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## SYNTHESIS OF ALLYLCAPRYLATE-STYRENE COPOLYMERS WITH STYROLE AND THEIR RESEARCH AS A VISCOSITY ADDITIVE TO LUBRICANT OILS

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**Abstract:** The article presents results of copolymerization of allyl ether of caprylic acid - allylcaprylate with styrene in line with radical mechanism, the influence of the main factors - the composition of primary monomers and initiator consumption on the process, as well as results of studies synthesized copolymer as a viscosity additive in the composition of lubricating oils. It found that samples of synthesized polymer compounds are on a par with industrial additives of the polyalkylmethacrylate type on improving viscosity-temperature properties, but have higher operational characteristics than industrial additives in terms of resistance to thermal effects due to the stabilizing effect of styrene units. The study into samples of synthesized copolymers as oil additives showed that depending on specific requirement, a polymer compound of any molecular weight can be synthesized in high yield for use as viscosity additive for these oils.

**Keywords:** caprylic acid, allyl alcohol, allylcaprylate, styrene, copolymer, viscosity additive, petroleum oil

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### Introduction

Obtaining of basic oils with high viscosity index is one of the urgent problems of present-day oil chemistry. The higher the viscosity index value which characterizes viscosity-temperature properties of oils, the lesser the viscosity of oils changes due to the effect of temperature and can be considered valuable. Viscosity-temperature properties of oils are determined with due regard for their chemical composition, purification degree, development level of production technology and so on. It is possible to obtain a required value of viscosity index by changing the above-mentioned factors. The simplest, economically profitable and rational way of oils production with high viscosity index is the use of petroleum oils - viscosity additives comprising a small amount of polymer compounds, i.e. it is possible to achieve any result with the least material expenses.

Oil-soluble polymers and copolymers of polyisobutylenes, polyalkylmethacrylates and other vinyl monomers are used as viscosity

additives [1-4]. However, these additives meet no requirements of modern techniques on resistance to destructive effects.

The analysis of research works on the synthesis and study of polymethacrylate additives shows that obtaining of complex ether polymers are more promising than hydrocarbon type polymers, for they are obtained by simple technology and improve viscosity-temperature properties of oils more effectively. From this point of view, to expand the feedstock of monomers used for obtaining of viscosity additives complex allyl ethers were synthesized and certain researches were carried out to obtain synthetic and petroleum oils by polymerizing them with vinyl monomers [5-8].

The present paper explores results of experiments performed to obtain viscosity additives for petroleum oils using allyl monomers - allyl ether of caprylic acid (octanoic acid) - allylcaprylate.

As is known, allyl monomers are not polymerized separately; however, they easily

enter into copolymerization reaction. That's why obtained monomers (allylcaprylate) were copolymerized with styrene. Styrene is one of the cheap monomers of oil chemistry and inclusion

of styrene units into open chain polymer macromolecule gives stability to copolymers to thermal impacts.

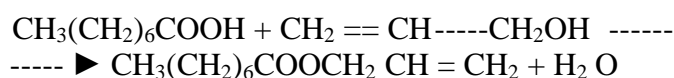
### Experimental part

Allylcaprylate is obtained by influencing caprylic acid with allyl alcohol through the well-known etherification reaction.

Caprylic acid (octanoic acid) and allyl alcohol were taken as a reactive. Both acid and allyl alcohol are included into etherification reaction in a freshly distilled form. Physical and chemical properties of an acid: mol. mass  $M_r = 144.2$ , melting temperature  $T_{\text{melt.}} = 16.63^\circ\text{C}$ , boiling temperature  $T_{\text{boil.}} = 239.3^\circ\text{C}/760 \text{ mm}$  ( $124^\circ/10 \text{ mm}$ ), refraction coefficient  $n_D = 1.4280$ , density  $d_4^{20} = 0.99089 \text{ g/cm}^3$ , physical and chemical properties of

allyl alcohol: mol. mass  $M_r = 58.8$ , melting temperature  $T_{\text{melt.}} = -129^\circ\text{C}$ , boiling temperature  $T_{\text{boil.}} = 97^\circ\text{C}$ , refraction coefficient  $n_D = 1.4133$ , density  $d_4^{20} = 0.854 \text{ g/cm}^3$ .

The reaction was methodically performed as follows. Calculated amount of reagents, certain amount of toluene (to separate water by azeotropic distillation), KU-2 cationite in the amount of 1% of reaction mixture were added to three necked flask supplied with Dean-Stark apparatus and the mixture was heated at  $110\text{--}120^\circ\text{C}$  temperature by mixing till water boiling:



Upon completion of the process, KU-2 catalyst was separated from the filtering system, the product was washed off with hot water distilled in vacuum after traces of toluene and allyl alcohol were separated. Obtained allyl ether was used in copolymerization with styrene.

Synthesized allylcaprate ether had the following physical and chemical properties:  $M_r = 184$ ,  $n_D = 1.4276$ ,  $d_4^{20} = 0.909 \text{ g/cm}^3$ .

Styrene was used as a chemical reagent in distilled form; its physical and chemical properties were as follows:  $M_r = 104.15$ ,  $n_D = 1.5465$ ,  $d_4^{20} = 0.909 \text{ g/cm}^3$ , melting temperature  $T_{\text{melt.}} = -30.06^\circ\text{C}$ , boiling temperature  $T_{\text{boil.}} = 145^\circ\text{C}$ .

### Results and discussion

As Table 1 shows, the main factors influencing the process are the composition of primary monomer and amount of an initiator (Table 1). The rise of styrene in monomer mixture from 5% to 25% causes the increase in the yield of copolymer from 25.0% to 91.3% and molar mass from 3000 to 8000. This is explained as being due to the fact that styrene has a high polymerization property and the rise

Copolymerization was performed in solution medium (hexane or heptane) with the presence of dinitrile of azo-(bis)-isooil acid as an initiator using radical polymerization mechanism. The effect of copolymerization condition on the properties of copolymer was studied and the results given in Table 1.

The composition and structure of synthesized compounds were studied using IR- and NMR-spectroscopy methods.

Thermal resistance of synthesized copolymer was determined by reduction of viscosity depending on the probation occurring in 5% of solution in Turbin "L" oil using known technique [10].

in its amount in monomer mixture causes the process acceleration and the rise in yield and molar mass. Allyl monomers are not polymerized separately, i.e. form no homopolymers and enter into polymer chain due to copolymerization. Thus, amount of allyl monomers must not be higher than 50 mol% and when the amount of it exceeds the given value the yield of copolymer and molar mass

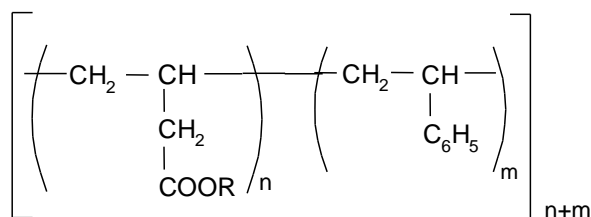
decrease. The increase of initiator amount from 0.3% to 1% raises the yield of copolymer, however causes the decreases of molar mass and this is typical for radical polymerization.

**Table 1.** Copolymerization of allylcaprylate with styrene

Copolymerization condition				Character of copolymerization	
Amount of styrene in monomer mixture, mass %	Amount of initiator, %	Duration of process, hour	Temperature (°C)	Yield, mass %	Molar mass
5	1	4	75	25.0	3000
10	1	4	75	53.4	4000
15	1	4	75	60.8	5000
20	1	4	75	85.5	7000
25	1	4	75	91.3	8000
20	0.3	4	75	50.1	9000
20	0.5	4	75	71.2	8000
20	0.7	4	75	77.3	7500
20	1	4	75	83.4	7000
20	1	3	75	77.8	7000
20	1	6	75	79.9	7100
20	1	4	65	76.5	7200
20	1	4	85	81.5	7000

Temperature changes in the range of 65-85°C and increase of polymerization duration do not influence the process sharply while an amount of initiator taken less than 1% causes the decrease in yield and increase in molar mass. That's why reaction conditions that provide the high yield and molar mass parameters can be selected as follows:

temperature 75 °C, process duration 4 hours, amount of an initiator for monomer mixture - 1.0%. The structure of synthesized copolymer was studied by IR- and NMR-spectroscopy methods and according to results obtained the following schematic general formula was proposed for obtained copolymers:



here  $n = 8-19$ ,  $m = 18-34$ ,  $R$  - caprylic acid radical

Synthesized copolymer was studied as viscosity additive for lubricants. The impact of viscosity-temperature properties of H-12A

petroleum oil on copolymer density with molar mass of 8000 was studied and the results given in Table 2.

**Table 2.** Impact of copolymer density on viscosity-temperature of H-12A oil

Density of copolymer, mass %	Kinematic viscosity of oil concentrated at 100°C, mm <sup>2</sup> /sec	Viscosity index (VI)
0	3.11	89
0,5	3.67	104
1	4.22	114
2	5.53	132
3	6.29	134
5	8.03	136
7	9.09	136

As Table 2 shows, rise in the density of oil copolymer from 0.5% to 5% led to the increase in viscosity index (VI) from 89 to 138. Further increase in density (7%) did not cause the increase of viscosity index and that was general regularity of concentrating oils. In considering that the demand VI for concentrated oils with viscosity of  $8 \pm 0.5$  mm<sup>2</sup>/sec at 100°C must not be less than 125, according to Table 2, we may obtain oil with required properties by adding 5% of copolymer into H-12A oil.

The influence of molar mass of synthesized copolymer on viscosity-temperature properties of H-12A oil was studied. Oil was concentrated and studied with copolymer at

100°C till kinematic viscosity reached 7.5-8.5 mm<sup>2</sup>/sec. Results were summarized in Table 3 and all samples used to concentrate oil met the requirements for VI value. However, with the reduction of molar mass it is necessary to increase the amount of copolymer in oil content to achieve the required value of viscosity of oil and this is not economically effective. The increase in molar mass causes decreases resistance of copolymer in oil content to destructive effects. Molar mass value of copolymer to be used as a viscosity additive is selected relevant to a certain demand put for resistance of concentrated oil.

**Table 3.** Influence of molar mass of synthesized copolymer on viscosity-temperature properties of H-12A oil

Characteristics			
copolymer		concentrated oil	
molar mass	density,%	kinematic viscosity at 100°C, MM <sup>2</sup> /C	viscosity index
10000	4.0	7.6	136
9000	5.5	7.9	133
8000	6.0	7.8	130
5000	9.0	7.9	128
3000	10.2	7.6	125
Polyalkyl methacrylate			
10000	4.1	8.1	138

According to Table 3, examined samples are in the same level with industrial viscosity additive - polyalkylmethacrylate for improving viscosity-temperature properties of H-12A oil.

Thermal resistance of synthesized copolymer samples was studied in comparison with known viscosity additives polyisobuthylene and polyalkylmethacrylate by

heating their 5% solutions in turbine "L" oil at 200°C for 12 hours. It was determined that synthesized copolymer exhibits higher operating characteristics than polyalkylmethacrylate type industrial additives due to its resistance to thermal effects. For oil concentrated with copolymer the reduction of viscosity due to destruction is 7.0-7.5%, and this indicator is into

the range of 9.5-11.4 and 13.7-17.9% for polyisobuthylene and polyalkylmethacrylates, accordingly. These results show that the inclusion of cyclic aromatic fragment in styrene molecule into copolymer increases resistance of obtained macromolecular compound to thermal effects

### Conclusion

Copolymers of allyl ether - allylcaprylate of caprylic acid with styrene were obtained by means of radical copolymerization. Also, the composition of primary monomers and amount of initiator - the main factors that influence the process were determined. It revealed that the rise in the styrene amount of monomer mixture caused the increase in yield of copolymer and molar mass. This was explained as being due to the fact that styrene had a high polymerization property and the increase in its amount in monomer mixture led to the process acceleration and increase in yield of molar mass. The amount of allyl monomers in copolymer of more than 50 mol% reduced the yield of copolymer and molar mass. The increase of initiator amount from 0.3% to 1%

raised the yield of copolymer, however, decreased the molar mass and this is believed to be typical for radical polymerization. Synthesized triple copolymer samples were studied as viscosity additives to petroleum oils and it found that depending on the demand may use these oils as viscosity additives by synthesizing any high molar mass copolymers with high yield.

Since synthesized copolymer samples are in the same level with polymethacrylate industrial additives in terms of improving viscosity-temperature properties of oils, the results showed their higher operating indicators in terms of thermal resistance and this case must be explained by stabilizing effect of styrene units.

### References

1. Kaplan S.Z., Radzevenchuk I.F. Viscous additives and thickened oils. L.: Himiya Publ., 1982. 132 p. (In Russian).
2. Kuliev A.M. Chemistry and technology of additives to oils and fuels. Leningrad: Himiya Publ., 1985, 312 p. (In Russian).
3. Akhmedov A.I., Farzaliev V.M., Aliguliev R.M. Polymer additives and oils, Baku: Elm Publ., 2000, 175 p. (In Azerbaijan).
4. Akhmedov A.I. State of research on the synthesis of viscous additives in the republic. *Azerbaydjanskoe Neftyanoe Khozyaystvo - Azerbaijan Oil Industry*. 2002, No. 4, pp. 37-39.
5. Akhmedov A.I., Askerova Kh.A., Isakov E.U., Gamidova D.Sh. Synthesis of viscosity additives for lubricating oils by copolymerization of butyl methacrylate with allyl naphthenates. *Nefttepeperabotka i Neftchemiya - Oil Processing and Petrochemistry*. 2009, no. 5, pp. 31-33. (In Russian).
6. Ahmadov A.I., Hamidova J.Sh., Isakov E.U., Adigozalova F.C. Synthesis of copolymers of allylnaphthenates with styrene as viscosity additives. *Azerbaijan Chemical Journal*. 2009, no. 2, pp. 119-121.
7. Farzaliyev V.M., Ahmadov A.I., Hasanova E.I. Synthesis of butylmethacrylate-o-allylphenol copolymers as viscosity additives to complex essential oils. *AMEA-nin meruzeleri - Report of ANAS*. 2009, no 6, pp. 79-83. (In Azerbaijan).
8. Kazimzadeh L.K., Hamidova D.Sh., Hasanova E.I. Co-oligomers of allyl ethers as viscosity additives. *Mejdunarodniy Nauchniy Jurnal - International Scientific Journal "Young Scientist"*. 2019, no. 52 (290), pp. 309-312. (In Russian).
9. Preparative Organic Chemistry. / Edited by N.S. Wulfson. Moscow: Himiya Publ., 1964, pp. 440-450.

**ALLİLKAPRİLAT-STİROL BİRGƏ POLİMERİNİN SINTEZİ VƏ SÜRÜKÜ YAĞLARINA ÖZLÜLÜK AŞQARI KİMİ TƏDQIQI**

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Məqalədə kapril turşusunun allil efirinin - allilkaprilatın stirolla birgə polimerinin radikal mexanizmi üzrə birgə polimerləşməsinin, prosesə əsas amillərin - ilkin monomer qarışığının və inisiatorun təsirinin və birgə polimerin sürükü yağlarının tərkibində özlülük aşqarı kimi tədqiqinin nəticələri verilmişdir. Müəyyən edilmişdir ki, sintez edilmiş birgə polimer nümunələri yağların özlülük-temperatur xassələrini yaxşılaşdırmağa görə polialkilmetakrilat tipli sənaye aşqarları ilə eyni səviyyədə olduğu halda, termiki təsirlərə qarşı davamlılıqlarına görə onlardan daha yüksək istismar göstəricilərinə malikdirlər ki, bu hal isə stirool manqalarının stabilləşdirici təsiri ilə izah olunmalıdır. Sintez olunmuş birgə polimer nümunələrinin neft yağlarına özlülük aşqarları kimi tədqiqi göstərmişdir ki, tələbatdan asılı olaraq istənilən molekul kütləyə malik yüksək çıxımlı birgə polimerlər sintez edərək, bu yağlara özlülük aşqarı kimi istifadə etmək olar.

**Açar sözlər:** kapril turşusu, allil spirti, allilkaprinat, stirool, birgə polimer, özlülük aşqarı, neft yağları

**СИНТЕЗ СОПОЛИМЕРОВ АЛЛИЛКАПРИЛАТА СО СТИРОЛОМ И ИССЛЕДОВАНИЕ ИХ В КАЧЕСТВЕ ВЯЗКОСТНЫХ ПРИСАДОК К СМАЗОЧНЫМ МАСЛАМ**

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В статье представлены результаты исследования сополимеризации аллилового эфира каприловой кислоты - аллилкаприлата со стиролом по радикальному механизму, влияния состава смесей исходных мономеров и расхода инициатора на процесс, а также результаты исследования синтезированного сополимера в качестве вязкостной присадки к смазочным маслам. Установлено, что образцы синтезированных полимерных соединений по улучшению вязкостно - температурных свойств находятся на одинаковом уровне с промышленными присадками полиалкилметакрилатного типа, но имеют более высокие эксплуатационные характеристики, чем промышленные присадки по устойчивости к термическим воздействиям, что обусловлено стабилизирующим действием стирольных звеньев. Исследование образцов синтезированных сополимеров в качестве присадок показало, что в зависимости от конкретных требований, предъявляемых к маслам, могут быть синтезированы полимерные соединения с различной молекулярной массой и высоким выходом для использования их в качестве вязкостной присадки к маслам.

**Ключевые слова:** каприловая кислота, аллиловый спирт, аллилкаприлат, стирол, сополимер, вязкостные присадки, нефтяные масла.