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Modified Copolymers Dextran-*graft*-Polyacrylamide

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The peculiarities of the alkaline hydrolysis of graft copolymers dextran-polyacrylamide with different molecular weights of the main polysaccharide and long grafted chains are studied by the potentiometric titration method. It is established that the degree of copolymers modification depends on the conformation of grafted polyacrylamide chains.

Keywords: alkaline hydrolysis; graft copolymer; polyacrylamide; structure

INTRODUCTION

Modified polymers can be obtained by a post-modification of materials which are difficult to be synthesized by the direct polymerization of the corresponding monomers. For example, partially hydrolyzed polyacrylamide having a better flocculating behaviour than polyacrylamide (PAM) itself [1] can be prepared by hydrolysis easily enough. It was pointed by Singh [2–5] that the graft copolymers based on polysaccharides and polyacrylamide exhibit much better flocculation characteristics than the conventional polysaccharide and synthetic polymer-based flocculants. Obviously, these systems should be very interesting due to the possibility of obtaining different samples with

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partially hydrolyzed grafted chains. With hydrolysis, the polyacrylamide chains acquire the polyelectrolyte character, because $-\text{CONH}_2$ groups of PAM chains are converted to $-\text{COOH}$ groups [6]. As a result, two adjacent negatively charged groups repel each other, so the chain will be expanded and straightened. However, the influence of the intramolecular structure of graft copolymers on the degree of transformation during alkaline hydrolysis has not been investigated till now.

The aim of the present work is the investigation of the effect of copolymer molecular structure on the alkaline hydrolysis for graft copolymers based on Dextran and Polyacrylamide.

EXPERIMENTAL

1. Polymer Sample Preparation

The ceric-ion-induced redox initiation method was used for the synthesis of graft copolymers Dextran-*graft*-Polyacrylamide (D-g-PAA) [7]. Dextrans with different molecular weights were purchased from Serva (Sweden), whose characteristics as given by the manufacturer are $M_w = 2 \times 10^4$ (designated as D20 throughout) and $M_w = 7 \times 10^4$ (designated as D70 throughout). A quantity of acrylamide monomer and the ratio of the molar concentrations of Ce(IV) ions (initiator) and dextran was kept constant for obtaining copolymers with the same number of grafts of comparable lengths.

These samples were freeze-dried after the synthesis and kept under vacuum for preventing them from hydrolysis. Potentiometric titration curves obtained for distilled water and for the copolymer solutions were the same. We can, therefore, conclude that the degree of hydrolyzation of the PAA moiety in the nascent copolymers is virtually zero.

Alkaline hydrolysis of graft copolymers samples was performed as follows: 2 g of D-g-PAA was dissolved in 200 cc of distilled water, and then the required amount of NaOH was added to it. The mixture was placed in a thermostated water bath at 50°C. At the end of the required reaction time (in 15, 30, and 60 min), the probes were precipitated by acetone and freeze-dried.

2. Experimental Methods

Potentiometry

The potentiometric titration was performed using a pH meter pH-340 (Russia), using a combined glass electrode. We used HCl (0.2N) as a titrant, and the polymer concentration was 0.2 g/dl. The measurements were made at 25°C under nitrogen, with constant stirring.

TABLE 1 Graft Copolymer Molecular Parameters Determined by Self-Exclusion Chromatography (SEC), Light Scattering (LS) and Viscometry Methods in Water

Sample	M_w (SEC)	M_w/M_n (SEC)	R_z , nm (SEC)	M_w (LS)	A_2 , cm^3/g (LS)	R_z , nm (LS)	$[\eta]$, dl/g
D20-g-PAA	6.9×10^6	1.81	167	5.2×10^6	5.3×10^{-4}	182	8.5
D70-g-PAA	4.7×10^6	1.65	162	3.2×10^6	3.7×10^{-4}	168	8.3

FTIR Spectroscopy

The FTIR spectra were obtained on a Nicolet NEXUS-475 (USA) spectrophotometer in the range $4000\text{--}400\text{ cm}^{-1}$ using thin copolymer films ($l = 6\text{--}9\ \mu\text{m}$). The films were cast from aqueous solutions.

RESULTS AND DISCUSSION

The results of characterization of the D-g-PAA samples [7] are presented in Table 1.

The values of the weight-averaged molecular weights are in rather good agreement with those derived from light scattering. Also, these samples possess a relatively low-molecular weight polydispersity.

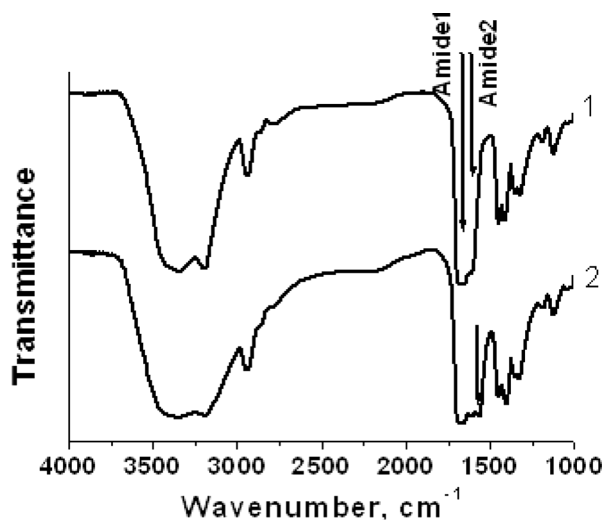


FIGURE 1 FTIR spectra of nonionic (1) and modified (2) D20-g-PAA samples (30 min of alkaline hydrolysis).

The value of the second virial coefficient A_2 reveals that the D-g-PAA samples are dispersed to individual molecules in a water solution.

Saponification of samples was carried out by alkaline hydrolysis. During hydrolysis, the $-\text{CONH}_2$ groups of PAA chains are converted to $-\text{COONa}$ groups according to the scheme

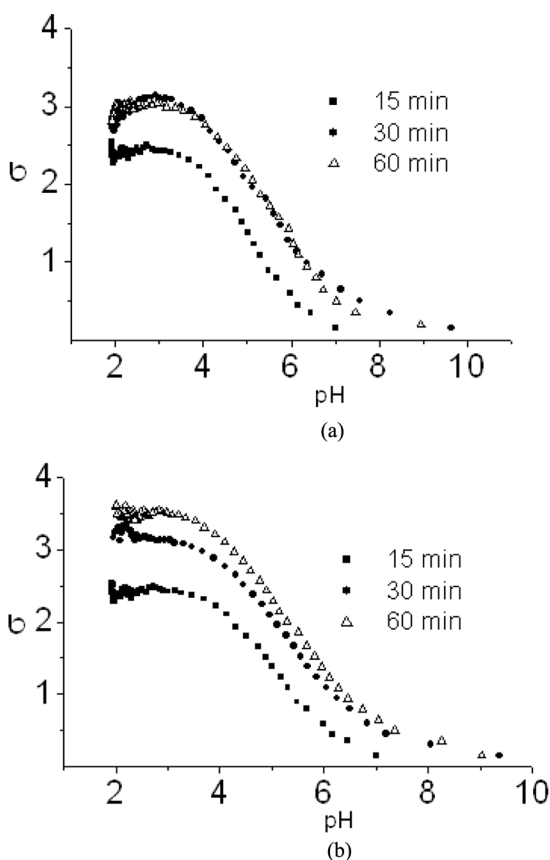
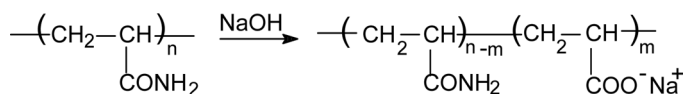


FIGURE 2 Dependence of the H^+ absorbance degree on pH for modified D20-g-PAA samples (a) and D70-g-PAA (b) in 15, 30, and 60 min of alkaline hydrolysis.

The FTIR spectra for nonionic and modified samples of D20-g-PAA are presented in Figure 1. A significant difference is observed between nonionic and modified samples. Additionally to the amide 1 ($1650\text{--}1660\text{ cm}^{-1}$, CO stretching) and amide 2 (1615 cm^{-1} , NH bending) regions [8], the peak at 1570 cm^{-1} (COO^- stretching) appears for saponified D-g-PAA samples [9]. This indicates that, under the saponification conditions, a part of the acrylamide moiety is converted into acrylate. Figure 2 (a, b) show the dependence of the extent of H^+ ion absorbance (σ) on pH for the different times of saponification. For D20-g-PAA, the degree of H^+ ion absorption achieves a maximum in 30 min and doesn't change afterwards, but continues to increase for D70-g-PAA. The degree of conversion, α , of amide groups to acrylate groups versus the time of hydrolysis is shown in Figure 3. In our opinion, this reflects the different initial molecular structures of the nonionic copolymers D20-g-PAA and D70-g-PAA, because the degree of conversion during the process of saponification will depend on the accessibility of a saponifier to the functional groups which can be hydrolyzed. Thus, the density of macrocoil structures affects a degree of copolymer hydrolysis. The intramolecular structure of D-g-PAA defines the mutual position of grafted polyacrylamide chains on the dextran backbone and their conformation in the solution. According to the synthesis conditions, the number of grafts in these copolymers should be the same. For D20-g-PAA, the grafted chains have extended worm-like conformation [7]. For D70-g-PAA, the grafts are highly extended close to its tethering points and more random far from the dextran backbone [7]. The space available to one graft is a cone, whose solid angle is related to the distance between adjacent grafts.

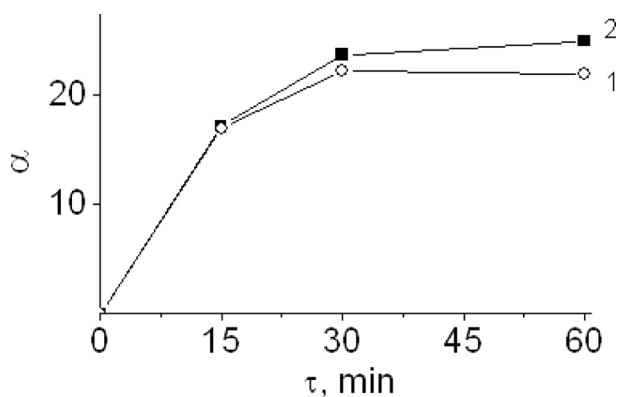


FIGURE 3 Effect of the hydrolysis time on the conversion (α) of amide to carboxylate groups in the graft copolymers. (1)- D20-g-PAA, (2)- D70-g-PAA.

Namely, the larger the distance, the larger is the cone solid angle [7]. As a result, the functional groups of grafted PAA chains are more accessible.

CONCLUDING REMARKS

Thus, we have investigated the alkaline hydrolysis of graft copolymers Dextran-g-Polyacrylamide with different lengths of the polysaccharide chain and long grafts. It is shown that the intramolecular structure, namely the conformation of the grafted polyacrylamide chains, affects the kinetics of hydrolysis and the degree of conversion of amide groups.

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