

Graft Copolymerization of N-vinyl Caprolactame onto Chitosan

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Abstract In the present work we studied the graft radical copolymerization of N-vinyl caprolactame onto chitosan, synthesized from the chitin of the silkworm pupae, in the presence of the potassium persulfate as initiator. The influence of the polymer, monomer and initiator concentration, as well as the temperature on the copolymer composition and the effectiveness of grafting are discussed.

Keywords Chitosan, N-vinyl caprolactame, Potassium persulfate, Graft radical copolymerization, Copolymers composition

1. Introduction

Chitosan (CS) is one of the most perspective polymers, as it is biocompatible, biodegradable, non-toxic and does not form threat for the environment. One of the most interesting approaches to CS chemical modification is obtaining grafted copolymers on their basis. Of particular interest are grafted copolymers of N-vinyl caprolactame (N-VCL) on chitosan, which can dissolve in water, have a stimulus responsive properties and antimicrobial activity. The authors [1, 2] provide a synthesis of grafted copolymers CS – poly N-VCL. The synthesis was performed in several stages. At the first stage the radical homopolymerization of N-VCL in the presence of chain transfer agent was carried out. Then conducted a grafting of the poly N-VCL chains onto CS account for the reaction terminal carboxyl group poly N-VCL and amino group of CS. Another approach is graft copolymerization of the vinyl monomer onto CS in the presence of the redox initiators [3-6]. Recently, we have established the fact of the grafted copolymers formation on the basis of crab chitosan and N-vinyl caprolactame [7]. For the countries of Central Asia are the interest of the study of chitosan derived syntheses from the chitin of the silkworm pupae, which differs from the crab CS both in composition and molecular weight. In Uzbekistan has been developed the technology of obtaining chitin and chitosan. Raw materials for their production are the pupa of the silkworm, which are the waste of silk production [8].

In connection with this, in the present work for the first time carried out grafted radical copolymerization N-VCL on

CS of silkworm pupae chitin in the presence of potassium persulfate (KPS). The influence of the concentrations of CS, N-VCL, KPS, and temperature on the composition of obtained copolymers and the effectiveness of grafting are discussed.

2. Experimental

For the experiments used the CS, synthesized from the chitin of the silkworm pupae, at the Institute of polymer chemistry and physics of the Academy of Sciences of Uzbekistan. CS has the following technical specifications: nitrogen content = 8.25%, degree of deacetylation = 77%, The intrinsic viscosity $[\eta] = 2.15$ dl/g in a solvent 0.25M $\text{CH}_3\text{COOH} + 0.25\text{M}$ CH_3COONa at 25 °C. Technical characteristics of chitosan comply with the standard TSh 88.2-13:2011 (Uzbekistan). The molecular weight of CS calculated by the equation $[\eta] = 1.4 \cdot 10^{-4} \times M_n^{0.83}$ [8]. The molecular weight $M_n = 110000$.

N-VCL monomer was manufactured at the Institute of Polymer Chemistry and Physics, Academy of Sciences of Uzbekistan, using acetylation of caprolactam. The obtained monomer was rectified by two vacuum distillations. Purity of the distilled N-VCL was tested using the method of reverse-phase thin-layer chromatography. The isopropyl alcohol—water mixture (volume ratio 50: 50) was used as a mobile phase. Visualization with iodine vapour showed only one chromatographic zone with $R_f = 0.66$. This fact together with the determined values of density ($d_4^{20} = 1.028$ g/cm³) and refraction index ($n_d^{20} = 1.5131$) that were in accordance with the literature data testified the complete purification of the monomer. All other reagents used were of chemical or analytical purity grade and were purchased from REAKHIM, Russia [9].

For the synthesis in homogeneous conditions was selected

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the complex solvent, in the capacity of which used a mixture of water, acetic acid and isopropyl alcohol (IPA). Synthesis of copolymers carried out at constant mixing in current of gaseous nitrogen. In the course of the experiment varied concentration of polymer, monomer, initiator and the temperature. For the copolymers extraction the solvent was evaporated at room temperature. Because in the presence of the KPS in the reaction mixture takes place as graft copolymerization of N-VCL onto CS, so homo polymerization of N-VCL. Therefore, the product of the reaction is a mixture of grafted copolymer and poly – N-VCL. For the separation of homopolymer and unreacted monomer N-VCL conducted extraction resulting mixture of isopropyl alcohol, not dissolved copolymer was separated and dried under vacuum up to a constant mass. Poly – N-VCL allocated by resedimentation from isopropyl alcohol to hexane with the subsequent drying to constant weights under vacuum. The fact of copolymer formation was confirmed by IR - spectroscopy, a method of gravimetry and elemental analysis. The composition of copolymer was calculated based on the content of total nitrogen, which was determined by the Dumas method. The standard deviation from the arithmetic average for the samples with a nitrogen content exceeding 9% did not exceed 0.15%, in the content of nitrogen in copolymer less than 9% of the standard deviation does not exceed 0.1%. These results correspond to the accuracy of determining the composition $\pm 8.2\%$ and $\pm 5.7\%$, respectively. The effectiveness of grafting (EG) of N-VCL in copolymers was determined on the basis of gravimetric data according to the formula:

$$EG = \frac{Mcpl - Mcs}{Mcpl - Mcs + M_{pvcl}} \cdot 100\%$$

Where:

$Mcpl$ - the mass of grafted copolymer

Mcs - the mass of Chitosan

M_{pvcl} - the mass of poly-N-VCL

3. Results and Discussion

Table 1 shows the dependence of the copolymer composition on concentration of CS and N-VCL in the reaction mixture. It is seen that the content of the N-VCL links in copolymer significantly depends on the ratio of CS:N-VCL (fig.1). The copolymers are enriched with N-VCL links at low concentrations of CS. An increase in the ratio CS:N-VCL leads to a rather sharp decrease of the content of the links of the N-VCL in the copolymer. Thus, by varying the concentration of polymer and N-VCL in the reaction mixture can significantly influence on the contents of the N-VCL in graft copolymer, synthesizing system in the widest range of grafting degrees. On the other hand, effectiveness of grafting (EG), which essentially

characterizes the relationship between the reactions of homo - and copolymerization remains in the whole range of relations CS/N-VCL quite low. It indicated about prevalence of homo-polymerization N-VCL reaction compared with copolymerization. It should be noted that copolymers containing a large number of links N-VCL (more than 80%) dissolved in the water.

To establish the influence of the initiator concentration on the copolymers composition and the effectiveness of grafting, the experiments were carried out at constant concentration of N-VCL and CS. The results (table 2) showed that the increase of the KPS concentration leads to reduction the content of the N-VCL links in copolymer. At this, the total yield of the reaction product (poly-N-VCL+graft copolymer) will slightly increase. This phenomenon can be explained as follows. Graft copolymerization of vinyl monomers onto CS accompanied by the low values of the reaction rate order on initiator concentration: less than 0.5 [10, 11]. At the same time, homo-polymerization of N-VCL is characterized, as a rule, the usual for radical polymerization reaction order of the initiator 0.5 [9]. Therefore, with the increase of the concentration of the initiator, the N-VCL homo-polymerization rate will increase faster than the increasing graft copolymerization rate. That is why, the share of poly-N-VCL in the reaction product will increase too. This is also confirmed by the data of the EG. As can be seen from table 3, with the increasing of the KPS concentration, the EG is reduced. Also the initiator concentration has a great influence on the copolymers structure. When KPS concentration $> 10^{-3}$ mol/l, the three-dimensional structure are formed.

The influence of temperature on the copolymers composition (table 3) have been studied. The experiments were carried out at the temperature range of 40-60°C. It is seen that the increase of temperature leads to the growth of output homo polymer, as well as the content of the N-VCL links in copolymer, which corresponds to the classical kinetic of radical polymerization.

It should also be noted that the interaction of CS with KPS the destruction of polysaccharide macromolecules carried out [12, 13]. This is confirmed by the fact that in the absence of N-VCL in reaction medium, decrease of molecular weight CS, obviously due to the rupture of a glycoside bound (table 4). The same phenomenon has been observed previously in the study of grafted of copolymerization of vinyl monomers in the crab chitosan [14].

It is known that the CS has antimicrobial properties, which are stored in obtaining his copolymers with synthetic monomers, not possessing their own antimicrobial activity [11]. Synthesized copolymers tested for their antibacterial activity in relation to 14 kinds of microorganisms. The results showed that copolymers have antibacterial effect, and do not have antifungicide actions and are of interest for the creation of new antimicrobial drugs for medical practice.

Table 1. The dependence of the nitrogen content in copolymer, composition and effectiveness of grafting on the CS and N-VCL concentration in the reaction mixture. $[KPS] = 1 \times 10^{-3}$ mol/l, $[CH_3COOH] = 0.15$ mol/l, conc. IPA = 19mass %. $T = 60^\circ C$. The time of synthesis 180 min

| [CS], mol/l | [N-VCL], mol/l | N, % | N-VCL links content in copolymer, % | EG, % |
|----------------|-------------------|---------|--|----------|
| 0.005 | 1.00 | 9.87 | 89.0 | 9.9 |
| 0.012 | 1.00 | 9.54 | 70.9 | 15.5 |
| 0.028 | 1.00 | 9.12 | 47.8 | 13.3 |
| 0.085 | 1.00 | 8.75 | 27.4 | 30.1 |
| 0.093 | 1.58 | 8.80 | 30.2 | 13.0 |
| 0.093 | 1.32 | 8.62 | 20.6 | 12.4 |
| 0.093 | 0.73 | 8.43 | 10.1 | 16.5 |
| 0.093 | 0.38 | 8.31 | 3.9 | 10.9 |

Table 2. The dependence of the mass of reaction products, the nitrogen content in copolymer, its composition and the effectiveness of grafting on the KPS concentration in the reaction mixture. Conc. CS = 1.5%, $[N-VCL] = 1.58$ mol/l, $[CH_3COOH] = 0.15$ mol/l, conc. IPA = 19mass %. $t = 60^\circ C$. The time of synthesis 180 min

| $[KPS] \cdot 10^3$, Mol/l | M_{pvcl} , g | M_{cpl} , g | N, % | N-VCL links content in copolymer, % | EG, % |
|-------------------------------|-------------------|------------------|---------|--|----------|
| 0.5 | 2.12 | 0.86 | 9.1 | 46.7 | 20.9 |
| 0.98 | 2.31 | 0.58 | 8.9 | 35.7 | 10.8 |
| 1.6 | 2.60 | 0.50 | 8.8 | 30.2 | 7.14 |
| 3.4 | 2.60 | 0.45 | 8.7 | 29.4 | 5.5 |

Table 3. The dependence of the mass of reaction products, the nitrogen content in copolymer, its composition and the effectiveness of grafting on the temperature of synthesis. Conc. CS = 0.32%, $[N-VCL] = 0.85$ mol/l, $[KPS] = 1 \times 10^{-3}$ mol/l, $[CH_3COOH] = 0.15$ mol/l, IPA = 19mass %. $t = 60^\circ C$. The time of synthesis 180 min

| $T, ^\circ C$ | M_{pvcl} , g | M_{cpl} , g | N, % | N-VCL links content in copolymer, % | EG, % |
|---------------|-------------------|------------------|---------|--|----------|
| 40 | 0.96 | 0.12 | 8.62 | 20.3 | 2.0 |
| 50 | 1.36 | 0.15 | 8.78 | 29.1 | 3.5 |
| 60 | 1.65 | 0.25 | 8.91 | 36.3 | 8.3 |

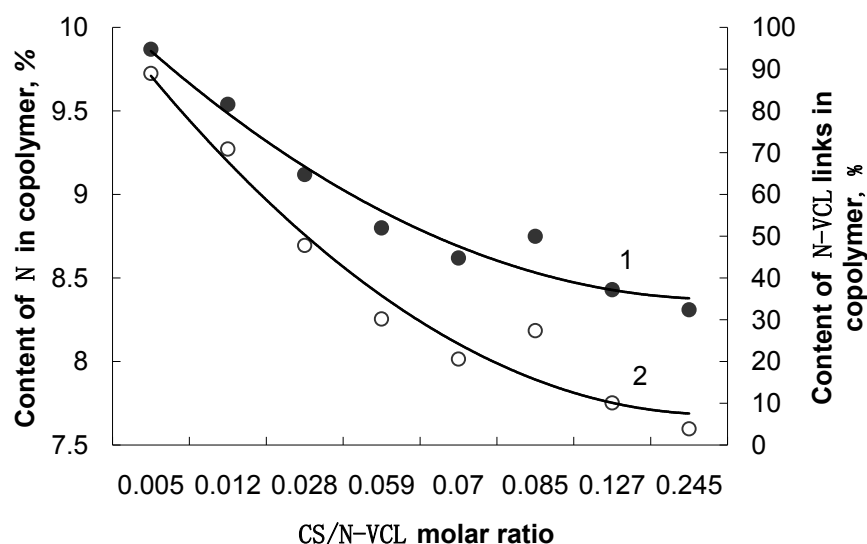
**Figure 1.** The dependence of the nitrogen content (1) in copolymer and content of N-VCL links in copolymer (2) on the molar ratio CS/N-VCL in the reaction mixture

Table 4. The effect of KPS concentration on the molecular weight of chitosan. $[\text{CH}_3\text{COOH}] = 0.15 \text{ mol/l}$, IPA = 19mass %. $t = 60^\circ\text{C}$. The time of synthesis 180 min

| № | $[\text{KPS}] \times 10^3, \text{ Mol/l}$ | $[\eta], \text{ dl/g}$ | M_n |
|---|---|------------------------|--------|
| 1 | 0 | 2.15 | 110000 |
| 2 | 0.4 | 1.95 | 98000 |
| 3 | 0.9 | 0.9 | 39000 |
| 4 | 1.7 | 1.05 | 46000 |

4. Conclusions

CS, synthesized from chitin, selected from the pupae of the silkworm, modified by grafting N-VCL in the conditions of radical initiation in the presence of the KPS. By varying the concentration of CS and VC in the reaction mixture can be synthesized graft copolymers in a wide range of ratios of components and, accordingly, the extent of grafting. Copolymers, enriched with N-VCL links, obtained in excess of the monomer at a temperature of 60°C . The initiator concentration in a more significant impact on the copolymers structure, than on their composition. Copolymerization characterized by low values of the effectiveness of grafting, that is caused by dominance of the reaction N-VCL homo-polymerization over graft copolymerization.

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