ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 8, Issue 11 , November 2021

Study of the Main Characteristics of Hydrolyzed Forms of Polyacrylonitrile

Ilxomjon Akhmadjonov, Sadatdin Tileubayev, Aziza Abdikamalova, Shakhnoza Kuldasheva

Junior researcher, AS RUz "Institute of General and Inorganic Chemistry", Tashkent, Uzbekistan
Junior researcher, AS RUz "Institute of General and Inorganic Chemistry", Tashkent, Uzbekistan
Leading researcher, DSc, AS RUz "Institute of General and Inorganic Chemistry", Tashkent, Uzbekistan
Professor, , DSc, AS RUz "Institute of General and Inorganic Chemistry", Tashkent, Uzbekistan

ABSTRACT: The molecular weight of the obtained polymers (Infinitely Better 1200 Infinity Series) was measured. The obtained results showed the possibility of changing the molecular weight of the polymer material as a result of hydrolysis. As it turns out, the conditions of hydrolysis and the nature of the hydrolyzing agent will affect the values of the molecular weight and the yield of the polymer. The results obtained show that there is an admixture of oligomers weighing about 3000-7000 in the composition of the initial polymer. However, after hydrolysis, these compounds were not identified, probably due to the formation of new bonds between oligomeric and polymer particles, which also contributed to an increase in the molecular weight of the final product.

KEYWORDS: polyacrylonitrile (PAN) waste, distiller's liquid, structure formation, microscopic images, temperature.

I. INTRODUCTION

It is well known that, polymer materials with hydroxyl, amine, carboxyl, and other groups have enhanced physicochemical and structure-forming characteristics. With a change in the ionic strength of solutions, which directly depends on the nature of the hydrolyzing agent, the degree of dissociation of polymers and the shape of their macromolecules change. Changing the shape leads to the transformation of operational characteristics.

As a result of dissociation, the number of kinetic units increases, i.e. the concentration of ions also increases, which also affects the hydrodynamic characteristics of their solutions. Many studies have been conducted on the physicochemical properties of water-soluble polymers. [1-3]. Research in this direction covers such experiments as determining the viscosity of their solutions, electrical conductivity, etc.

The aim of the research is to study the structure-forming characteristics of hydrolyzed forms of polyacrylonitrile (PAN) obtained using sodium hydroxide, liquid glass, sodium carbonate, and distiller's liquid.

II. SIGNIFICANCE OF THE SYSTEM

The molecular weight of the obtained polymers (Infinitely Better 1200 Infinity Series) was measured. The obtained results showed the possibility of changing the molecular weight of the polymer material as a result of hydrolysis. The study of methodology is explained in section III, section IV covers the experimental results of the study, and section V discusses the future study and conclusion.

III. METHODOLOGY

Polyacrylonitrile (PAN) waste (Navoiyazot JSC) was used as a feedstock. Sodium hydroxide, liquid glass, sodium carbonate, and distiller's liquid were studied as hydrolyzing agents. A solution of hydrochloric acid-HCl (p=1.025 g/cm^3) was also used to regulate the pH of the medium.

The pH of the solutions was measured according to a generally accepted method on a GMH-Greisinger 3500 Series laboratory pH meter with glass electrodes.

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 8, Issue 11 , November 2021

The acid number (AN) was determined by the method of reverse titration of the polymer solution and its hydrolysis product. According to the found values of QF, the change in the number of carboxyl groups during hydrolysis of the initial copolymers was judged.

The nitrogen content in polymers was determined by the generally accepted Kjeldahl's method [4]. Kjeldahl's method consists of the fact that when the polymer is heated with concentrated sulfuric acid in the presence of a small amount of CuSO4 catalyst, the bound nitrogen turns into ammonium sulfate. After the decomposition of the sample, a solution of caustic soda was added to it and ammonia was distilled, absorbing HCl with a standard hydrochloric acid solution [4]. The nitrogen content was determined by the amount of ammonia absorbed.

The specific viscosity (η_{sv}) of polymer sample solutions was determined using an Ostwald viscometer (water expiration time of 58 sec, capillary diameter of 0.56 mm) at a temperature of 250 °C, depending on the concentration [5]. For this purpose, appropriate solutions with different concentrations (0.50-0.01 g/100 ml) were prepared by dilution with water or 0.1 N KCI solution.

The characteristic viscosity (η_x) of AA solutions was determined graphically by the dependence of η_s on the concentration of C (η_s/C). To determine the effect of the pH of solutions on their viscosity, polymer solutions were prepared by adding various volumes of 0.1 N solutions of HCI and KOH to the initial solution.

To carry out the alkaline hydrolysis process, 50 g of distilled water was poured into the reaction vessel (V = 500 ml) and 10 g of PAN was added. Then the system was thermostated at the process temperature with constant stirring. Temperatures ranging from 50 to 98 °C were studied, with temperatures chosen in accordance with known literature data. Upon reaching the set temperature in the reaction medium, 50 ml of a 10% solution of the hydrolyzing agent was added with vigorous stirring, while taking this moment as the beginning of the process. The reaction was carried out for 0.5–3 hours. The kinetics of hydrolysis were controlled by a potentiometric method. The degree of hydrolysis was determined by taking a sample of 2 mL, which underwent potentiometric titration. The polyelectrolytes obtained using the hydrolyzing agent's sodium hydroxide, liquid glass, sodium carbonate, and distiller liquid, respectively, were conventionally named Na-PAN, NaSi-PAN, NaC-PAN, and Ca-PAN.

IV. EXPERIMENTAL RESULTS

The original PAN is not soluble in water. Hydrolyzed forms, depending on the duration of the process, are significantly well soluble in water, which also leads to a change in the viscosity characteristics of their solutions.

The manifestation of a change in the dependence of the specific viscosity on the concentration of the solution of hydrolyzed polymers has a similar nature. However, significant structure formation in the CaPAN solution in the region of high concentrations is likely due to different values of molecular weight as well as the structure-forming characteristics of Ca^{2+} ions associated with the carboxyl group. The dependence of the specific viscosity and pH of solutions on the concentration of PE is given in Table 1.

Table 1.

Dependence of the characteristics of solutions on the concentration

Sample	Concentration							
	0,01		0,05		0,1		0,5	
	$\eta_{уд}$	pH	$\eta_{уд}$	pH	$\eta_{уд}$	pH	$\eta_{уд}$	pH
Na-ПАН	0,29	9,7	0,77	10,3	0,98	10,7	3,32	11,4
NaSi-ПАН	0,16	7,6	0,71	8,8	0,87	9,02	3,03	10,01
NaC-ПАН	0,12	9,4	0,61	10,2	0,83	10,6	2,92	11,07
Ca-ПАН	0,20	7,8	0,73	8,9	0,90	9,3	3,14	10,09

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 8, Issue 11 , November 2021

As the table data shows, an increase in concentration leads to an instant increase in viscosity values for all the samples studied, which is especially noticeable in aqueous solutions of samples obtained by hydrolysis of NaOH and Na2SiO3. The presence of a viscosity anomaly is less pronounced for Ca-PAN.

Further investigation of the structure was carried out on the basis of electron and optical microscopy (binocular digital microscope model NLCD-307B). As it turned out, the difference in the characteristics of hydrolyzed forms of PAN is associated with the conformational state of macromolecules in solution. At low concentrations of hydrolyzed PAN macromolecules, shapeless aggregates of particles are detected, especially for NaC-PAN samples. Sodium carbonate is a weaker base compared to other hydrolyzing mixtures, and probably the hydrolysis process proceeds largely without the formation of amidine.

Consequently, the complete disappearance of nitrile groups does not occur in this process since the already formed carboxyl groups screen them, which leads to a stoppage of the hydrolysis reaction. Therefore, macromolecules have a more folded shape. Microscopic images of the obtained samples are shown in Figures 1 and 2.

Fig. 1. Micrographs of samples of structure-forming agents obtained with a binocular microscope: 1) Na-PAN; 2) NaSi-PAN; 3) NaC-PAN; 4) Ca-PA

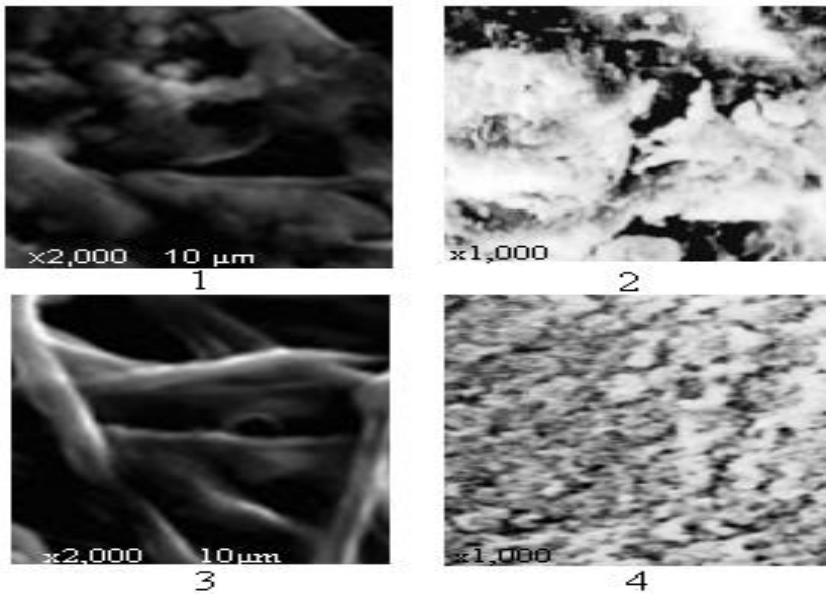


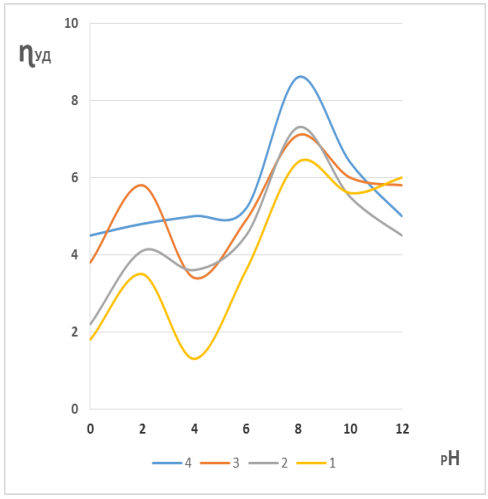
Fig. 2. Electron microscopic images: 1) Na-PAN; 2) NaSi-PAN; 3) NaC-PAN; 4) Ca-PAN.

The appearance of fibrous structures is associated with increased yields of the hydrolysis process and the straightening of macromolecules due to the steric effects of neighboring functional groups. However, in the case of the Saipan sample, the formation of completely fibrillar filaments was observed during the storage of these samples. It is probably that further hydrolysis occurs during storage. [6-9]

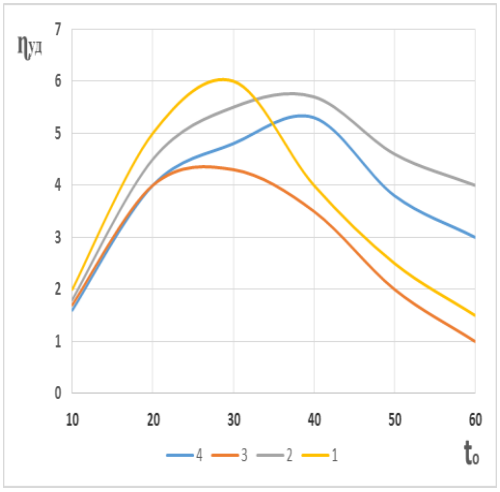
The viscosity of solutions of hydrolyzed forms of PAN, with the exception of their NaSi forms, practically does not change during long-term storage. There is evidence that polymers hydrolyzed in liquid glass form a precipitate of silicic acid. This is probably the reason for this change.

The influence of temperature on the viscosity of hydrolyzed PAN solutions has been studied. The study found that increasing the temperature to 40–45°C causes a slight increase in the viscosity of Ca- and NaSi-based solutions, regardless of the initial polymer. A further increase in temperature causes a sharp decrease in the value of the viscosity characteristics. For other studied objects, a similar dependence is not observed, but only an increase in temperature reduces the value of the viscosity of solutions. The results of studying the effects of changes in temperature and pH of solutions on their viscosity are shown in Fig. 3.

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 8, Issue 11 , November 2021



А



Б

Figure 4.5. Dependence of the specific viscosity of solutions: 1) Na-PAN; 2) Nazi-PAN; 3) NaC-PAN; 4) Ca-PAN from a) pH, b) temperature;

According to the literature data, it is known that at different pH values of the medium, macromolecules of water-soluble polymers have different structures. The experimental results show that the viscosity of solutions of polymer preparations at different pH values of the medium changes identically to the viscosity of known polymers (hypane). Thus, at pH > 10, rectification occurs due to the presence of carboxyl groups and dissociation of salt groups, due to which the viscosity increases sharply. As shown by the curves of the figure and their nature in highly alkaline media, the viscosity characteristics of these PE do not differ from each other. In highly acidic conditions, the PE data differ slightly from one another.

An increase in temperature to 30°C causes an increase in the viscosity of the medium, and a further increase in temperature contributes to a decrease in all polyelectrolytes. Consequently, changes in the viscosity of solutions of all PE are subject to general laws.

To establish the composition and ratio of the functional groups of the obtained PE, the acid number and nitrogen content were determined (Table 2).

Table 2.
Characteristics of hydrolyzed polymers

Sample	Consistent with the Nitrogen in the polymer, %.	Degree of hydrolysis, %	Acid number, mg/g
Na-ПАН	11,25	43,2	118,4
NaSi-ПАН	11,58	41,9	167,7
NaC-ПАН	14,38	31,1	141,7
Ca-ПАН	13,63	37,9	131,9

As the table data shows, during hydrolysis with sodium hydroxide and silicate, the process yields have the highest values, thereby reducing the amount of nitrogen in the composition of polymers. At the same time, the values of QF have comparatively lower values, probably due to saponification and the formation of COONa groups. [6]

Thus, macromolecules of these polymers at pH values of the medium (3-4.5) pass from one form to another. The maximum structure formation for individual polymers lies in the range of values of 6.5–9.

The molecular weight of the obtained polymers (Infinitely Better 1200 Infinity Series) was measured. The obtained results showed the possibility of changing the molecular weight of the polymer material as a result of hydrolysis. As it turns out, the conditions of hydrolysis and the nature of the hydrolyzing agent will affect the values of the molecular weight and the yield of the polymer. The results obtained are shown in Table 3.

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 8, Issue 11 , November 2021

Table 3.
Molecular weight of polymers and their composition

Sample	Molecular weight of the main substance and impurities	The content of the main substance and impurities
ПАН	560000 5000 3000	80,7 9,8 9,5
Na-ПАН	1200000	99,8
NaSi-ПАН	1290000 1500	98,9 1,0
NaC-ПАН	920000 2200	99,0 1,0
Ca-ПАН	1000000 1500	99,0 1,0

V. CONCLUSION AND FUTURE WORK

The results obtained show that there is an admixture of oligomers weighing about 3000-7000 in the composition of the initial polymer. However, after hydrolysis, these compounds were not identified, probably due to the formation of new bonds between oligomeric and polymer particles, which also contributed to an increase in the molecular weight of the final product.

REFERENCES

[1]. Nechaev, A.I. Investigation of radical polymerization and structure of anti-turbulent terpolymers based on acrylamide, acrylonitrile and 2-acrylamide-2-methylpropanesulfonic acid / A.I. Nechaev, M.N. Gorbunova, I.I. Lebedeva et al. // Journal. prikl. chemistry - 2017. - Vol. 90. - No. 9– - 1234-1242 p.
[2]. Strelnikov, V.N. Development of acrylate copolymers with increased acid, salt and heat resistance as a basis for import-substituting drilling lubricants / V.N. Strelnikov, V.A. Valcifer, A.I. Nechaev // Collection of theses of the XX Mendeleev Congress on General and Applied Chemistry. - Yekaterinburg, 2016. - Vol. 3. - 283 p.
[3]. Nechaev, A.I. Investigations in Acrylate Polymer Composition, in its Structure and DragReducing Properties under Conditions of High Temperatures and Highly Mineralized Aqueous Media / A.I. Nechaev, V.A. Valtsifer and V.N. Strelnikov. // The optimization of the composition, structure and properties of metals, oxides, composites, nano and amorphous materials. Proceedings of the sixteenth Israeli – Russian Bi-National Workshop. –Israel, Ariel, 2017.– 91 p.
[4]. Fundamentals of analytical chemistry / edited by Yu. A. Zolotov. - 3rd, pererab. and additional - M.: Higher School, 2004. - Vol. 2. - 503 p.
[5]. GOST 11034-82 polyamides. Method for determining the number of viscosity of dilute solutions.
[6]. A.I. Sharipova., I.L. Akhmadjonov., A.B. Abdikamalova., Kh.I. Akbarov., Sh.A. Kuldasheva Synthesis of New Fixings of Mobile Sands (2021). Alinteri Journal of Agriculture Sciences 36(1): 356-361
[7] Feruz Tukhtaev, Dilorom Karimova, Dilnavoz Kamalova. Research of Kinetic Sorption of Pb^{2+} Ions in $Pb(NO_3)_2$ Solution by Composite Polymeric Sorbents Under Various Conditions //International Journal of Advanced Research in Science, Engineering and Technology. Vol. 7, Issue 6, June. 2020. pp 14036-14043.
[8]. Feruz Tukhtayev, Iroda DJalilova, Nargiza Shonazarova. Development of Sorption Technology of Composition Polymer Sorbents // International Journal of Advanced Research in Science, Engineering and Technology. Vol. 7, Issue 10 , October 2020. pp. 15414-15417
[9]. Feruz Tukhtaev, Dilorom Karimova, Ayzada Malikova, Dilnavoz Kamalova. Research Of Kinetic Sorption Of Cu^{2+} Ions In $CuSO_4$ Solution By Composite Polymeric Sorbents Under Various Conditions // Journal of Advanced Research in Dynamical & Control Systems, DOI: 10.5373/JARDCS/V12SP6/SP20201058. Vol.12, Special Issue-06, 2020. pp. 505-511.