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Intramolecular Polycomplexes Formed by Dextran-Grafted Polyacrylamide: Effect of the Components Molecular Weight

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Summary: Graft copolymers of Polyacrylamide-*g*-Dextran were synthesized using ceric-ion-initiated solution polymerisation technique. It is shown that the macromolecular parameters of these copolymers and their molecular structure strongly depend on the molecular weight of the Dextran part.

Keywords: dextran; graft copolymer; intramolecular bond; polyacrylamide

Introduction

Graft copolymerisation is one of the techniques employed for modifying the chemical properties of polymer. In the last decade in-depth study has been made on the synthesis and application of graft copolymers based on natural and synthetic polymers as these copolymers are very efficient flocculants [1]. A number of copolymers have been synthesized by grafting polyacrylamide (PAA) onto starch [2], carboxymethyl cellulose [2], guar gum [3], xanthan gum [4], and s.o.. It was concluded that by grafting flexible PAA chains onto the polysaccharide backbone, it is possible to develop efficient, shear-stable polymers for treatment of industrial effluents and for mineral processing. So far, systematic characterization of such copolymers is missing, although its knowledge is very important for understanding the mechanism involved in the capture of pollutants. Clearly, the copolymer microstructure will have a direct bearing upon the final properties.

This paper is devoted to the synthesis and the characterization of water-soluble graft copolymers based on Dextran and Polyacrylamide. These systems should be interesting due their propensity to form hydrogen bonds between the main and the grafted chains as well as between grafts leading to various and unusual inter and intramolecular structure [5].

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Experimental

Dextran (Leuconostoc) with characteristics: M_w=500 000 g/mol (D500) was obtain from Fluka. Dextrans with characteristics: M_w=20 000 g/mol (D20) and M_w=70 000 g/mol (D70) were obtain from Serva (Sweden). Ammonium cerium (IV) nitrate (CAN) from Aldrich (USA) was used as initiator. Acrylamide (AA) was obtain from Reanal (Hungary). It was recrystallized from chloroform and dried under vacuum at room temperature for 24 h.

Synthesis of Dextran-graft –Polyacrylamide copolymers

0.02 mmol of Dextran was dissolved in 100 ml of distilled water. The contents of the flask were stirred and bubbled with argon gas for 20 min to remove the dissolved oxygen. Then, 0.12 mmol of CAN in 4 ml of 0.125 N HNO_3 was added to reaction mixture and allowed to react for 10 min, followed by the addition of calculated amount of AA. The polymerisation proceeded under argon atmosphere generally for 24 h. At the end of the reaction, the polymer was precipitated by adding an excess of acetone, dissolved in water again and then freeze-dried.

The elemental analysis of all samples was carried out for the four elements, i.e. carbon, hydrogen, oxygen and nitrogen.

The FT-IR spectra were obtained by Spectrophotometer Nicolet NIXUS-475 (USA) in the range 4000-400cm^{-1} using KBr pellets.

H^1 NMR spectra were recorded on an AVANCE spectrometer equipped with an xyz gradient unit, operating at 600.13 MHz. For the H^1 NMR measurements, the samples were run in D_2O.

Viscosity measurements were performed for dilute solution in a bath thermostated at 25±0.05°C, using an Ostwald type viscometer. The data were analyzed according to:

$$\eta_{sp}/C= [\eta]+k_H[\eta]^2C$$

where η_{sp} is the specific viscosity, $[\eta]$ the intrinsic viscosity and k_H the Huggins constant.

Results and Discussion

Two series of graft copolymers Polyacrylamide grafted to various molecular weight of Dextran (D20, D70, D500) named D20-g-PAA1, D70-g-PAA1, D500-g-PAA1 – *I series* and D20-g-PAA2, D70-g-PAA2, D500-g-PAA2 *-II series* were synthesised. The AA monomer concentration for copolymers of I and II series differed twice for getting various length of grafted chains.

For characterization of graft copolymers molecular parameters we calculated the percentage of PAA and Dextran in graft copolymers, ratio of PAA and Dextran monomers in copolymers β ($\beta=\alpha_1/\alpha_2$), where α_1 is the number of PAA monomers in macromolecules, α_2 the number of Dextran monomers in macromolecules of graft copolymer) from the data of elemental analysis. Take into account molecular weight of Dextran (M_D), the total molecular weight of all PAA grafts M_{PAA}, the molecular weight of the graft copolymers M_G ($M_G= M_{PAA}+M_D$) was calculated. It has been found also a significant percentage of water for all samples. The results are gathered in Table 1.

Table 1. Molecular characteristics of graft copolymers calculated from the elemental analysis.

Series	Sample	β	$M_D\times 10^{-3}$	$M_G\times10^{-6}$	$M_{PAA}\times10^{-6}$	Moisture, weight %
I	D20-g-PAA1	31	20	0.41	0.39	9.22
	D70-g-PAA1	20	70	0.69	0.62	8.23
	D500-g-PAA1	3	500	1. 11	0.61	8.13
II	D20-g-PAA2	45	20	0.28	0.26	8.21
	D70-g-PAA2	11	70	0.41	0.34	9.14
	D500-g-PAA2	2	500	0.92	0.42	9.79

The total molecular weight of grafted PAA chains within I and II series is different. With increasing the molecular weight of Dextran in the graft copolymer also increases the total molecular weight of PAA component, however the ratio of total molecular weight of PAA grafts in the corresponding copolymers (based on the same molecular weight Dextran) of the I and II series is approximately equalled: for samples D20-g-PAA -1.5, for D70-g-PAA - 1.82 and for D500-g-PAA - 1.45.

In IR spectrum of D70-g-PAA (Fig.2), one can also observe the characteristic Amid I (stretching vibration of C=O groups) and Amid II (deformation vibration of NH_2 groups) bands of PAA at 1730-1580 cm^{-1} in addition to the characteristic absorption bands of Dextran glucosidic rings at 600-950 cm^{-1}, 1100-1200 cm^{-1} [6,7]. This is consistent with the occurrence of graft copolymerisation.

The chemical structure of graft copolymer was further examined by ^{1}H-MNR spectroscopy. A typical example of a ^{1}H-MNR spectra of the samples D20-PAA2 is drawn in Fig. 3. The characteristic resonance peaks corresponding to the protons in the methylene groups and other five methine groups of dextran at 3.40-3.92 ppm and 4.91 ppm [8] are apparently presented. The weak strip intensity of Dextran components in graft copolymers (Fig.3) is explained by the low content of Dextran in this samples – 6.35%, calculated from the elemental analysis data. In addition, the signals of protons in PAA graft also appear in the spectrum at 2.2-2.3 ppm (methine groups), 1.6-1.7 ppm (methylene groups), which a close to experimental results, has been obtain in [9] for individual PAA. These results also testifies the existence of grafting.

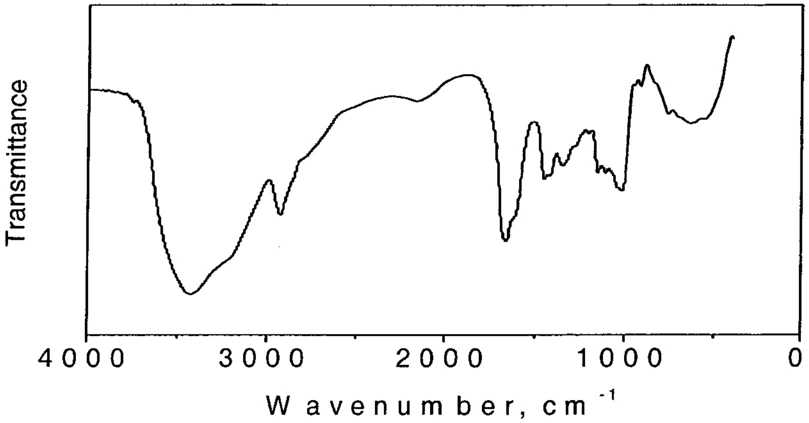

Figure 1. FTIR spectrum of D500-g-PAA.

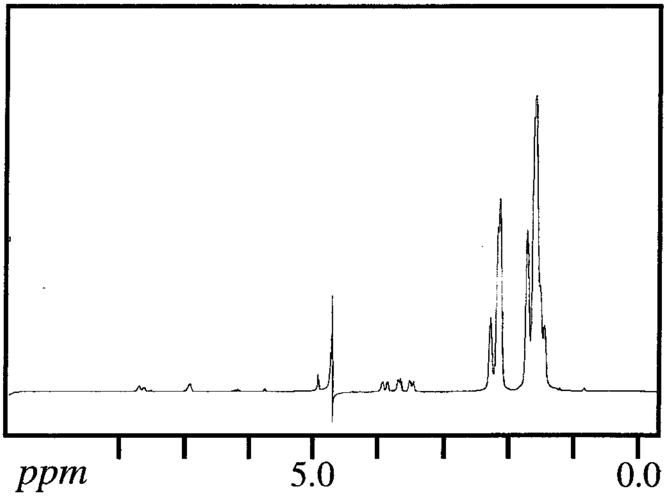

Figure 2. ^{1}H-NMR spectrum of D20-g-PAA2 copolymer.

Figure 3 shows the plots of the reduced viscosity (η_{sp}/C) versus concentration for D500-g-PAA2, D70-g-PAA2 and D20-g-PAA2. Through extrapolation to zero concentration the intrinsic viscosity [η] of the graft copolymers was obtained (Table 2).

Table 2. Molecular parameters of graft copolymers determined by viscometry and elemental analysis methods.

Series	Sample	$M_G \times 10^{-6}$	[η], m^3kg^{-1}
I	D20-g-PAA1	0.41	0.40
	D70-g-PAA1	0.69	0.65
	D500-g-PAA1	1, 11	0.51
II	D20-g-PAA2	0.28	0.23
	D70-g-PAA2	0.41	0.20
	D500-g-PAA2	0.92	0.31

We did not observe a drastic change in intrinsic viscosity for copolymers within I and II series in spite of the differing molecular weight of these copolymers (Table 2). Taking into account that intrinsic viscosity characterizes the hydrodynamic volume of the coil in solution, we can therefore conclude that the structure of graft copolymer D-g-PAA depends strongly on the molecular weight of Dextran component. This may arise from the possibility of Dextran and PAA components to form intramolecular H-bonds. Parameter β in Table 1 characterizes the ratio of Dextran and PAA monomers in the copolymers. The smallest value of this parameter is for copolymers based on D500. This suggests that in this case the bonding between the main chain and the grafted chains is more efficient.

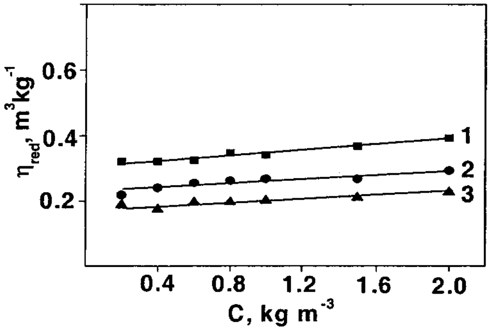

Figure 3. Dependence of reduced viscosity vs concentration for D500-g-PAA2 (1), D70-g-PAA2 (2) and D20-g-PAA2 (3).

The temperature dependence of the reduced viscosity for D70-g-PAA1(a) and D500-g-PAA2 (b) is shown in Fig.4. Significantly differing types of behaviour are seen. This also suggests that the intramolecular bonding varies with the number of grafts.

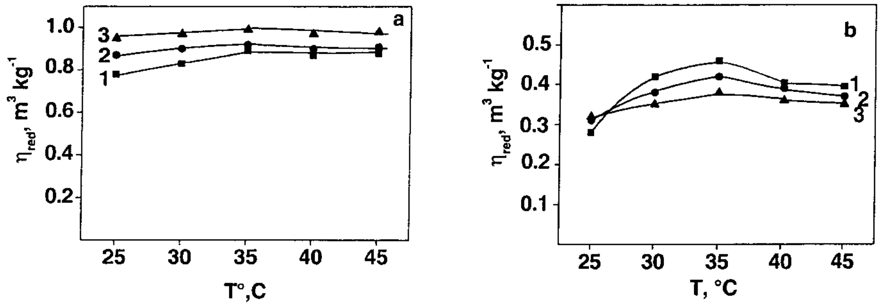

Figure 4. Temperature dependence of reduced viscosity for D70-g-PAA1(a) and D500-g-PAA2 (b). C=0.01 (1), 0.02 (2), C=0.6 kg m^{-3} (3).

Conclusion

It can be concluded that the macromolecular structure of D-g-PAA copolymers strongly depends on the molecular weight of Dextran component. The structure of such compounds can be easily monitored through the ratio of the main chain length to the grafts length.

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