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SYNTHESIS OF POLYCARBOXYLATE PLASTICIZER BASED ON ACRYLIC ACID AND APEG AND ITS GEL CHROMATOGRAPHIC ANALYSIS

JALILOV ABDULAKHAT

Director of the Tashkent scientific research institute of chemical technology, Tashkent, Uzbekistan
E-mail.: ooo_tniixt@mail.ru
*Corresponding author.

SOTTIKULOV ELYOR

Senior research of Tashkent scientific research institute of chemical technology, Tashkent, Uzbekistan.
E-mail.: elyor-s88@mail.ru

KARIMOVA MASUDA

Professor of Tashkent scientific research institute of chemical technology, Tashkent, Uzbekistan.
E-mail.: masudkarimov27@gmail.com

BOYMIRZAEV AZAMAT

Professor of Namangan Institute of Engineering and Technology, Namangan, Uzbekistan
E-mail.: a.boymirzayev@nammti.uz

Abstract: The purpose of this work is not only to develop a method for synthesizing a new plasticizer but also to study its properties using gel chromatography, which will allow for the optimization of its use in concrete production. The research includes the synthesis of polycarboxylate-based plasticizers and the determination of their polyelectrolyte properties using gel chromatography. The work employed multifaceted experimental approaches aimed at determining the molecular mass and structure of the new products. The distribution of molecular masses, hydrodynamic parameters, and polyelectrolyte properties of the synthesized copolymers are discussed. The study successfully synthesized a new polycarboxylate-based plasticizer and determined its molecular mass and structure using gel chromatography. The copolymer's molecular mass was 10 kDa, and the monomer fraction was 1.8 kDa. The plasticizer improved concrete mixture properties, enhancing flowability, hardening time, and strength.

Keywords: polycarboxylate, plasticizer, molecular mass, Gel-chromatography, acrylic acid, unsaturated macromer, polyelectrolyte, molecular mass distribution, unsaturated polyethylene glycol, copolymer.

Introduction. Currently, the importance of improving the properties of construction materials such as concrete is increasing. One of the most promising directions in this field is the production and use of polycarboxylate plasticizers, which significantly improve the flowability and other performance characteristics of concrete mixtures. Polycarboxylate plasticizers are the best way to reduce the water requirement of the mixture. At the same time, they allow for an increase in the strength and durability of ready-made concrete products.

This article is devoted to the synthesis of a new type of polycarboxylate plasticizer and its investigation using gel chromatography as the exclusive method. The synthesis of polymers with desired properties requires precise control of molecular masses, which in turn affects their efficiency and cost-effectiveness in use. Gel chromatography, the most

effective method for molecular mass distribution and structure analysis, plays a key role in evaluating the quality and functionality of the synthesized polymers.

The purpose of this work is not only to develop a method for synthesizing a new plasticizer but also to study its properties using gel chromatography, which will allow for the optimization of its use in concrete production. The introduction of new information on the structure and properties of polycarboxylate plasticizers helps to better understand the relationship between molecular structure and performance, opening new opportunities for innovation in the construction industry.

Scientists of the Faculty of Chemistry at the Technical University of Munich, including J. Plank and other researchers, synthesized polycarboxylate-based plasticizers and conducted many studies. One of these studies involves the synthesis of a plasticizer based on methacrylic acid and unsaturated polyethylene glycol. The study confirms that hydroxy-terminated PEG side chains in methacrylic acid and unsaturated polyethylene glycol superplasticizers are effective and can serve as viable alternatives to conventional methoxy-terminated polymers. The advantages of using side-chain termination with a hydroxyl group include potentially simpler synthetic processes and reduced by-product formation. The synthesized superplasticizers were studied using gel chromatography. Additionally, the role of cement mixtures in the development of high-performance concrete composition has been proven [1].

A chromatograph equipped with a differential refractometer is used to determine the molecular mass of various polymer samples. This method allows absolute molecular weight-dependent scaling of the size for only one sample of each polymer in the polymer solution. In this study, water-soluble polyethylene oxide was used to calibrate the chromatographic column. The scaling law allows us to understand the solution characteristics of polymers because it reflects how the molecular weight is related to the polymer size, representing the interactions between the polymer chain segments and the solvent molecules [2].

Gel chromatography or Exclusive liquid chromatography (ESX) is currently one of the highly effective physico-chemical analytical methods for determining the molecular mass distribution of polymers, the degree of polydispersity, and the hydrodynamic parameters of macromolecules [3,4].

In this paper, the synthesis of an unsaturated polyethylene glycol and acrylic acid copolymer and its polyelectrolyte properties in ESX are investigated.

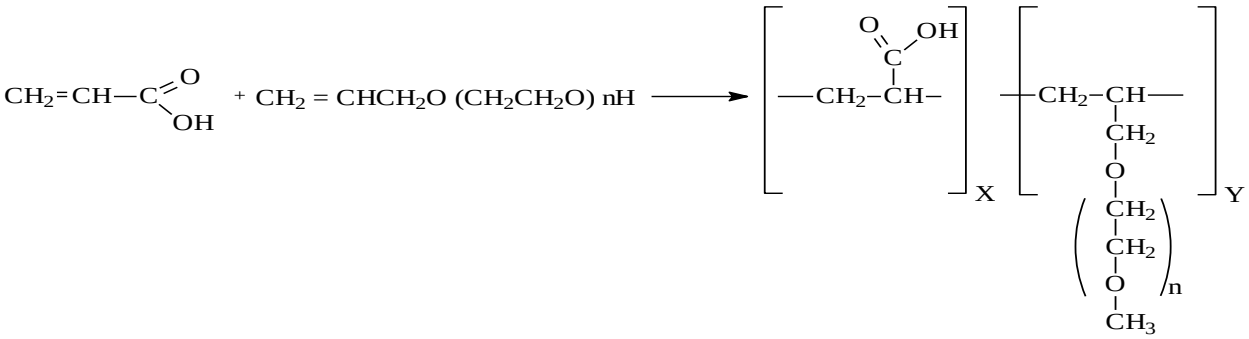
Materials and methods. Synthesis Process. The copolymer synthesis based on acrylic acid (AA) and unsaturated macromer (APEG) was carried out as follows. The synthesis process of the polycarboxylate plasticizer was conducted in a three-necked flat-bottomed flask equipped with a reflux condenser, a thermometer, and a dropping funnel. Mixing and heating of the reaction mass were performed using an MS7-H550-S magnetic stirrer.

First, 100 ml of distilled and deionized water was added to the reaction flask. Acrylic acid (AA), the unsaturated macromer (APEG), and a chain transfer agent were then dissolved in distilled and deionized water. The initial 100 ml of water was heated to 80°C

and maintained at this temperature for 15 minutes. The aqueous solution of the initial reagents was added to the flask, and the reaction temperature was increased to 80°C. Then, the initiator solution was added dropwise to the reaction mass using a dropping funnel. The initiator solution was calculated based on the molar amount of the initial monomers. The reaction process was conducted following a laboratory protocol developed for obtaining a polycarboxylate plasticizer based on acrylic acid and unsaturated polyethylene glycol.

The synthesized polycarboxylate plasticizer was tested without preliminary cleaning. It was reduced to 30% on a dry basis, and the amounts used in the test procedures were calculated based on this concentration. The resulting plasticizer belongs to the group of polyelectrolytes and contains carboxyl groups and oxyethylene groups in its chain structure. The average molecular mass and structure of the product obtained during the synthesis of the polycarboxylate plasticizer are of great importance.

The synthesis of the copolymer (plasticizer) from AA and APEG was carried out based on the following reaction mechanism.



(X =? ; Y=? listed below)

APEG macromer is 40 (n=40). The mutual values of acrylic acid and APEG macromer in the reaction product were estimated based on gel chromatography analysis and the structure was worked out.

The molecular weight and macromolecular structure of plasticizers have a significant impact on the plasticization process, the hardening time of cement-based building mixtures, and the strength indicators of the final product. Therefore, it is important to determine the molecular weight of high-quality plasticizers.

Research Method. The molecular mass parameters of the samples were determined using an Agilent 1260 Infinity high-performance liquid chromatograph. A refractometric detector was used in the analysis. The concentration of the polymer solution and the volume of the dispenser were 2 mg/ml and 20 µl, respectively. The eluent flow rate was 0.8 ml/min. The chromatographic column was made of cylindrical stainless steel, with a length of 25 cm and an inner diameter of 0.8 cm, filled with TSK GM PW XL (Toya Soda, Japan) sorbent. The molecular masses of the copolymers were calculated using Windows Chemstation 7 software and Benoit's universal calibration method.

Determination of the molecular mass of polyelectrolytes in ESX is carried out by eliminating one or more electrostatic effects. These phenomena are known as ion

exclusion, polyelectrolyte precipitation (PB), molecular adsorption, and ion inclusion. If there are residual hydroxyl or anionic groups on the surface of the sorbent, ion exclusion occurs in the chromatography of anionic polyelectrolytes. If the surface of the sorbent is neutral under these conditions, polyelectrolyte precipitation occurs. When water is used as an eluent in a hydrophilic sorbent, and if the polyelectrolyte has a positive charge, molecular adsorption occurs. These effects disrupt the molecular sieve of ESX, that is, the mechanism of separation of macromolecules according to their geometric (hydrodynamic) dimensions. The phenomenon of PB is manifested in chromatograms by the elongation of the front part of the elution curve and a sharp decrease in the rear part. This is due to the fact that the polymer solution is initially introduced into the chromatographic column in the form of a narrow rectangular shape through a dispenser.

When the polymer solution, together with the eluent (or solvent), moves along the column, the macroions corresponding to the front and back sides of the chromatographic peak increase in their geometric size due to the phenomenon of polyelectrolyte precipitation. This results in asymmetric elution curves. To eliminate these phenomena, neutral salts with a concentration of 0.1 mol/l, such as NaCl or $NaNO_3$, are added to the eluent. As a result, the cations of the salts neutralize the Coulomb forces created by the anionic groups in the macroions, and the chromatograms become symmetrical. This phenomenon is illustrated by superimposed gel chromatograms of the copolymer sample solution taken in water at different concentrations, as shown in Figure 1a.

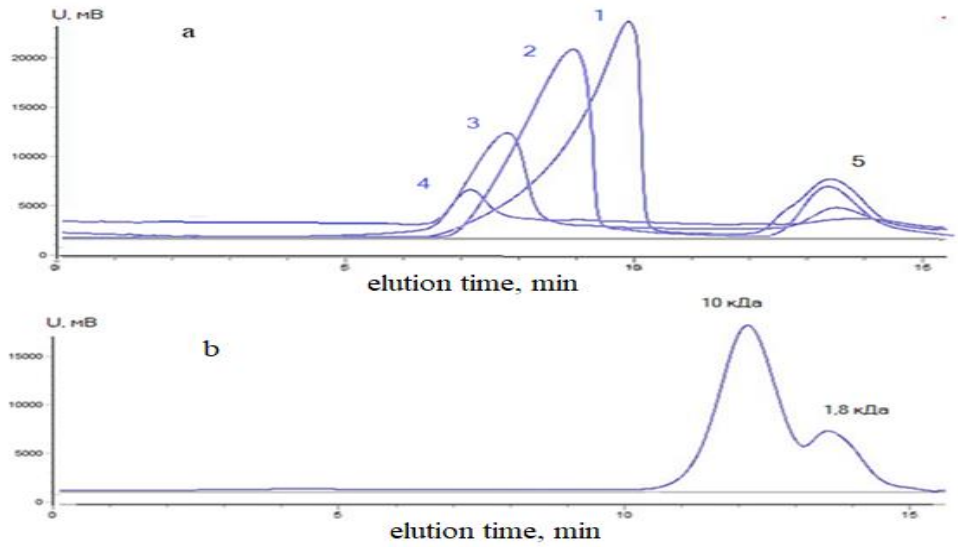


Figure 1. The result of gel chromatography analysis of the obtained plasticizer. a) Gel chromatograms of copolymer sample solution 1 in water at different concentrations. Concentration values, %: 1 - 2%; 2 - 1.5%; 3 - 0.75%; 4 - 0.3%; 5 - PEG. b) Gel chromatogram obtained in a 0.1 M $NaNO_3$ aqueous solution of the sample.

The concentrations in samples 4 and 1 in the gel chromatograms presented in Figure 1 vary from 0.3% to 2%, respectively. An increase in the concentration of the sample corresponds to an increase in the elution time because, in this case, a reduction in the

mechanism of polyelectrolyte precipitation is observed. This leads to a decrease in the geometric size of the macroions. Gel chromatogram 5 in Figure 1a showed the separation of the monomer fraction from the copolymer. The phenomenon of polyelectrolyte precipitation was not observed in the monomer fraction at all concentrations. If the monomer and macromer are denoted by the letters AA (A) and APEG (B), respectively, this indicates that the copolymerization reaction does not occur in the form -A-A-A-B-, but rather in the form -A-A-B-A-.

Results and Discussion. Figure 1b shows the gel chromatogram of the copolymer sample where a 0.1 M $NaNO_3$ aqueous solution was used as the eluent. It can be seen that the gel chromatogram became symmetrical in the saline solution, indicating that the PB effect was eliminated and the molecular sieve separation mechanism of ESX was activated. In the gel chromatogram, it was determined that the molecular mass of the copolymer is 10 kDa, and that of the monomer is 1.8 kDa.

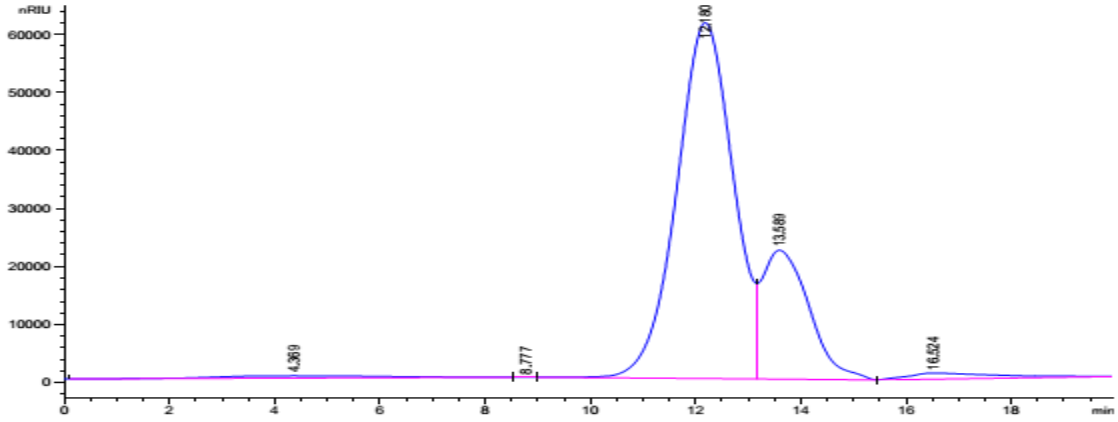


Figure 2. Chromatogram of the resulting plasticizer.

From Figure 2, it can be seen that the high molecular mass copolymer is separated in the range of about 11-13.3 minutes, while the macromer mass retained in the sorbent pores is separated in the range of 13-14.5 minutes.

Table 1. Chromatography results of the obtained plasticizer.

peak	RetTime [min]	Type	Width [min]	Area [nRIU*s]	Height [nRIU]	Area %
1	4.369	BV	2.3937	8.59484 e4	421.57,028	1.3941
2	8.777	BB	0.1911	93.49422	5.978 0 5	1.517 e-3
3	12.188	BV	1.1460	4.57761 e6	6.13 0 8 4e 4	74.2517
4	13,589	VB	0.9750	1.37851 e6	2.2215 0e4	22.3683
5	16,524	BBA	1.5025	1.22882 e5	1039.03711	1.9923

From Table 1 above, it can be seen that the main mass was separated in 12.188 minutes, which accounts for 74.25%. The next major mass was separated at 13.589 minutes, accounting for 22.36%. The first major mass belongs to the 10 kDa molecular

mass fraction, that is, the copolymer, and the next mass belongs to the macromer with a mass of 1.8 kDa. Based on this information, we can calculate the macromer and monomer values in the resulting copolymer chain.

The amount of macromer and the amount of copolymer increased in the synthesized product were calculated. When calculating the masses of the initial reagents, 97% belong to the monomer and macromer. If the molar ratio of the initial monomer and macromer is 1:1, conditionally AA-98 and APEG-1800, then 98 g of acrylic acid corresponds to 1800 g of APEG. The total mass is 1898 g. Based on the dry residue, 22.36% of the main mass, the part with a mass of 1.8 kDa, belongs to the macromer, which is 21.68% of the initial monomer and macromer. When calculated:

$$C_{\%(makr)} = \frac{M_{residual\ makr}}{M_{умум}} * 100\%; \textit{ from this:} M_{residual\ makr} = \frac{M_{common} * C_{\%(makr)}}{100\%}$$

$$\textit{originates, } M_{residual\ makr} = \frac{1898 * 21.68}{100\%} = 411{,}49 \text{ гр},$$

$$\textit{or } \frac{411{,}49}{1800} = 0{,}228\ \textit{mole},$$

Therefore, the amount of unreacted macromer is 22.8% of the macromer obtained from the reaction. It follows that the ratio of the initial monomer to macromer is 1:0.771. Based on the obtained results and calculation data, the values of the unknown numbers (x, y) in the aforementioned reaction mechanism are derived and, accordingly, x=1 and y=0.771.

Conclusion. The information presented in the article allows for the improvement of the efficiency of synthesized polycarboxylate plasticizers and the expansion of their fields of application. Additionally, these studies are of great importance in the development of high-performance concrete compositions, as they enhance the performance characteristics of building materials and help optimize engineering solutions. Furthermore, these studies contribute to a deeper understanding of the relationships between the reaction mechanisms of copolymers and the molecular structure of their products.

Future research should focus on developing more optimized synthesis methods for these plasticizers and expanding their practical applications. Further research is also needed on the environmental safety and sustainability of these plasticizers. New knowledge obtained through targeted scientific research can lay the groundwork for further progress in this field.

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