Peculiarities of the oxidative polycondensation of aniline derivatives in solution of polyvinyl alcohol

Halyna Stasyshyn, Galyna Zastavska, Mariia Koval, Volodymyr Dutka

Ivan Franko National University of L'viv, UKRAINE
Kyryla & Mefodiya Str. 6, L'viv 79005,
natalia.matsyuk@gmail.com

Abstract – Studied oxidative polycondensation of aniline peroksydysulfatom ammonia in solution of polyvinyl alcohol. It is shown that water-soluble polymer can interact with aniline. Kinetic curves are characterized by oxidative polycondensation of two plots that indicate the nature of the avtokatolitychnyy. During the process available polymer-polymer materials that have film-forming and conductive properties.

Key words – aniline, polyaniline, polyvinyl alcohol, viscosity, electrically conducting

I. Introduction

Electrically conducting polymer-polymer materials possess unique properties because the study of conditions of their receipt and of investigation of physical and chemical parameters received considerable attention. [1, 2].

II. Objects of research

In our work studied specific oxidative polycondensation of aniline derivatives peroksodysulfat amaniyu the presence of polyvinyl alcohol (PVA). Under these conditions can be formed of polymer-polymer composites (PPK) who have film-forming properties, and the presence of a PPK polyaniline (PAN) will predetermine the electrical conductivity of the polymer material.

The resulting composites can be used to produce conductive coatings. On the formation mechanism of the composite method of preparation will affect the reaction mixture. The first stage of the process of obtaining PPK is to obtain aqueous solutions of PVA. In contact with water PVA polymer swelling is observed, the degree of swelling depends on the pH.

In the table 1 shows the extent of swelling water-soluble polymers of methacrylic acid (PMAK), poly acrylic acid (PAK) and polyvinyl alcohol (PVA).

The kinetics of of swelling has a classic look dependencies with the release of the plateau area, with water molecules capture polymeric matrix lasts 30-50 minutes.

TABLE 1.
THE DEGREE SWELLING OF INVESTIGATED POLYMERS (D) AT DIFFERENT VALUES OF PH SOLUTION

pH	The degree of swelling (H) ml / g		
	PVA	PMAK	PAK
6,86	10,5	3,99	4,62
1,68	4,25	3,64	4,45

The degree of swelling of H found by the ratio of the volume of water absorbed to the mass of the polymer. As you would expect numerical values of H depend on the pH. At pH = 6.86 degree of swelling of and PAC for PMAK up 3.93 and 4.62 ml / g, while PVA value H proved to be more a factor of 2 than for other polymers. When reducing the pH to 1.68 numerical value N for PVS decreases more than in 2 times, while PMAK PAC and the degree swelling of varies slightly. The intensive mixing and heating the of samples PVS that are absorbed the water leads to the formation of viscous polymer solutions. Increasing the number of PVA in aqueous solution spends significant growth of the relative to the viscosity of the derived gel (Fig. 1).

Introduction to the aqueous solution of 0.002 mol of aniline leads to an increase in viscosity compared to the original of PVA solution. This fact indicates the interaction of the polymer matrix - aniline, that results in conformational changes of macromolecules state and growth the viscosity of the polymer.

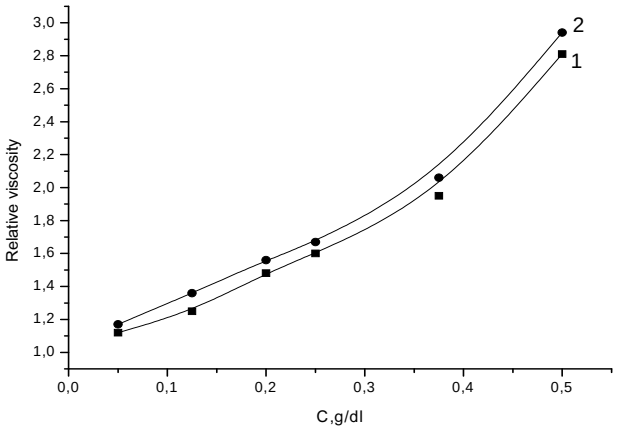

Fig. 1. Relative viscosity the contents of PVA 1, and with the addition of 0.002 mol of aniline 2.

Investigation of conductivity solutions with of PVA and of PVA plugins 0.002 mol aniline confirms the conclusion of the interaction with aniline polymer matrix (Fig. 2)

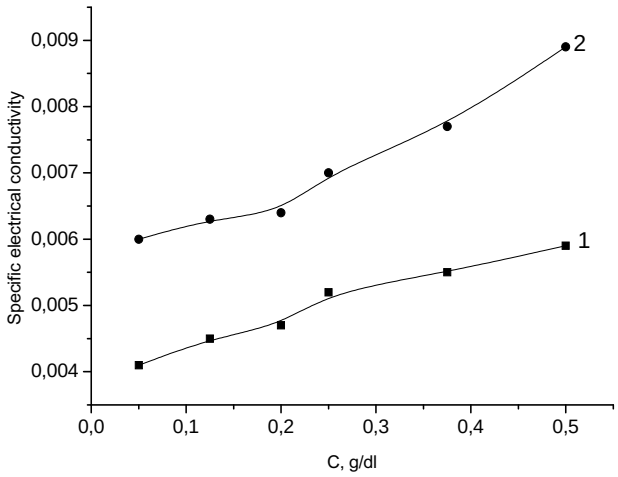

Fig. 2. The dependence specific conductivity the contents of PVA 1, and with the addition of 0.002 mol of aniline 2

Adding to the aqueous solutions of of PVA and aniline-oxidant ammonium peroksodysulfat will lead to the formation of polyaniline. As known in the oxidation of aniline in solution peroksodysulfatamy formed PAN, with the optical density of the reaction mixture increases. As known in the oxidation of aniline peroksodysulfatamy PAN formed by in solution and the optical density of the reaction mixture increases. By measuring change in optical density (D) from the time the polycondensation can be obtained kinetic curves oxidative polycondensation. Obviously aniline interaction with polymer matrix will affect the kinetics of oxidative polymerization. The kinetic curves oxidative polycondensation of aniline are shown in (Fig. 3)

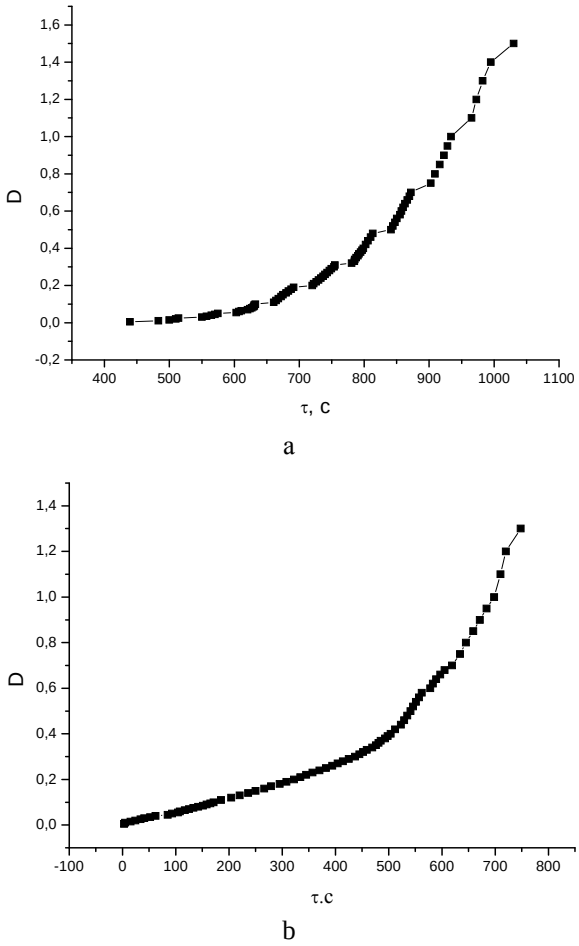

Fig. 3. Change in optical density (D) the reaction mixture with time in the presence of 2% of PVA. Peroksydysulfatu ammonium concentration of 0.1 M, C_{AH} = 0.01 (a), C_{AH} = 0.05 (b)

The kinetic curves are characterized by two stages (Figure 3) At the initial process stage the optical density varies slightly, but after a defined period reaction rate increases sharply, indicating the character avtocatalitical oxidation of aniline peroksidisulfat ammonium. Construction of kinetic curves in logarithmic coordinates has allowed determine the total rate constants of the first and second 2 1 process, numerical values are given in Table 2.

TABLE 2.

THE TOTAL RATE CONSTANTS OXIDATIVE POLYCONDENSATIONS OF ANILINE MONOMER WITH DIFFERENT CONTENT OF 2% OF PVA SOLUTION (peroksydysulfatu ammonium concentration of 0.1 mol / l.)

The concentration of aniline	$k_1 \times 10^3$, c^{-1}	$k_2 \times 10^3$, c^{-1}
0,01	4.23	11.87
0,025	4.35	11.95
0,05	6.65	13.87

Conclusions:

The obtained data indicate that changing the concentration of aniline in the reaction mixture can change the speed of the first and second process stage. The rate of oxidative polymerization will affect the nature of the polymer, which is used to produce the PPK. The resulting polymer-polymer composites have electrically conductive and film-forming properties.

References

[1] Volkov S. A., Kovalchuk Ie. P., Ohenko V., Reshetniak O. V. Nanokhimiia. Nanosystemy: Nanomaterialy". K. Nauk. dumku. p.424. 2008.

[2] A. Mirmohseni, G.G. Wallace, Preparation and characterization of processable electroactive polyaniline–polyvinyl alcohol composite", Polymer., vol. 44. pp. 3523-3528, 2003.

[3] Tongfei Wu, Kevin O'Kelly. Biqiong Chen. Poly(vinyl alcohol) particle-reinforced elastomer composites with water-active shape-memory effects", European Polymer Journal ., vol. 53. pp. 230-237, 2014.