}$ catalysts.

Catalyst support for $\text{CoPc}(\text{NaSO}_3)_4$	pH	K_m (M)	$10^{-2} k_2$ (s^{-1})
Catalyst type B	8.0	0.3 ± 0.1	1.2 ± 0.2
Soluble PVAm	7.4	0.09 ± 0.02	28 ± 4

Silica Anchored Polymeric Catalysts

From all these observations it may be deduced that the catalytic sites ($\text{CoPc}(\text{NaSO}_3)_4$ situated at or nearby the outer surface of the crosslinked polymeric particle) are the most effective ones, since then reaction rate is hardly limited by the matrix diffusion. This ineffectiveness of the catalyst interior prompted us to substitute this inner part by an inert substance e.g. silica.

A silica anchored $\text{CoPc}(\text{NaSO}_3)_4/\text{PVAm}$ catalyst was synthesized and characterized (see Experimental), and its activity (see Tab. 6) was found to be even higher than observed for system A, but nevertheless less active than

Tab. 6. Initial reaction rate and pH optimum for several catalyst systems.

Catalyst support for $\text{CoPc}(\text{NaSO}_3)_4$	pH Optimum	10^{-2} Initial rate ^a ($\text{ml}/\mu\text{mol} \cdot \text{min}$)
OH^-	10	0.1
Catalyst type B (D.C. = 4%)	7.5	0.3
Catalyst type A (D.C. = 2.5%)	— ^b	1.6
Silica anchored PVAm	8	2.7
Soluble PVAm	8	10.6

^a At pH = 8.2; $c_{\text{RSH}} = 0.19 \text{ mole dm}^{-3}$.

^b Not determined.

the soluble non-crosslinked polymeric system. Thus, an improved accessibility of the catalytic sites leads to an enhanced reaction rate as compared to system A, but decelerated it as compared to the polymeric catalyst system,

due to multi-anchoring of the PVAm onto the silanized surface, thus lowering conformational freedom and accessibility or due to a specific effect of the silica surface¹⁷. It seems therefore that a polymeric catalyst anchored by a single link on a small rigid inert carrier particle as shown recently by Verlaan et al.¹⁸, will offer an approach to an even more active, immobilized polymeric catalyst.

Conclusions

1. α,α' -dichloro-p-xylene appeared to be an efficient crosslinker of PVAm. The reaction proceeds almost quantitatively under the applied conditions.

2. The main effect introduced by crosslinking the very active water soluble polymeric catalyst, $\text{CoPc}(\text{NaSO}_3)_4/\text{PVAm}$, is the occurrence of a rate limitation by matrix diffusion. At the applied stirring speed ($3 \cdot 10^3$ rpm) rate limitation by mass transfer in bulk has not been observed. Therefore, more active immobilized catalysts of this type will only be obtained, when the accessibility to the very active catalytic sites is improved, as is the case for a silica anchored macromolecular catalyst.

3. As expected, kinetic resemblance has been found between the soluble polymeric catalyst system, $\text{CoPc}(\text{NaSO}_3)_4/\text{PVAm}$, and the insoluble cross-linked polymeric catalysts; e.g. Michaelis-Menten kinetics in thiol and a shift of the optimal pH value from that of the polymer free systems.

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