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THE RESEARCH OF COPOLYMERIZATION REACTIONS OF ALLYL AND VINYL ACETYLSALICYLATES WITH MALEIC ANHYDRIDE

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The copolymerization reactions of allyl- and vinyl ether of salicylic acid with maleic anhydride (MA) have been researched. It was shown that with transferring charge copolymer monomer pairs make complex and these complexes form rotational structure macromolecules with entering polymerization reaction easily. Equilibrium constant of complex among monomer pairs was defined with the help of PMR spectrums: for Al_{asp}…MA couple K_c=0.097 and for V_{asp}…MA K_c=0.028. Via Chromatographic method – Jaaks equation relative activities of monomers have been identified. For Al_{asp}–MA comonomer is r_1=0.022, r_2=0.038 and for V_{asp}– MA comonomers r_1=0.036, r_2=0.028. Being close to zero of relative activities of monomer in both case in copolymerization reactions prove that, those monomer pairs are inclined to copolymerization. The relativity of monomer pairs and the influence to the reaction of the concentration of monomer mixture in the copolymerization reactions of V_{asp} and MA is studied. The nature of curves is proved that the copolmerization reactions occurs by ″mixture″ mechanizm by the presence of free monomers and monomer complex.

Keywords*: allylacetilsalicylic ether, vinylacetilsalicylic ether, copolymerization, complexes made by transfer of charge.*

Introduction

Recent years the interest to the synthesis of polymers keeping biological active groups is increasing. Thus, such kind of polymers are widely used in obtaining long effective medications, antiseptic polymer coverings, paint and so on.

On the other hand, such kind of polymers being used as bactericidal additions in obtaining antibacterial polymer composites are considered more perspective. Because washing out polymer additions from material surface happens during longer time in comparison with little molecular antibacterial compounds and using time of such coverings increases. One of the polymers with antibacterial property are polymers containing salicylic groups. One of the obtained methods of polymers is polyvinyl salicylate polymers obtained with mutual effects of polyvinyl alcohol and acetylsalicylic acid by polymer analogy conversion method [1]. In our earlier investigations it was shown that polymers keeping salicylic groups have high antibacterial properties [2].

In our earlier investigations the obtaining methods of monomers – (met)acryloyl salicylates keeping salicylic groups and copolymers on the base of them were reported. It was shown that these monomers and also methyl methacrylate copolymers obtained on their base have high antibacterial properties [3].

The purpose in presented work is the research of copolymerization reaction of allyl and vinyl ethers (Al_{asp} and V_{asp}) of acetylsalicylic acid with maleic anhydride (MA) for the obtaining polymers keeping acetylsalicylic group. MA is chosen as comonomer because of the solubility of obtained copolymers.

Experimental part

The synthesis of monomers. V_{asp} monomer was obtained due to mutual effect of vinylacetate with aspirin by *trans*-vinylization reaction [4]. d_4^{20}=0.93 and n_D^{20}=1.4200. The synthesis of Al_{asp} monomer was carried out on the base of exchange reaction of Na salt of aspirin with allylchloride [5].

The synthesis of copolymers of V_{asp} and MA. 0.059 mol (10.30 g) vinylacetil salicylic ether (V_{asp}), 0.05 g (4.99 mol) maleic anhydride, 0.2% benzoyl peroxide and 35 ml dioxane mixture are poured into the glass ampoule. After freezing solution its air is take off with nitrogen. Reaction product is precipitated in methanol, is washed with ether and dried at

40^0C temperature in vacuum wardrobe till it gets constant weight.

The obtained white power polymer methyl-ethyl-ketone is solved well in benzol and chlorine hydrocarbon. Yield is 9.89 g (68%) T_{mel} – 131^0C, characteristic viscosity is identified in benzol solution in ″Ubbelohde″ viscozimetry [η] 0.11dl/g were recorded.

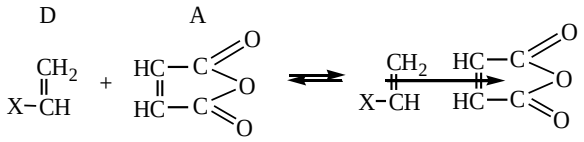
The kinetics of copolymerization reaction is studied by dilatometric way [6].

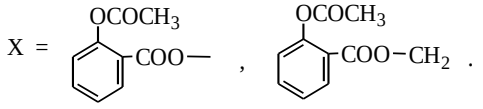
The content of monomer mixture before and after reactions is identified by the ″Chrom-5″ gas-liquid chromatograph.

IG spectrums in ″VARIAN″, PMR spectrums were recorded in dayterium chloroform in ″Bruker″ spectrometry.

Results and their discussions

The formation of donor (D)–acceptor (A) type complexes (complexes formed by charge transfer) among the molecules of allylacetilsalicylate maleic anhydride was mentioned ago [7]. Taking into account this PMR spectrum of monomers in separate and in different proportions mixture have been recorded. Rate change of chemical sliding of protones belonging to MA molecule in PMR spectrum of different composition mixtures of MA and V_{asp} monomers show the formation of [D…A] type complex.





The changing in sliding rate increases with enhancing of mol proportion of donor in monomer mixture. Equilibrium constant (K_c) of complex forming process was graphically calculated by Ketalaar equation [8] (Table 1).

$$[D]+[A] \xrightleftharpoons{K_c} [D...A],$$

$$K_c = \frac{[D...A]}{[D]\cdot[A]}.$$

Table 1. Indicators for the calculation of complex forming constants (K_c) of allyl and vinyl acetylsalicylates (D) with maleic anhydride

Monomer pairs	[A], mol/l	[D], mol/l	$1/\Delta_{eks}$, ppm	1/D, l/mol
Al_{asp}–MA	0.1	1.0	42.0	1.00
	0.1	2.0	17.0	0.50
	0.1	4.0	12	0.25
V_{asp}–MA	0.1	1.0	71.0	1.0
	0.1	2.0	39.0	0.50
	0.1	4.0	11.0	0.25

According to the calculation for Al_{asp}–MA monomer pairs is K_c=0.097 and for V_{asp}–MA monomer couple is K_c=0.028.

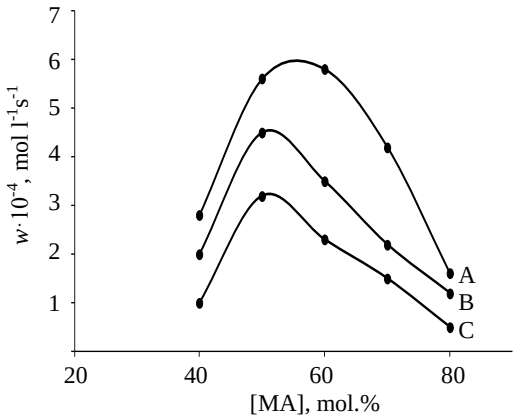
Rates of copolymerization constants of Al_{asp} and V_{asp} with MA were calculated by chromatographic Jaaks method [9] (Table 2).

Table 2. Results of copolymerization reactions of allyl and vinyl acetylsalicylic ethers with maleic anhydride

Preliminary composition of monomer mixture, mol.%		Composition of monomer mixture after reaction, mol.%		r_1	r_2
$[M_1]_0$	$[M_2]_0$	$[M_1]_t$	$[M_2]_t$		
Al_{asp}	MA				
10	90	8.73	89.53	0.022	0.038
90	10	85.6	5.85		
V_{asp}	MA				
10	90	8.47	89.53	0.036	0.028
90	10	87.9	8.76		

For Al_{asp}–MA monomer pair r_1=0.022, r_2=0.038 and r_1=0.036, r_2=0.028 for V_{asp}–MA monomer pair. Being close to zero of rates of relative and activities in copolymerization reactions in monomers prove that copolymers have alternative structure. Having C=O (1725 sm^{-1}), C–O–C (1150 sm^{-1}) copolymer strips in IR spectrums and (1630–1640) absorption strips belonging to C=C contact are one the factors proving copolymer formation.

One may come to conclusion that, complex formed among monomers effect their relative reactivity. MA macro radicals formed from monomer pairs MA molecule cannot join MA molecule and (MA...V_{asp}) complex by MA component. The created complex behaves like free monomer. The dependence on the composition of monomer mixture of general speed of copolymerization reactions for V_{asp}–MA monomer pairs was studied (Figure).



The dependence of initial velocity of the copolymerization reaction V_{asp} and MA's on content of MA at different summary concentrations of monomers [M] in the reaction system: mixture with: A – [M]=4.0 mol/l, B – [M]=3.2 mol/l, C – [M]=2.8 mol/l.

As is seen in the Figure this dependence is extremal. Displacement of curves depending on the general concentration of monomer mixture of maximum is observed. This fact proves participation of both free monomers and complex in copolymerization reaction [10].

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ALLİL- VƏ VİNİLASETİLSALİSİLATLARIN MALEİN ANHİDRİDİ İLƏ SOPOLİMERLƏŞMƏ REAKSİYALARININ TƏDQİQİ

N.Ş.Rəsulzadə, A.H.Əzizov, G.M.Səfərova, N.Ş.Rəsulov

Salisil turşusunun allil və vinil efirlərinin malein anhidridi ilə sopolimerləşmə reaksiyaları tədqiq edilmişdir. Göstərilmişdir ki, sopolimerləşən monomer cütləri yükün ötürülməsi ilə kompleks əmələ gətirir ki, həmin komplekslər asanlıqla polimerləşmə reaksiyalarına daxil olaraq növbəli quruluşlu makromolekullar əmələ gətirir. Monomer cütləri arasında yaranan kompleksin tarazlıq sabitləri PMR spektrlərin köməyilə təyin olunmuşdur: Al_{asp}…MA cütü üçün K_c=0.097 və V_{asp}…MA cütü üçün isə K_c=0.028. Xromatoqrafik üsulla – Jaaks tənliyinin köməyilə monomerlərin nisbi aktivlikləri təyin edilmişdir. Al_{asp}−MA somonomerləri üçün r_1= 0.022, r_2= 0.038 və V_{asp}−MA somonomerləri üçün isə r_1=0.036, r_2=0.028-dir. Sopolimerləşmə reaksiyalarında hər iki halda monomerin nisbi aktivliklərinin sıfıra yaxın olması həmin monomer cütlərinin sopolimerləşməyə meyilli olduğunu sübut edir. V_{asp} və MA-nın sopolimerləşməsi reaksiyalarında monomer cütlərinin nisbətinin və monomerlərin ümumi qatılığının reaksiyanın başlanğıc sürətinə təsiri öyrənilmişdir. İlkin monomerlərin ekvimolyar nisbətlərində *w* maksimum qiymətlərində müxtəlif ümumi qatılıqlarında sopolimerləşmənin başlanğıc sürətinin MA-nın tərkibindən asılılığı əyrilərinin ekstremal xarakteri zəncirin böyüməsinin həm sərbəst monomerlərin, həm də monomer-kompleksin iştirakı ilə baş verdiyini sübut edir.

Açar sözlər: *allilasetilsalisil efiri, vinilasetilsalisil efiri, sopolimerləşmə, sopolimerləşmə sürəti, yükün ötürülməsilə yaranan kompleks.*

ИССЛЕДОВАНИЕ РЕАКЦИИ СОПОЛИМЕРИЗАЦИИ АЛЛИЛ- И ВИНИЛОВЫХ ЭФИРОВ АЦЕТИЛСАЛИЦИЛОВОЙ КИСЛОТЫ С МАЛЕИНОВЫМ АНГИДРИДОМ

Н.Ш.Расулзаде, А.Г.Азизов, Г.М.Сафарова, Н.Ш.Расулов

Исследован реакции сополимеризации аллил- и виниловых эфиров ацетилсалициловой кислоты (Al_{asp} и V_{asp}) с малеиновым ангидридом (МА). Показано, что мономерные пары образуют комплексы с переносом заряда (КПЗ), которые легко превращаются в сополимер чередующейся структуры. Константы комплексообразования вычислены на основе спектров ПМР−смеси сомономеров методом Кетаалара; для Al_{asp}…МА K_c = 0.097, для V_{asp}…МА K_c = 0.028. Относительные активности мономеров при сополимеризации определены методом Яакса с использованием данных хроматографического анализа смеси мономеров до и после реакции сополимеризации. Они соответственно равны r_1=0.022, r_2=0.038 для мономеров Al_{asp}− МА и r_1=0.036, r_2=0.028, для мономеров V_{asp}−МА. В обоих случаях относительные активности сополимеризующихся мономеров близки к нулю, что доказывает высокую тенденцию к сополимеризации мономерных пар. Изучены зависимости начальной скорости реакции сополимеризации V_{asp} и МА от состава исходной мономерной смеси при различных суммарных концентрациях мономеров в реакционной смеси. Экстремальный характер кривых зависимости начальной скорости сополимеризации от содержания МА при различных суммарных концентрациях мономеров с максимумами значений *w* при эквимольном соотношении исходных мономеров позволяет предположить протекание роста цепи с участием свободных или комплексно-связанных мономеров.

Ключевые слова: *аллиловый эфир ацетилсалициловой кислоты, виниловый эфир ацетилсалициловой кислоты, сополимеризация, комплекс с переносом заряда.*