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Chemical modification of macroreticular 2-Hydroxyethyl methacrylate – Ethylene dimethacrylate copolymers

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SUMMARY

Several chemical modifications of commercial macroreticular 2-hydroxyethyl methacrylate-ethylene dimethacrylate copolymers are described. The derivatives containing pendant imidazole, primary amino groups and complexon (EDTA and DTPA) groupings as well as oligo(N-acetyliminoethylene) and oligo-(iminoethylene) grafts were prepared.

INTRODUCTION

Poly(2-hydroxyethyl methacrylates) containing primary alcoholic groups are reactive polymers and, by chemical transformations of their hydroxy groups, many new polymers with various functional groups can be prepared (1). Strongly cross-linked macroreticular copolymers of 2-hydroxyethyl methacrylate (HEMA) and ethylene dimethacrylate (EDMA) are known under the commercial generic name Spheron ® (Lachema Brno) and Separon ® HEMA (Laboratory Instrument Works Prague). They themselves and their derivatives are used as sorbents, carriers of biologically active substances and ion exchangers for various types of chromatography. In this paper several chemical modifications of HEMA-EDMA copolymer leading to new potentially useful derivatives are described.

EXPERIMENTAL

Materials

HEMA-EDMA, macroreticular copolymer 2-hydroxyethyl methacrylate-ethylene dimethacrylate (Separon ® HEMA 300 or 1000, Laboratory Instrument Works, Prague), grain size 180-315 μm or 400-630 μm. Alkylating derivatives of HEMA-EDMA (1): 1a tosylated macroreticular copolymer HEMA-EDMA was prepared by the reaction of HEMA-EDMA (9 g) with p-toluenesulfochloride (10.2 g) in anhydrous pyridine (20 ml). The mixture was shaken at laboratory temperature for 10 hours. The product was filtered off and washed with water and methanol. S content 5.45%; 1b brominated macroreticular copolymer HEMA-EDMA (Spheron ® 1000-Br, Lachema Brno), Br content 25.86%; 1c 2,3-epoxypropy-

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lated macroreticular copolymer HEMA-EDMA (Separon® HEMA-E_{max}, Laboratory Instrument Works Prague), grain size 15-25 μm, epoxy group content 1.2 mmol/g. 2-Methyloxazoline was prepared according to the literature (2), b.p. 109.5-110.5°C, assay (GLC) 99.11%. Oligo(N-acetyliminoethylene), MW 1500, m.p. 100-120°C, N content 15.38%, was obtained as a byproduct in grafting experiments (see further). Oligo(iminoethylene) was prepared by hydrolysis of oligo(N-acetyliminoethylene) with dilute hydrochloric acid (1:1) according to ref. (3). Branched polyethylenimine, 50% aqueous solution (Polymin P, BASF).

All starting and product polymers were dried in the vacuum of a water pump at 50-60°C.

Imidazole derivatives of HEMA-EDMA

A mixture of 2 g of 1 and 25 ml of methanolic solution of the sodium salt of imidazole (prepared from 0.46 g Na, 25 ml anhydrous methanol and 1.85 g imidazole) was heated under stirring to 80°C for 8 hours. The product was extracted with boiling methanol for 12 hours and dried in vacuo at 50°C. The products obtained from 1a and 1b contain 2.48 and 3.15% N, i.e. 0.9 and 1.13 mmol of bound imidazole/g, respectively.

Derivatives of HEMA-EDMA with primary amino groups

1 g of 1 was swollen in 15 ml chloroform and heated with a solution of 2 g hexamethylenetetramine in 15 ml $CHCl_3$ at 70°C for several hours. The polymer was then washed with hot $CHCl_3$ and dried in vacuo. 0.2 g of the hexamethylenetetraminium salt formed was hydrolyzed by boiling 6 hours with 20 ml of ethanolic hydrochloric acid (3:1 by vol.). The product was washed with water and methanol. NH_2 groups were detected in the product by a colour reaction with sodium 2,4,6-trinitrobenzenesulfonate. The products obtained from 1a and 1b contain 2.57 and 2.27% N, i.e. 1.8 and 1.6 mmol NH_2/g, respectively. The corresponding hexamethylenetetraminium salts contain 5.08 and 9.10% N, respectively.

Oligo(N-acetyliminoethylene)-grafted HEMA-EDMA

Before the reaction, 1 was swollen in a five-fold excess of 2-methyloxazoline for 24 hours. The reaction was performed in a glass ampoule at 80°C under continuous shaking for 50 hours. In the reaction, the homopolymer of 2-methyloxazoline was also formed which was separated from the grafted polymer by dissolution in methanol. The grafted polymer was extracted with methanol in a Soxhlet apparatus for 12 hours.

Oligo(iminoethylene)-grafted HEMA-EDMA

- by hydrolysis of oligo(N-acetyliminoethylene)-grafted HEMA-EDMA: The hydrolysis was performed with concentrated or dilute (1:1) hydrochloric acid at boil for 48 hours, or with 50% aqueous NaOH at 100°C for 48 hours. In both cases, the hydrolysis products showed a distinctly lower IR absorption of acetyl groups;

- by reaction of oligo(iminoethylene) with 1: A mixture of 2 g

Table 1. Nitrogen content (%) in grafted HEMA-EDMA polymers

Starting polymer	Graft			
	$(NAcCH_2CH_2)_n$[a]	hydrolyzed $(NAcCH_2CH_2)_n$	$(NHCH_2CH_2)_n$	PEI[b]
1a	9.07	8.55[c]	2.39	5.09[d]
1b	10.50	-	4.45	-
1c	1.03	-	2.71	4.49

[a] Strong IR absorption of acetyl group at 1640 cm^{-1}. [b] Polyethyleneimine. [c] Acid hydrolysis, chelating capacity 58.4 mg Cu^{++}/g. [d] Chelating capacity 13.1 mg Cu^{++}/ml.

oligo(iminoethylene) in 50 ml 1-propanol and 0.3 g of 1 previously swollen in 1-propanol was heated under shaking in a glass ampoule at 75°C for 24 hours. The product was extracted with boiling methanol for 10 hours;

- by reaction of polyethyleneimine with 1: A mixture of 7.2 g Polymin P and 1 g of 1 was heated to 100°C for 24 hours. The product was washed with hot water.

The characteristics of all the products are given in Table 1.

Ethylenediaminetetraacetic acid ester of HEMA-EDMA

A mixture of 17 g HEMA-EDMA, 450 ml anhydrous pyridine and 37.5 g EDTA dianhydride was heated under stirring at 75°C for 24 hours. The reaction mixture was diluted with water, the polymer was filtered off and successively washed with the filtrate and water. N content 3.53% N, total exchange capacity 1.1 mmol Cu^{++}/g. Diethylenetriaminepentaacetic acid ester of HEMA-EDMA was prepared in a similar way.

RESULTS AND DISCUSSION

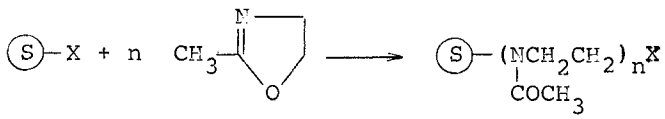
We have synthesized several new derivatives of macroreticular HEMA-EDMA copolymer (denoted (S)—OH in the equations): with imidazole, primary amino groups and complexon groupings, as well as with oligo (N-acetyliminoethylene) and oligo(iminoethylene) grafts.

Polymer-immobilized imidazoles are already known, with polystyrene used as the matrix. The hydrophobic nature of the polymer may be inconvenient in some cases. This is why other carriers were sought. Imidazole moieties had already been introduced in HEMA-EDMA, via the corresponding glycidyl derivative (4). An alternative method based on the alkylation of imidazole with an alkylating derivative of HEMA-EDMA is described in this paper. By employing this method, an imidazole content up to 1.1 mmol/g was reached.

A derivative of HEMA-EDMA containing primary amino groups may be an important intermediate. Its synthesis via azide derivative has been described in the literature (5). The syn-

thesis of the polymeric primary amine by the Delépine reaction, i.e. by the alkylation of hexamethylenetetramine and subsequent hydrolysis of the hexamethylenetetraminium salt formed which is described here seems to be simpler. In this way, products containing up to 1.8 mmol NH_2/g were obtained.

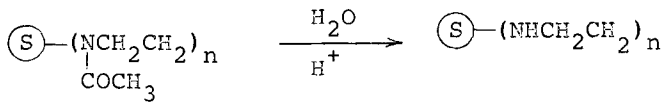
We grafted oligo(N-acetyliminoethylene) chains on HEMA-EDMA by the cationic oligomerization of 2-methyloxazoline initiated with polymer alkylating groups



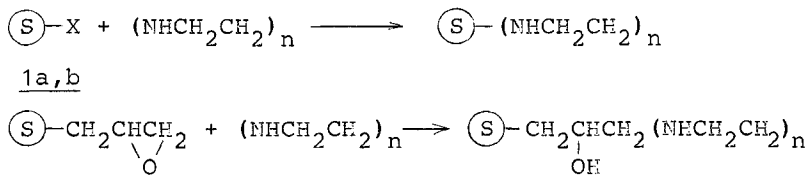
1a,b (X=Br,OTs)

In this way products with the average DP of grafts (n) up to 10 and with the N-acetyliminoethylene group content up to 5.4 mmol/g were obtained. These groups are very polar by nature and actually model the active moiety of well-known dipolar aprotic solvents, i.e., dimethylformamide and/or diethylacetamide. Therefore, it is not surprising that HEMA-EDMA polymers containing these moieties are adequately active as phase-transfer catalysts in alkylation reactions (6). In addition to this, they also possess some interesting properties as sorbents in the gas chromatography of polar substances (7).

Acid hydrolysis of oligo(N-acetyliminoethylene) grafts on HEMA-EDMA gives products containing iminoethylene groupings, but the hydrolysis of acetyl groups is not complete (8).



Due to iminoethylene groupings, the products of hydrolysis possess chelating properties for heavy metals, such as Cu and Ni. Similar products were obtained by the reaction of alkylating derivatives of HEMA-EDMA with linear oligo(iminoethylenes) (prepared by the acid hydrolysis of oligo(N-acetyliminoethylene)) and by the reaction with branched polyethylenimine (9).

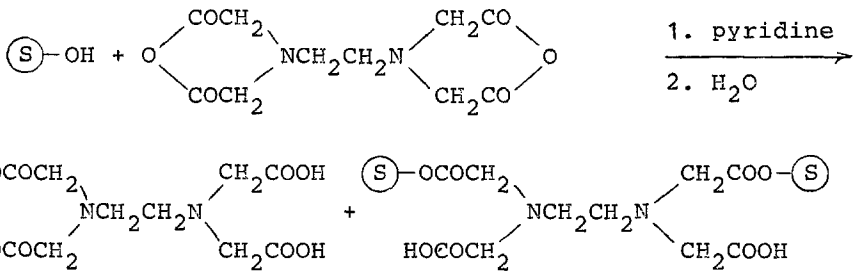


1a,b

1c

HEMA-EDMA polymers containing multidonor chelating groupings may be of some importance. In the patent literature only iminodiacetic acid derivatives have been described (10). Com-

plexon polymers based on HEMA-EDMA are described here. We have obtained polymeric complexon esters by the reaction of hydroxy groups of HEMA-EDMA with complexon dianhydrides, e.g. the EDTA ester (11)



The products contain up to 1.6 mmol bound EDTA/g. Similarly, diethylenetriamine pentaacetic acid esters can also be obtained (12). Complexon esters of HEMA-EDMA form stable chelates with the same metal ions and under the same conditions as analogous low-molecular complexons - EDTA and DTPA. The complexon esters are relatively stable in an acid and neutral aqueous medium, while in alkaline solutions they are rapidly hydrolyzed (13).

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