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Complexes of poly(2-*N,N*-dimethylaminoethyl) methacrylate with heavy metals II. Oxidation of cyclohexene with *tert*-butylhydroperoxide

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Summary

Metal complexes of poly(2-*N,N*-dimethylaminoethyl) methacrylate were prepared by complex-forming with aqueous solutions of salts of $FeSO_4.2H_2O$; $CoCl_2.6H_2O$; $CuCl_2.2H_2O$; $VOSO_4.5H_2O$; $Na_2MoO_4.2H_2O$ and $Na_2WO_4.2H_2O$. The catalytic activity of the complexes was studied in the oxidation of cyclohexene as a model reaction. The activities of the complexes synthesized towards the reaction of cyclohexene epoxidation can be arranged by the following order: PDMAEM-MoO_2^{2+} > PDMAEM-VO^{2+} > PDMAEM-WO_2^{2+} > PDMAEM-Co^{2+} > PDMAEM-Fe^{3+} > PDMAEM-Cu^{2+}. The complexes catalyzing the homolytic decomposition of *tert*-butylhydroperoxide increased the maximum yield of 2-cyclohexene-1-ol and 2-cyclohexene-1-on. The yield of cyclohexene oxide and 2-cyclohexene-1-ol were 58% and 13%, respectively.

Introduction

The development of heterogenated polymer catalysts with high concentration of active centers with certain co-ordination sphere, as well as the preparation of stable catalytic systems with good reproducibility, activity, selectivity and easily removable from the reaction mixture, is interesting for the practice. These requirements determine the use of scientifically based approach to the selection of an immobilized catalyst and prediction of its catalytic effect under certain reaction conditions. Recently, the search for suitable conditions for synthesis of new polymer carriers containing catalytically active centers is quite intense.

The scientific research related to the synthesis of heterogeneous catalysts on the basis of copolymerization of suitable metal-containing monomers has been reviewed by Mastrorilli [1]. The catalytic application of these metal-containing complexes can be summarized in the following fields: hydrogenation of alkenes and functional olefins, oxidation of various substrates like olefins, sulphates, alcohols and aldehydes. The main factors derived from this analysis are related to the use of metal-containing monomers for synthesis of polymers with defined molecular structure which can be used as catalysts or catalyst carriers.

Recently were obtained chitosan-metal complexes as an antimicrobial agent [2] and metal complexes of polybutylacrylate which exhibit electrochemical activity and dielectric properties [3].

The manuscripts of D.S.Sherrington are analytic summary of the tendencies in the development of the immobilized metal-polymer complexes for catalytic epoxidation of alkenes[4-6]. Our group reported for highly selective immobilized catalysts for the reactions of epoxidation, obtained from copolymers of cross-linked polyoxyethene with 4-vinylpyridine, methacrylic acid [7,8] and radiation grafted acrylic acid and 4-vinylpyridine onto polyethene and polytetrafluoroethene films [9,10]. Vanadium complexes have been prepared on the basis of polyoxyethene in organic solvents with different donor numbers [11]. The complexes of poly(2-*N,N*-dimethylaminoethyl) methacrylate (PDMAEM) with metals of various degrees of oxidation is interesting for polymer chemistry due to their potential use as immobilized catalysts in various chemical reactions. One possibility to use PDMAEM has been discussed in a previous publication where the activity of tungsten (VI) peroxocomplexes was studied in the epoxidation of styrene with hydrogen peroxide by three-phase catalysis [12].

In this paper we report studies on reaction of oxidation of cyclohexene with polymer-supported metal ions as catalysts.

Experimental Part

Chemicals

Cyclohexene, $(CH_3)_3COOH$ (Fluka,), $C_6H_5CH_3$ (Aldrich,) glacial CH_3COOH, KJ, $Na_2S_2O_3$, starch (Chimsnab, Bulgaria) were analytical grade. *Tert*-butylhydroperoxide was purified by vacuum distillation. Cyclohexene was distilled prior to use. Toluene was dried with molecular sieve 5A and used as solvent.

Metal complexes of Poly(2-N,N-dimethylaminoethyl) methacrylate

The metal complexes of poly(2-*N,N*-dimethylaminoethyl) methacrylate were obtained by the methods described in our previous paper [13].

Oxidation of cyclohexene

Cyclohexene was oxidized with *tert*-butylhydroperoxide (*t*-BHP) in a glass reactor (batch) equipped with a magnetic stirrer at T=85°C for 90 min.

The following reagents were introduced into the reaction vessel:
Polymer content 5.10^{-3}mmol metal/l; (in all cases the catalysts used as powder)
0.1ml *t*-BHP (0.081g; $8.79.10^{-4}$M);
1.0ml cyclohexene (0.8g, $9.8.10^{-3}$M);
4.0ml toluene (solvent).

The reaction occurs under continuous stirring and the initial sample was taken immediately after thermostating the reaction mixture. Then, samples of the reaction mixture were taken at certain time intervals for identification of hydroperoxide and reaction products obtained.

Analysis

EPR analysis and Moesbauer analysis of the metal complexes

EPR and Moesbauer analysis before test reaction were described in our paper[13].

Thermal analysis

The thermal properties of the polymers and their metal complexes were determined on an OD-102 derivatograph type , system F.Paulik-J.Paulik-L.Erdey (MOM, Budapest, Hungary) by TG curves and following conditions: rate of heating 6°C/min, temperature range 20-600°C, amount of samples 100±0.5mg in air medium.

Gas Chromatographic Analysis

The Gas Chromatographic analyses (GC) of all samples were performed on a Perkin-Elmer Sigma 2000 gas chromatograph (Norwalk, CT, USA) , equipped with dual flame-ionization detectors (FID), an all-glass split-type sample injector and Chromatographics 2 Data Systems. The chromatograph was fitted with Permaphase DMS [poly(dimethyl siloxane)] fused-silica capillary column [50mx0.25mm i.d. (two columns in series) connected with a butt connector)]; film thickness $d_f = 1.0$ μm (Perkin-Elmer). The column oven temperature was programmed from 35°C to 180°C at $1°C.min^{-1}$. Nitrogen with high purity (99.999%) was used as carrier gas at flow rate $0.9\ mL.min^{-1}$. The detector and injector temperatures were held at 250°C and 200°C, respectively, the split ratio was 1:80 and the sample volume 0.2 μl. The peak identification of the components was made on by reference substances.

The *t*-BHP concentration ($C_{t\text{-bhp}}$, M) was determined iodometrically while conversion (X,%) was calculated using:

$$X = \frac{C_{ot-bhp} - C_{ft-bhp}}{C_{ot-bhp}}.100 \qquad \textbf{(1)}$$

where $C_{o\,t\text{-bhp}}$ and $C_{f\,t\text{-bhp}}$ are initial and final concentrations of *t*-BHP, respectively.

Results and discussion

The metal complexes of PDMAEM, synthesized and described in paper [13] were studied in reaction of cyclohexene oxidation with *tert*-butylhydroperoxide.

The materials obtained possess catalytically active centers and were studied as immobilized catalysts. Metal-polymer complexes of carboxyl- and nitrogen-containing radiation grafted copolymers were studied earlier [9,10], as well as their use as catalysts for cyclohexene oxidation.

When polymer complexes of metals are used as heterogenized catalytic systems, the effectiveness of the chemical processes is determined by the swelling of the carrier in the reaction medium. This facilitates reagents diffusion and increases products yields. The cross-linked PDMAEM macromolecules possess balanced hydrophilic-lipophilic properties which stipulate their swelling in polar and non-polar solvents.

The swelling behavior of PDMAEM and its complexes in different solvents was studied. It was found that the introduction of metal ions affected the sorption solvent molecules – it decreased compared to that of the initial polymer. The samples cross-linked with 5% divinylbenzene (DVB) showed twice higher swelling compared to these prepared with 10% cross-linking agent. This can be explained with the lower density of the network of crosslinks between polymer macromolecules and DVB. The change of the swelling values of the different complexes can be explained with affinity of each metal ion to formation of complexes. The latter changes the number of amphiphilic groups in the film and as a results affects the swelling degree. The nature of the solvent exerts significant effect on the aptitude of polymer metal complexes to swelling. The experimental results showed that, depending on solvent nature, the swelling of polymer metal complexes can be arranged by the following order: water < water:ethanol (50:50) < ethanol ≤ toluene. The nature of metal ion depends on the degree of swelling of polymer carrier. This dependence for all solvents can be described in the order: PDMAEM-VO^{2+} < PDMAEM-Fe^{3+} < PDMAEM-MoO_2^{2+} < PDMAEM-Cu^{2+} < PDMAEM-Co^{2+} < PDMAEM-WO_2^{2+} < PDMAEM. These data correlate well with the results obtained from the spectrophotometric quantitative determination of mg bonded metal ions per g PDMAEM, presented in previous paper [13]. With a view to the use of the polymer carriers with immobilized catalytically active centers synthesized for reactions of organic synthesis taking place at high temperatures, differential thermal analyses were carried out. The results obtained are presented in Table 1. The complexes of all the samples do not form individual phases having its own stage of destruction. The temperatures of the beginning of destruction of the pure polymer and that of the metal complexes were affected positively by the content of cross-linking agent DVB.

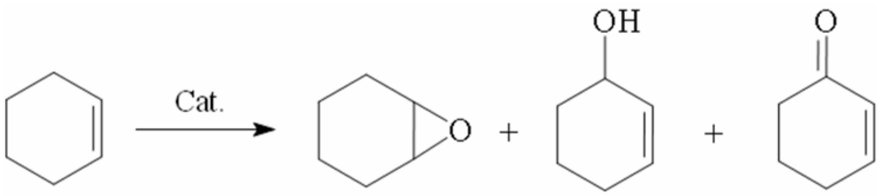
Table 1. Thermal properties of PDMAEM and their metal complexes

Temperature	PDMAEM		PDMAEM-VO^{2+}		PDMAEM-MoO_2^{2+}		PDMAEM-WO_2^{2+}		PDMAEM-Co^{2+}		PDMAEM-Cu^{2+}	
	Amount of DVB, %											
°C	5%	10%	5%	10%	5%	10%	5%	10%	5%	10%	5%	10%
T_b^*	190	250	210	180	190	210	210	230	190	230	210	210
T_{10}^*	245	300	250	232	222	220	250	290	230	288	270	235
T_{50}^*	380	400	420	390	500	430	415	360	365	410	512	460

T_b^* - $T_{\text{begining of destruction}}$
T_{10}^* - $T_{\text{10 mass \% loss}}$
T_{50}^* - $T_{\text{50 mass \% loss}}$

The only exceptions were the complexes of PDMAEM with Cu^{2+} and VO^{2+}. Similar tendency was observed for the other two characteristics – the temperatures of 10% and 50% weight loss. The data obtained from the thermal analysis of PDMAEM and its metal complexes showed that all the samples studied have good thermal stability up to 180°C. The processes of oxidative destruction began in the interval 180-230°C. Therefore, the complexes have the necessary thermal stability to be used as catalysts in reactions taking place in temperature interval (20-180°C).

The processes involving homogeneous, heterogeneous and immobilized catalytic systems play an important role in chemical industry. The oxidation of alkenes is a method for direct introduction of oxygen. These processes require the presence of a complex of transition metal and source of oxygen. The most often used oxidants are oxygen, hydrogen peroxide, ozone, sodium hypochloride, *tert*-butylhydroperoxide, potassium persulphate and iodosylbenzene [14]. Further, the catalytic activities of the polymer metal complexes prepared from Mo (VI), V (IV), W(VI), Co(II), Cu(II) and Fe(III) with PDMAEM were studied in the reaction of cyclohexene oxidation. The oxidizer used was *t*-BHP. All the experiments were carried out under the same conditions presented in Table 2. The following scheme can be suggested for the reaction of cyclohexene (1) oxidation with *tert*-butylhydroperoxide:



(1) (2) (3) (4)

Scheme 1.

Table 2. Oxidation of cyclohexene with *tert*-butylhydroperoxide in presence of immobilized catalysts

№	Complexes №1-6;5% (DVB) №7-12;10% (DVB)	Conversion*, %	Yield **,%		
			Cyclohexene oxide	2-cyclohexene-1-ol	2-cyclohexene-1-on
1	PDMAEM-VO^{2+}	63	47	13	11
2	PDMAEM-MoO_2^{2+}	67	58	4	2
3	PDMAEM - WO_2^{2+}	37	18	11	9
4	PDMAEM - Co^{2+}	64	8	8	3
5	PDMAEM - Fe^{3+}	78	4	6	8
6	PDMAEM- Cu^{2+}	45	3	8	6
7	PDMAEM - VO^{2+}	51	42	11	10
8	PDMAEM-MoO_2^{2+}	66	51	4	1
9	PDMAEM - WO_2^{2+}	35	16	10	8
10	PDMAEM - Co^{2+}	50	7	11	9
11	PDMAEM - Fe^{3+}	67	8	7	8
12	PDMAEM - Cu^{2+}	44	4	6	7

*- according to equation (1) shown in Experimental part

**- according data from gas-chromatographic analysis.

It is possible to obtain three products: cyclohexene oxide (2), 2-cyclohexene-1-ol (3) and 2-cyclohexene-1-on (4). Figure 1 shows the chromatogram of the initial reagents and the products obtained from the cyclohexene oxidation. The chromatogram confirmed the information that suitable conditions for separation and identification of the products obtained have been found.

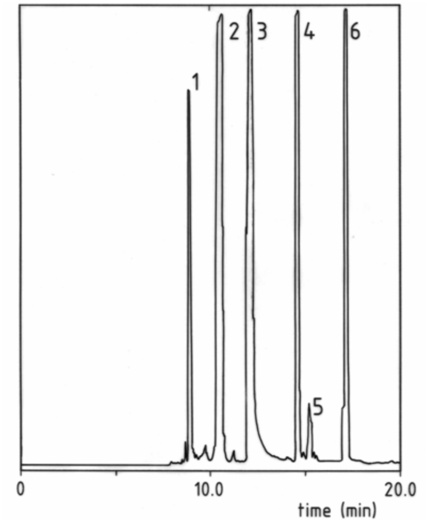


Figure 1. GC Chromatograme
1) t-Butylhydroperoxide (t-BHP)-8.77 min; 2) Cyclohexene-10.53 min; 3) Toluene-12.00 min; 4) Cyclohexene oxide (Epoxycyclohexene)-14.47 min; 5) 2-cyclohexene-1-ol- 15.07 min; 6) 2-cyclohexene-1-on- 16.90 min

The experimental data for the polymer complexes with DVB 5% are shown in Table 2. As can be seen, high yields of cyclohexene oxide were observed with molybdenum and vanadium catalysts, 58 and 47%, respectively. The yields of 2-cyclohexene-1-ol and 2-cyclohexene-1-on were considerably lower with molybdenum catalyst compared to vanadium one, despite that the degree of conversion of *t*-BHP was about the same – 67% and 63%, respectively. These results suggest that molybdenum is much more selective in the heterolytic decomposition of organic hydroperoxide. It may be supposed that the use of tungsten would give cyclohexene oxide yields higher than 18% since it is well known that metals with high oxidation potential and low Lewis acidity are active catalysts for epoxidation of unsaturated compounds [15]. With Fe (III), Co (II) and Cu (II), the yields of cyclohexene oxide, 2-cyclohexene-1-ol an 2-cyclohexene-1-on were significantly lower – within 3-8%. The conversion was much higher 45-78%. It means that these metals are not selective in the decomposition of the organic peroxide. Similar results were obtained by the use of manganese complexes with Schiff bases in cyclohexene oxidation reaction [16]. The cyclohexene oxide yield was 36%, while that of 2-cyclohexene-1-ol and 2-cyclohexene-1-on were 8% and 14%, respectively.

Experiments were carried out with the same complexes but with divinylbenzene 10%. The results are presented in (Table 2, rows 7-12). The higher content of cross-linking agent of cross-linking is supposed to impede the reagents diffusion to the catalytic centers and, as a result, the yields were expected to be lower. The analyses carried out, however, showed that both the yields and conversion were not quite different. This was probably due to the good swelling of the polymer matrix in toluene which is used as solvent for reactions of oxidation.

The catalytic systems discussed can be regarded as active unit deposited onto polymer and they have significant advantage in the separation of the catalysts from the reaction mixture and their reuse. Part of the polymer metal complexes synthesized - Mo (VI), V (IV) and Fe (III) with degree of cross-linking 5% were used twice in the test reaction to assess the change of their catalytic activity. The experimental data did not show significant differences in both degree of conversion vs *t*-BHP and product yields. The yield of cyclohexene oxide when Mo was used was 54% while with vanadium it was 44%. This means that the metal ions were not washed away from the polymer carrier after one operation cycle. Similar results were obtained with molybdenum complexes of cross-linked copolymer of polyoxyethylene and polyvinylpyridine [8] by epoxidation of styrene where it was established that the molybdenum catalyst did not lose its activity for 50 h.

The results obtained on the catalytic activity correlate well with the data from EPR and Moesbauer spectroscopies.

The electron configuration of the vanadyl ions in the metal complexes of PDMAEM after test reaction was studied by EPR (Figure 2).

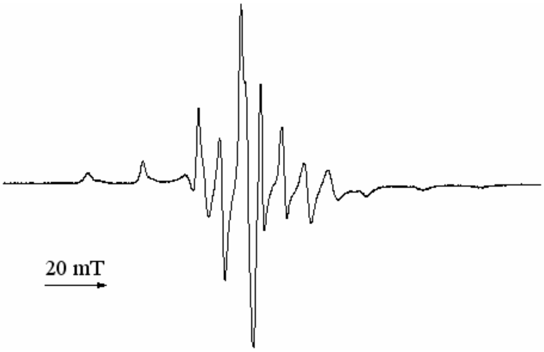


Figure 2. EPR-spectra of PDMAEM-VO^{2+} complex after test-reaction

The spectra observed were very close to g-factors and A-constants of superfine interaction and there was quite large overlapping in the range of perpendicular lines and the last three lines with parallel orientation. Therefore, the lines before the catalytic reaction were a little wider than that after the catalytic test. The EPR parameters of the spectrum after the catalytic reaction were $g_{||} = 1.941$; $g_{\perp} = 1.984$; $A_{||} = 18.6 \pm 0.3$ mT; $A_{\perp} = 6.7 \pm 0.3$ mT.

The experimental Moesbauer spectra after test reaction (Figure 3) were composed of paramagnetic component (doublet - Db) and a component with superfine magnetic structure (sextet - Sx). A model including the lines of one doublet and one sextet was used for the mathematical processing. The parameters determined are presented in Table 3.

Table 3. Parameters of the Moesbauer spectra after the test reaction

Polymer complexes	Components	IS, mm/s	QS, mm/s	H_{eff}, T	FWHM, mm/s	G, %
Poly(2-*N,N*-dimethyl-aminoethyl)metha-crylate-Fe^{3+}	Sx	0.38	-0.12	33.7	1.07	32
	Db	0.37	0.55	-	0.30	68

The comparison of the spectra of samples taken before and after catalytic test reaction showed that they are similar by type and value of the parameters determined.

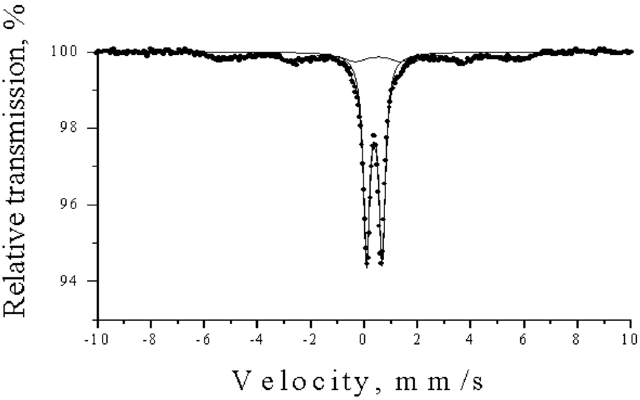


Figure 3. Moesbauer spectra of PDMAEM - Fe^{3+} complexes after test-reaction at room temperature

This may be regarded as indication that the catalyst is stable and its stationary state under conditions of catalytic reaction is formed without change of its composition. Since the experimental apparatus was transmission one, i.e. the results refer to samples volume, if insignificant changes take place (mainly on the surface and affecting small number of the iron atoms) they would be manifested by insignificant changes in the spectra observed.

Conclusion

Complexes of poly(2-*N,N*-dimethylamioethyl) methacrylate with heavy metals were synthesized. The complexes have the necessary thermal stability to be used as catalysts in reactions taking place in temperature interval 20-180°C. The polymer carriers with immobilized metal ions were tested in a model reaction of oxidation of cyclohexene with *tert*-butylhydroperoxide. It was proved that the highest yields can be obtained with the complexes containing Mo (VI). The degree of cross-linking of the polymer carrier did not have significant influence on the yields of the products obtained. The complexes of Mo (VI), V (IV) and Fe (III) with content of DVB 5% were studied twice in the test reaction to asses the change of their catalytic activity and it was proved that the latter remained unchanged.

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