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Modified polyacrylamide-supported chlorochromate as a new polymeric oxidizing agent

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Abstract: Modified polyacrylamide-supported chlorochromate was synthesized and used as a versatile and efficient oxidizing agent for the oxidation of various organic compounds, such as hydroxyl compounds, silylethers, oximes, thiols, and others. Over oxidation of the products (aldehydes to carboxylic acids) was not observed with this oxidizing agent. The oxidant was insoluble in the oxidation media and the chromium(VI) ions remained firmly bound to the insoluble polymeric support after the oxidation reaction. The mild reaction condition, easy work-up, short reaction times, regenerability of the reagent and its easy preparation and handling are among the advantages of this new polymeric chlorochromate reagent.

Keywords: chromium(VI) oxidant; modified polyacrylamide; polymeric oxidizing agent; chlorochromate.

INTRODUCTION

During the past years, there have been several important advances in the field of organic synthesis; the use of polymer-supported reagents is one of them.¹ Polymeric reagents can be defined as functionalized polymers used in stoichiometric amounts in one-step processes to transform low-molecular-weight substrates into products.² They have been investigated widely and a very large range of reactions can be realized using such reagents.³ The most important benefits of these reagents over their soluble counterparts are simple filtration procedures, ease of separation from the reaction mixture, selectivity and low toxicity.⁴ These reagents have been developed for use in simple reactions, such as oxidation, reduction, condensation, acylation, alkylation, halogenation, the Wittig reaction, *etc.*⁵

Chromium(VI)-based oxidizing reagents have been extensively used in organic synthesis.⁶ Among these, pyridinium chlorochromate (PCC),⁷ prolinium chlorochromate,⁸ caffenilium chlorochromate,⁹ tetrahexylammonium chlorochro-

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mate,¹⁰ 2,6-dicarboxypyridinium chlorochromate,^{11,12} and tributylammonium chlorochromate¹³ are a number of oxidizing agents based on chlorochromate that have been reported.

Numerous heterogeneous polymer-supported oxidizing agents with different functionalities have been reported in the literature that offers some advantages over their more traditional soluble counterparts. Among these, polymer-bound metallic oxidants and especially polymer-supported chromium(VI) reagents have received considerable attention.¹⁴ Heterogeneous polymeric reagents such as poly[vinyl(pyridinium chlorochromate)] and dichromate,^{15,16} poly(*n*-butyl-4-vinylpyridinium)dichromate,¹⁷ poly(4-vinylpyridinium nitrate),¹⁸ poly(*N*-vinylpyrrolidone)-hydrotribromide,¹⁹ poly(*n*-butyl-4-vinylpyridinium)periodate, iodate and bromate,²⁰ polystyrene supported *t*-butylchromates²¹ and poly[vinyl (pyrrolidonium chlorochromates)]²² are among those reported in the literature.

In continuation of our interest on modified polyacrylamides,^{23–26} the synthesis and use of a modified polyacrylamide-supported chlorochromate as new polymeric oxidizing agent for the oxidation of various organic compounds, such as hydroxyl compounds, oximes, silylethers, thiols and some other compounds, are described herein.

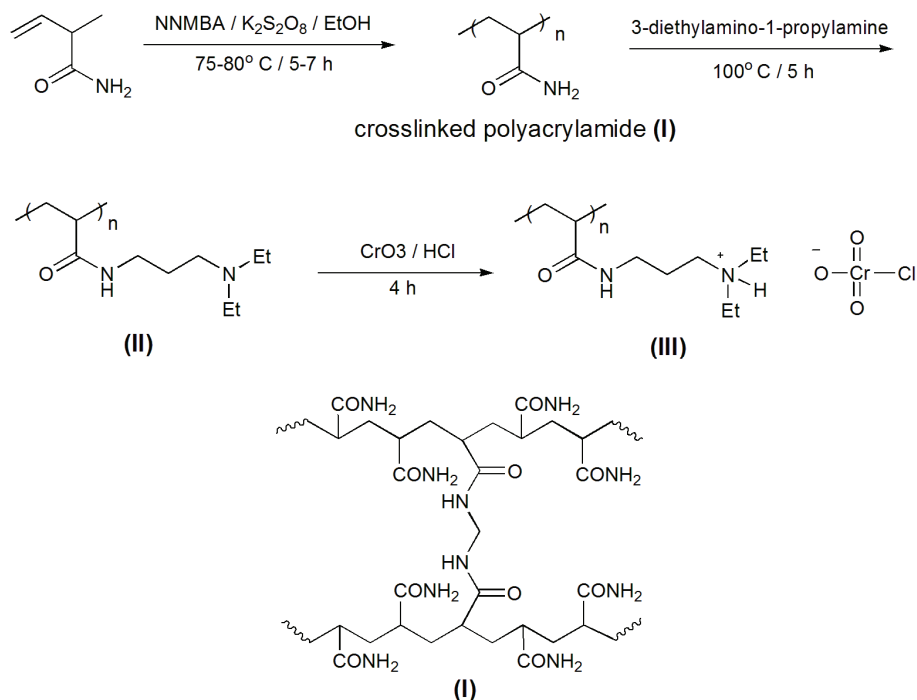
EXPERIMENTAL

Chemicals were purchased either from Merck or Fluka, or were synthesized in the laboratory. Acrylamide and the cross-linking agent, *N,N'*-methylene bisacrylamide (NNMBA), were commercial products obtained from Merck. Trimethylsilyl ethers were prepared by a reported procedure.²⁷ All products were characterized by comparison of their IR and/or ¹H-NMR spectra and physical data with those of authentic samples. All yields refer to the isolated products.

The purity determination of the substrates and products and monitoring of the reaction were accomplished by thin layer chromatography (TLC) on silica gel polygram SIL/UV 254 plates. The FTIR spectra were run on a Shimadzu FTIR-8300 spectrophotometer. The ¹H-NMR (250 MHz) and ¹³C-NMR (62.5 MHz) were recorded on a Bruker Advanced DPX instrument. Melting points were recorded on a Büchi B-545 apparatus (Switzerland) in open capillary tubes.

Preparation of different cross-linked polyacrylamides (I)

Cross-linked polyacrylamide (Scheme 1) was synthesized by the free-radical precipitation polymerization technique using *N,N'*-methylene bisacrylamide (NNMBA) as a cross-linking agent.^{26,28} As an example for the preparation of 5 % cross-linked polyacrylamide, acrylamide (5.00 g, 69.0 mmol) and (NNMBA) (0.56 g, 3.6 mmol) were dissolved in ethanol (40 mL). Potassium persulfate (0.017 g, 0.070 mmol) was added as an initiator and the mixture was heated at 75–80 °C under stirring for 7 h. The polymer was collected by filtration, washed several times with ethanol and dried under vacuum at 50 °C. A white powder was obtained in almost quantitative yield. The same procedure was repeated for the preparation of 2, 10, 15 and 20 % cross-linked polyacrylamides using 0.22, 1.18, 1.85 and 2.66 g of NNMBA, respectively.



Scheme 1. Cross-linked polyacrylamide synthesis route.

Incorporation of (3-diethylamino-1-propylamine) function onto cross-linked polyacrylamide

In a round bottomed flask, excess 3-diethylamino-1-propylamine (35 mL) was added to 5 % cross-linked polyacrylamide **(I)** (5.00 g). The reaction mixture was stirred at room temperature to allow complete swelling of the polymer by the diamine. The reaction mixture was then heated at 100 °C for 5 h. The aminated gel was filtered and washed with sodium chloride solution (0.1 M) many times; it was then washed with water and ethanol. The product was dried under vacuum at 60 °C to give the aminated resin **(II)** in 42 % yield (7.25 g).

Incorporation of chlorochromate function onto the aminated cross-linked polymer

In a round bottomed flask, chromium trioxide (4.50 g, 45.0 mmol) was added to aminated cross-linked polymer **(II)** (5.00 g) suspended in HCl (50 mL, 1 M). The mixture was stirred in an ice bath for 4 h and filtered. The brown beads were filtered off and washed extensively with acetone until the filtrate was clear. The resin was then dried under vacuum (60 °C, 5 h) in the presence of CaCl_2 to give a stable brown powder **(III)**. The capacity of this resin was determined by the iodometric titration method to be 1.64 mmol $\text{CrO}_3 \text{ g}^{-1}$ polymeric reagent, which was in agreement with the value of 1.58 obtained by the atomic absorption technique.²⁹

Determination of capacity of 5 % cross-linked polymer (III) by atomic absorption technique

A series of standards containing 0.00, 0.90, 1.50, 3.00, 4.50, 6.00, 7.50, 9.00 ppm of CrO_3 (with respect to Cr) were prepared in water and their atomic absorptions were determined (Fig. 1). To a solution of potassium hydroxide (0.40 g) in water (10 mL) was added polymeric reagent **(III)** (0.08 g), which was then stirred for 12 h. The mixture was filtered and

washed with distilled water several times. Activated carbon black was added to the combined filtrates and the mixture was stirred for 20 min at 40 °C. Then, the mixture was filtered and washed with distilled water. The solution of the combined filtrates was diluted to 500 mL in a volumetric flask; then 10 mL of this solution was diluted to 250 mL. Atomic absorption spectroscopy of the final solution with respect to chromium gave an absorbance value of 1.014 using the calibration curve (Fig. 1). The capacity of the reagent was determined to be 1.58 mmol of CrO₃ per gram of the reagent.

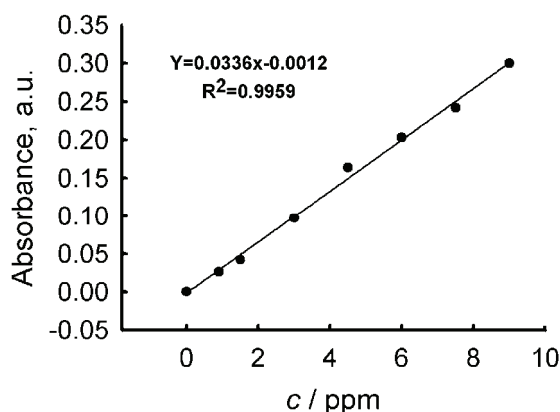


Fig. 1. Calibration curve for the atomic absorption spectroscopy method.

General procedure for the oxidation of organic compounds with the 5 % cross-linked polymer (III)

In a round bottomed flask (25 mL), a mixture of the organic compound (1.00 mmol) and polymeric reagent (III) (2.00–4.00 mmol, based on the molar ratio of oxidant to substrate) in cyclohexane or *n*-hexane (10 mL) was stirred at room temperature for an appropriate time. The progress of the reaction was followed by TLC. When the reaction was completed, the resin was filtered off and washed twice with solvent. Evaporation of the combined filtrates afforded pure products (in the few cases when the reaction did not go to completion, the crude product was purified on a silica gel plate with an appropriate eluent).

Regeneration of the 5 % cross-linked polymer (III)

The spent polymeric reagents obtained from different oxidation reactions were combined and washed thoroughly with CH₂Cl₂ to remove any residual soluble organic substrate or product; then it was washed with HCl (1 M) until the filtrate was colorless, neutralized with NaOH (1 M), washed with water and acetone and finally vacuum dried. The polymer (10.00 g) was suspended in HCl (100 mL, 1 M) for 0.5–1.0 h, chromium trioxide (9.00 g) added and the mixture stirred for 4.0 h at 0 °C. It was filtered and washed with acetone until the filtrate was clear. The obtained polymer was dried under vacuum (50 °C) in the presence of CaCl₂ overnight. The capacities of the regenerated resins were determined as described previously.

RESULTS AND DISCUSSION

Copolymers of acrylamide with NNMBA as a cross-linking agent (2, 5, 10, 15 and 20 %) were prepared by free-radical precipitation polymerization using potassium persulfate as the initiator (Scheme 1). White polymers were obtained as irregularly-shaped amorphous particles. The IR spectra of the polymers showed

characteristic absorptions of amide (N–H), and carbonyl groups at 3421 and 1666 cm^{-1} , respectively (Fig. 2).

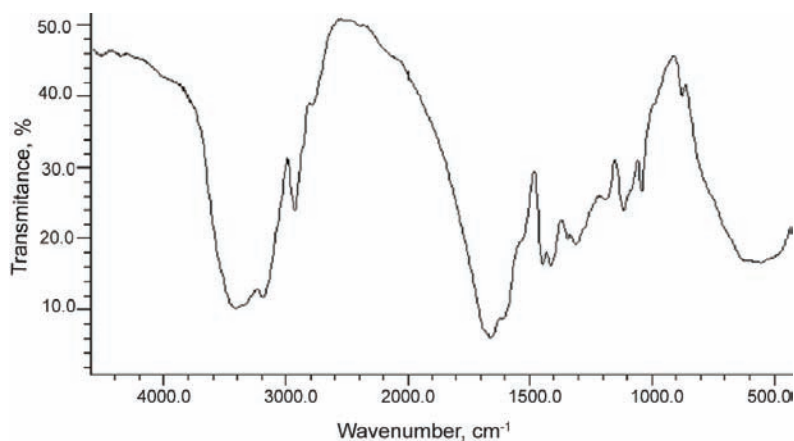


Fig. 2. FTIR spectrum of **I**.

Poly[*N*-3-(diethylamino)propyl] acrylamides (**II**) with different degrees of cross-linking were prepared by transamidation reaction of excess 3-diethylamino-1-propylamine with the polyacrylamides having different degrees of cross-linking (Scheme 1). The amino polymer exhibited strong absorption bands at 3202 and 3329 cm^{-1} (N–H stretching), 1655 cm^{-1} (C=O amide stretching) and 1528 cm^{-1} (N–H amide bending) (Fig. 3). The average amine value (4.70 mmol amine g^{-1} of polymer) was calculated by the back acid–base titration method. It was noticed that as the proportion of the cross linking agent increased, the capacity of the polymer decreased because of the highly cross-linked network structure.

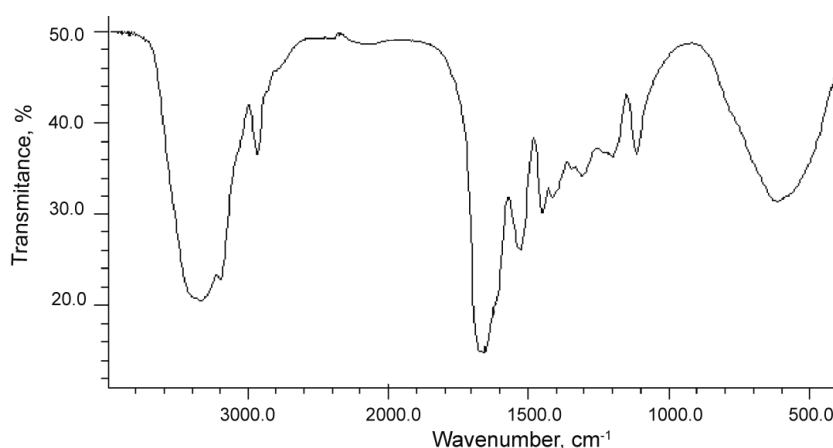


Fig. 3. FTIR spectrum of **II**.

Polymeric oxidizing agents containing chlorochromate (**III**) were prepared very easily by addition of chromium(VI) oxide to a suspension of the cross-linked poly[*N*-3-(diethylamino)propyl] acrylamides in dilute HCl (Scheme 1). The presence of the chlorochromate anion in the oxidizing agents was confirmed by their IR spectra, showing bands at 945 and 769 cm^{-1} , which are characteristic peaks for the chromate anion (Fig. 4). Capacity of the polymeric oxidizing agent (5 % cross-linked) was measured easily by titration with an appropriate reducing agent ($\text{S}_2\text{O}_3^{2-}$) and by atomic absorption spectroscopy. The obtained values were 1.64 and 1.58 $\text{mmol Cr(VI) g}^{-1}$ polymeric reagent, respectively.

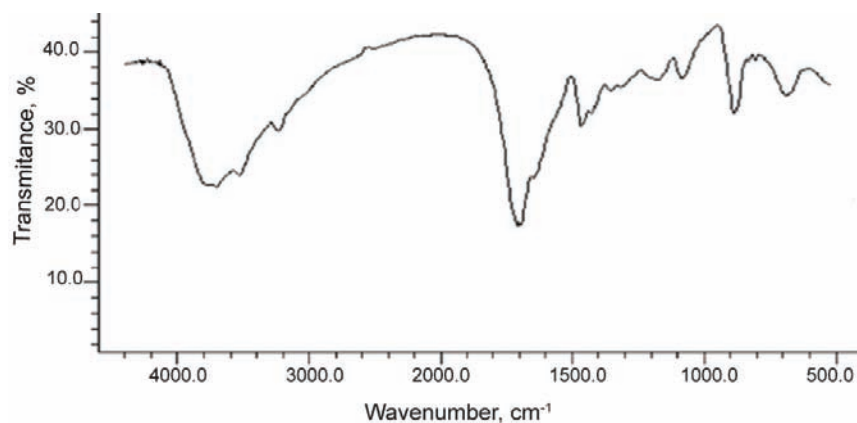


Fig. 4. FTIR spectrum of **III**.

As a model, the oxidation reaction of benzyl alcohol with the polymeric reagents having different percentage crosslinking was performed in cyclohexane at room temperature (Table I). The best results were obtained using the gel-like 2 % cross-linked polymer, which was difficult to handle however; thus the 5 % cross-linked sample was chosen for the general study, due to its better stability.

TABLE I. Oxidation of benzyl alcohol with polymer **III** of different degrees of cross-linking in cyclohexane (molar ratio of polymeric oxidant to substrate was 2:1; wet polymer was used; conversion in all cases was 100 %)

Entry	Content of III in polymer %	Average capacity of polymer mmol g^{-1}	Time, h
1	2	1.80	2.5
2	5	1.64	3.0
3	10	1.10	4.0
4	15	1.04	4.5
5	20	0.81	5.0

The choice of solvent in organic reactions using polymeric reagents is extremely important. A solvent should be chosen in which the insoluble polymeric

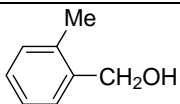
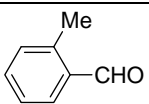
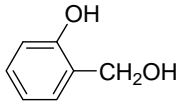
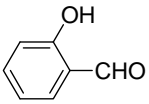
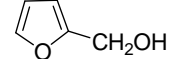
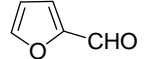
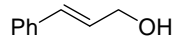
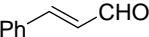
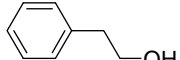
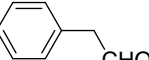
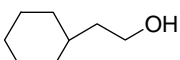
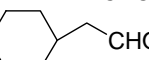
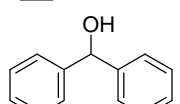
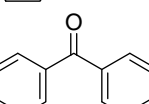
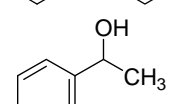
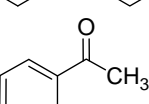
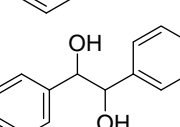
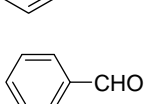
oxidizing agent swells well. The effect of solvent on the oxidation reaction showed that less polar solvents gave the best results. For the oxidation reaction, cyclohexane and *n*-hexane were the best solvents compared to toluene, ethyl acetate, CH₃CN, THF, CHCl₃ and H₂O. This is probably due to the higher compatibility of these two solvents with the polymeric reagent and the substrates. The polymeric oxidant was insoluble in the reaction media and the chromium ions remained firmly bound to the insoluble polymer support after the oxidation reaction, which was confirmed by atomic absorption spectroscopy (chromium ions were not observed in reaction solvent after filtration). This advantage is one of the advantages of this polymeric reagent over monomeric chromium(VI)-based oxidants.

The generality of this polymeric oxidant was tested for different alcohols (Table II) and other functionalities (Table III). The oxidant was capable to convert primary and secondary alcohols to their corresponding aldehydes and ketones. Over-oxidation of the products to carboxylic acids was not observed. Electron donating groups increased the rate of conversion. Aliphatic alcohols had a low yield so the oxidant could oxidize selectively benzylic alcohols in the presence of aliphatic alcohols.

TABLE II. Oxidation of benzylic alcohols with 5 % cross-linked polymer **III** (these reactions were carried out in cyclohexane at r.t.; wet polymer was used; molar ratio of polymeric oxidant to substrate was 2:1)

Entry	Substrate	Product	Time, h	Yield, %
1			3	90
2			6	80
3			6	70
4			10	45
5			4	90
6			4	85
7			4	92

TABLE II. Continued

Entry	Substrate	Product	Time, h	Yield, %
8			5.5	85
9			5	92
10			5	95
11			12	80
12			20	85
13			10	40
14			3.5	90
15			3	95
16 ^a			3	93

^aMolar ratio of polymeric oxidant to substrate was 3:1

Aldoximes, ketoximes, and silylethers were oxidized to their corresponding aldehydes and ketones without over-oxidation in good to high yields. Deoxygenation of oximes required a long reaction time compared to the oxidation of alcohols. The oxidation of thiols to their corresponding disulfides was performed easily by this polymeric reagent. The oxidation of *p*-hydroquinone, benzylamine, and benzoin were also investigated.

The oxidant was not able to oxidize α -hydroxyl carboxylic acids, toluene, naphthalene, epoxides and sulfides. Hence, hydroxyl compounds, oximes, silylethers and thiols can be selectively oxidized in the presence of these functional groups.

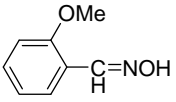
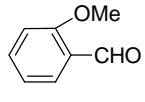
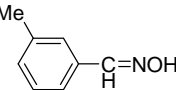
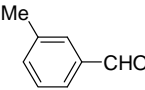
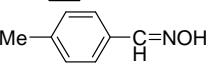
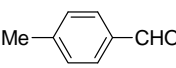
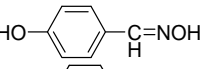
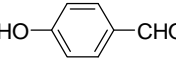
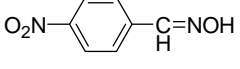
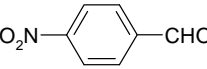
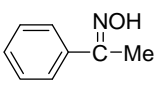
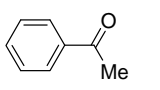
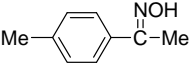
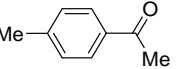
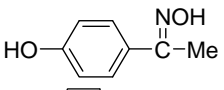
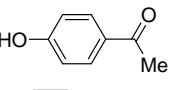
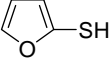
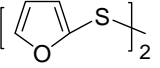
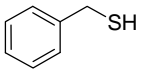
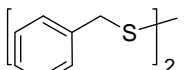
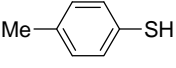
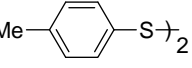
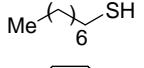
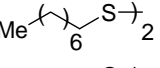
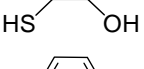
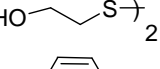
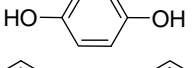
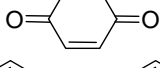
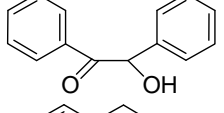
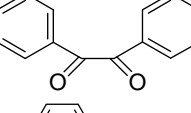
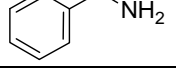
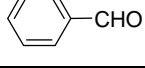
Regenerability and reuse of the spent polymeric reagent is one of the main advantages in the use of this polymeric reagent. The reagent could be recycled at least three times (Table IV). There was a small decrease in the capacity of the

resins after each regeneration, which might have been caused by mechanical degradation of the polymeric reagent.²² This polymeric reagent can be stored several months without loss of its activity.

TABLE III. Oxidation of other organic compounds with 5 % cross-linked polymer (III); these reactions were realized in cyclohexane at room temperature; wet polymer was used

Entry	Substrate	Product	Time, h	Yield, %
1 ^a			4.5	93
2 ^a			4.0	90
3 ^a			4.5	82
4 ^a			5.5	95
5 ^a			7.0	90
6 ^a			7.0	93
7 ^a			5.0	90
8 ^a			6.0	85
9 ^a			5.0	73
10 ^a			5.0	78
11 ^b			10.0	90
12 ^b			8.0	75

TABLE III. Continued

Entry	Substrate	Product	Time, h	Yield, %
13 ^b			9.0	78
14 ^b			11.0	75
15 ^b			10.0	82
16 ^b			8.0	95
17 ^b			10.0	40
18 ^b			10.0	90
19 ^b			9.0	90
20 ^b			12.0	70
21 ^c			5.0	85
22 ^c			1.0	95
23 ^c			5/6	92
24 ^d			9.0	50
25 ^d			9.0	10
26 ^a			45/60	96
27 ^a			8.0	60
28 ^a			5.0	75

^aMolar ratio of polymeric oxidant to substrate was 2:1; ^bMolar ratio of polymeric oxidant to substrate was 4:1 and reactions were realized in *n*-hexane at r.t.; ^cMolar ratio of polymeric oxidant to substrate was 3:1; ^d% conversion and molar ratio of polymeric oxidant to substrate was 3:1

TABLE IV. Capacity of the polymeric reagent after regeneration

Number of regenerations	Capacity of polymer, mmol g ⁻¹
1	1.30
2	1.15
3	0.92

A comparison of the efficiency of the presented polymeric reagent (**III**) with a number of other reported polymeric oxidants based on chromium(VI) is given in Table V. The polymeric reagent (**III**) is more efficient in the oxidation of 1-phenylethanol than most of the other reagents.

TABLE V. Comparison of the efficiency of **III** with those of different chromium(VI)-based polymeric oxidants in the oxidation of 1-phenylethanol

Entry	Oxidizing agent	Time, h	Molar ratio	Yield, %
1 ^a	III	3	2/1 (r.t)	95
2 ^a	ref. 15	3.5	4.5/1 (reflux)	69 ^d
3 ^a	ref. 16	5	1.1/1 (reflux)	89 ^d
		24	1.1/1 (reflux)	>99 ^d
4 ^a	ref. 17	12.5	2/1 (reflux)	91
5 ^b	ref. 22	44	5/1 (reflux)	96
6 ^c	ref. 30	25/60	1/1 (reflux)	95

^aReactions were realized in cyclohexane; ^b reaction was realized in chloroform; ^c reaction was realized in toluene; ^d% conversion

CONCLUSIONS

In conclusion, this modified polyacrylamide-supported chlorochromate is a useful oxidant for the oxidation of different organic compounds, such as hydroxyl compounds, silylethers, oximes, thiols, *etc.* Over oxidation of the products was not observed with this oxidizing agent. It was able to oxidize the aforementioned functional groups in the presence of α -hydroxyacids, benzylic acids, epoxides, sulfides, aldehydes and double bonds. The handling and use of this heterogeneous reagent is environmentally safer than its monomeric soluble counterparts. The mild reaction conditions, stability, selectivity, good to excellent yields of the products, simple recovery of the reaction products and regenerability of the reagent make this heterogeneous polymeric oxidizing agent useful in organic synthesis. The reagent can be stored for months without any loss in its activity.

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ИЗВОД

ПОЛИАКРИЛАМИД МОДИФИКОВАН ДИЕТИЛПРОПИЛАМОНИЈУМ-ХЛОП-ХРОМАТОМ – НОВИ ПОЛИМЕРНИ ОКСИДАЦИОНИ АГЕНС

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Полимерни носач, на бази умреженог полиакриламида, модификован диетилпропил-амонијум-хлорхроматом, показао се као веома ефикасан реагенс за оксидацију различитих органских једињења: алкохола, силелетра, оксима, тиола, итд. У реакцијама оксидације алкохола, производи оксидације су били алдехиди или кетони, и није се одвијала даља оксидација алдехида у карбоксилне киселине. Оксидациони агенс је нерастворан у реакционој средини, а хром(VI) јони остају везани за полимерну матрицу и након реакције оксидације. Предности овог новог полимерног оксидационог реагенса, диетилпропиламонијум-хлорхромата, су: благи реакциони услови, једноставан начин и кратко време извођења реакције оксидације, као и једноставна и лака регенерација реагенса.

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