CHEMISTRY AND TECHNOLOGY OF MEDICINAL COMPOUNDS AND BIOLOGICALLY ACTIVE SUBSTANCES

ХИМИЯ И ТЕХНОЛОГИЯ ЛЕКАРСТВЕННЫХ ПРЕПАРАТОВ И БИОЛОГИЧЕСКИ АКТИВНЫХ СОЕДИНЕНИЙ

ISSN 2686-7575 (Online)

https://doi.org/10.32362/2410-6593-2021-16-5-399-413

UDC 541.64+678.55+632.952

RESEARCH ARTICLE

Synthesis and properties of vinyl benzyl alcohol copolymers with styrene

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Abstract

Objectives. *Synthesis and study of the properties of copolymers of vinyl benzyl alcohol (VBA) with styrene with antimicrobial properties.*
Methods. *The study employed infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy, thin-layer chromatography, viscometry, and elemental analysis. The sessile drop method and the pencil method were respectively utilized to determine the contact angles and hardness of the films. The process of testing the film coatings' resistance to the effects of molds consisted of contaminating the film coatings applied to the glass with mold spores of the All-Russian Collection of Microorganisms in a solution of mineral salts without sugar (Czapek–Dox medium).*
Results. *Homopolymers of vinyl benzyl acetate and its copolymers with styrene were synthesized in this study. Homo- and copolymers of VBA were obtained by saponification. IR and proton NMR (^1H NMR) spectroscopy determined the composition of the copolymers. Employing IR spectroscopy, the degree of saponification was monitored by the appearance of the hydroxyl group absorption band and the disappearance of the ester group absorption band. According to the IR spectroscopy data, only an insignificant (~3%) amount of ester groups remains in the saponified copolymers. The influence of the copolymers' composition on their solubility in various solvents is demonstrated. IR spectroscopy of the copolymers revealed hydrogen-bond formation between the unreacted ester groups and hydroxyl groups formed due to the saponification. The viscometry of the solutions of mixtures of saponified and unsaponified copolymers, solutions of mixtures of saponified copolymer with polyvinyl acetate, and viscometry of saponified*

copolymers in various solvents all support this conclusion. These bonds' concentration depends on the copolymer's composition and can be controlled by the nature of the solvent from which these copolymers' films are formed. Saponified copolymer solutions form smooth, transparent film coatings with excellent adhesion to metals and silicate glass surfaces. The contact angle of these films, like the hardness, decreases as the VBA units' concentration in the copolymers increases and depends on the solvent polarity used to form the films. It has been demonstrated that increasing the VBA units concentration suppresses the microorganisms' growth.

Conclusions. *Film coatings made of copolymers of styrene with VBA have been shown to have high biocidal activity against molds; can be used to protect structural materials and products from the effects of microorganisms.*

Keywords: *biocidal properties, vinyl benzyl acetate, hydrogen bonds, saponification, film coatings, polyvinyl benzyl alcohol, copolymerization, styrene*

For citation: Gusarov M.V., Krylov A.V., Deshevaya E.A., Tverskoy V.A. Synthesis and properties of vinyl benzyl alcohol copolymers with styrene. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2021;16(5):399–413 (Russ., Eng.). https://doi.org/10.32362/2410-6593-2021-16-5-399-413

НАУЧНАЯ СТАТЬЯ

Синтез и свойства сополимеров винилбензилового спирта со стиролом

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Аннотация

Цели. *Синтез и изучение свойств сополимеров винилбензилового спирта (ВБС) со стиролом, обладающих антимикробными свойствами.*

Методы. *В работе использованы такие методы как ИК- и ЯМР-спектроскопия, тонкослойная хроматография, вискозиметрия и элементный анализ. Краевые углы смачивания и твердость пленок определяли методом сидячей капли и «методом карандаша», соответственно. Метод испытаний стойкости пленочных покрытий к воздействию плесневых грибов заключался в заражении пленочных покрытий, нанесенных на стекла, спорами плесневых грибов Всероссийской коллекции микроорганизмов в растворе минеральных солей без сахара (среда Чапека-Докса).*

Результаты. *В работе синтезированы гомополимеры винилбензилацетата и его сополимеры со стиролом. Их омылением получены гомо- и сополимеры ВБС. Состав сополимеров определен ИК- и ^{1}H ЯМР-спектроскопией. Степень омыления контролировали ИК-спектроскопией по появлению полосы поглощения гидроксильной группы и исчезновению полосы* *поглощения сложноэфирной группы. По данным ИК-спектроскопии в омыленных сополимерах остается лишь незначительное (~3%) количество сложноэфирных групп. Показано влияние состава сополимеров на их растворимость в растворителях различной природы. ИК-спектроскопией сополимеров показано образование водородных связей между непрореагировавшими сложноэфирными группами и образовавшимися в результате омыления гидроксильными группами. Этот вывод подтвержден вискозиметрией растворов смесей омыленного и неомыленного сополимеров, растворов смесей омыленного сополимера с поливинилацетатом и вискозиметрией омыленных сополимеров в растворителях различной природы. Концентрация этих связей зависит от состава сополимера и может регулироваться природой растворителя, из которого формируются пленки этих сополимеров. Из растворов омыленных сополимеров формируются гладкие прозрачные пленочные покрытия с высокой адгезией к поверхностям металлов и силикатного стекла. Краевой угол смачивания этих пленок, как и твердость, уменьшается с увеличением концентрации в сополимерах звеньев ВБС и зависит от полярности растворителя, из раствора в котором сформированы пленки. Показано, что увеличение концентрации звеньев ВБС приводит к подавлению роста микроорганизмов.*

Выводы. *Показано, что пленочные покрытия из сополимеров стирола с ВБС обладают высокой биоцидной активностью по отношению к плесневым грибам и могут быть использованы для защиты конструкционных материалов и изделий из них от воздействия микроорганизмов.*

Ключевые слова: *биоцидные свойства, винилбензилацетат, водородные связи, омыление, пленочные покрытия, поливинилбензиловый спирт, сополимеризация, стирол*

Для цитирования: Гусаров М.В., Крылов А.В., Дешевая Е.А., Тверской В.А. Синтез и свойства сополимеров винилбензилового спирта со стиролом. *Тонкие химические технологии.* 2021;16(5):399–413. https://doi.org/10.32362/2410-6593-2021-16-5-399-413

INTRODUCTION

The synthesis and investigation of the properties of polymers containing functional groups of diverse nature with antimicrobial properties have piqued the interest of researchers in recent years, as summarized in reviews and monographs [1–9]. Unlike low molecular weight compounds, polymer biocides allow the formation of protective films that are resistant to microorganism colonization, and they do not “sweat out” the biocide. The biocidal properties of such polymers should, of course, depend on the concentration of the functional groups that provide these properties. In most cases, these polymers are obtained by chemically modifying precursor polymers containing functional groups that can be converted through chemical reactions into biocidal ones or introducing groups with biocidal properties into the structure of a macromolecule [10].

Phenols, other aromatic alcohols, and their derivatives are known to have a broad spectrum of biocidal action [11]. Carbon-chain polymers containing phenolic groups can only be obtained through chemical modification, which is associated with the inhibition of polymerization of monomers containing groups of aromatic phenols and a benzyl alcohol group with properties similar to them. Thus, in [12–16], polymers containing units of vinyl benzyl alcohol (VBA) were obtained by chemical modification of polymers containing units of vinyl benzyl chloride (VBC). The modification included the acylation of the polymers’ benzyl chloride groups with potassium acetate, followed by their saponification with the VBC units formation. However, according to [14–16], intermolecular simple ether bonds are formed in polymers with a high content of chloromethyl groups, resulting from saponification, and benzyl alcohol groups, resulting from the interaction of residual chloromethyl groups with benzyl alcohol groups. It was proposed in [17] that obtaining copolymers of VBA by copolymerization of vinyl benzyl acetate (VBAc) followed by saponification of these copolymers will lead to excluding the formation of these intermolecular bonds.

This study employed this method to synthesize polyvinyl benzyl alcohols and copolymers of VBA with styrene and study their properties.

EXPERIMENTAL

Materials

VBC (*Sigma-Aldrich*, USA), which is a mixture of *m*-(60%) and *p*-isomers (40%) stabilized with 4-*tert*-butylpyrocatechin (*Sigma-Aldrich*), is used for VBA synthesis without additional purification.

Styrene, *pur.* (*Angara-Reaktiv*, Russia), was washed from hydroquinone using a 30% aqueous solution of caustic potassium, washed with water from excess alkali to a neutral reaction of washing waters, dried over calcined calcium chloride, and distilled under vacuum, selecting a fraction at 46°C and a pressure of 30 mm Hg.

Potassium acetate, *puriss.* (*Reachim*, Russia), was drained by azeotropic distillation of water with benzene.

Dimethyl sulfoxide (DMSO), *puriss*. (*Chimmed*, Russia), was dried by holding over calcined calcium chloride for several days, then held over calcium hydride for 6 h at 80°C, followed by distillation over a fresh portion of calcium hydride at 130°C and a residual pressure of 25 mm Hg.

Before use, azobisisobutyronitrile (AIBN) was recrystallized from methyl alcohol.

The remaining reagents and solvents were used without additional purification because they were purely reactive.

Methods of analysis

Using ^{1}H NMR and IR spectroscopy, the composition of VBAc copolymers with styrene and the degree of their saponification were calculated. The ^{1}H NMR spectra of the VBAc copolymer solutions in C_6D_6 and VBA copolymers in DMSO-d_6 were recorded on a DPX-300 spectrometer (*Bruker,* Germany). Quantitative processing of ^{1}H NMR spectra was carried out in the MestReNova program[1]. IR spectroscopic studies were performed on an Equinox 55 spectrometer (*Bruker*) in KBr tablets and polymer films formed on germanium plates.

Viscometric measurements were conducted in a Ubbelohde viscometer at 30°C.

Films were formed from polymer solutions on silicate glass substrates to determine the film coatings' hardness, the wetting edge angles, and the resistance of these films to the effects of mold fungi.

The wetting edge angles at the sample-water-air interface were determined by the sedentary drop method.

The films' hardness was determined by the pencil method [18] according to GOST P 54586-2011 (ISO 15184:1998)[2].

The film coatings' resistance to the effects of mold fungi was evaluated using mold fungi of the All-Russian Collection of Microorganisms of the following species according to GOST 9.049-91[3] (method 1): *Aspergillus niger van Tieghem*, VKM F-1119; *Aspergillus terreus Thom*, VKM F-1025; *Aspergillus oryzae (Ahlburg) Cohn*, VKM F-55; *Chaetomium globosum Kunze*, VKM F-109; *Paecilomyces varioti Bainier*, VKM F-378; *Penicillium funiculosum Thom*, VKM F-1115; *Penicillium chrysogenum Thom*, VKM F-245; *Penicillium cyclopium Westling*, VKM F-265; *Trichoderma viride Pers. ex S. F. Gray*, VKM F-1117.

In the absence of mineral and organic contaminants, this method establishes the materials' fungus resistance and their components. An association of fungal spores with a concentration of $9 \cdot 10^6$ in 1 mL ($1 \cdot 10^6$ in 1 mL of each type of spore) was used for infection.

The films were tested using the following method, which establishes the mushroom resistance of the materials in the absence of mineral and organic contaminants under optimal conditions for the mold fungi development, but without an additional power source.

The test method consisted in infecting the film coatings applied to the glass with mold fungi spores in a solution of mineral salts without sugar (Chapek–Doks medium). As a result, fungi could only grow in the nutrients contained in the material.

Infection of samples in sterile Petri dishes was carried out by evenly applying a prepared suspension of fungal spores to the surface of the dishes. The open Petri dishes with samples were kept for 28 days, after which the content and composition of microorganisms were taken into account on experimental samples according to the six-point scale (GOST 9.049-91) given in Table 1.

Synthesis methods

The acylation of VBC was done using a method similar to that described in [12, 19]. DMSO (85 mL), VBC (34 mL, 0.24 mol), and potassium acetate

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[1] Mestrelab Research S.L. https://mestrelab.com/

[2] GOST P 54586-2011 (ISO 15184:1998). Paints and varnishes. Determination of film hardness by pencil test. Moscow: Standartinform; 2012.

[3] GOST 9.049-91 (Method 1). Unified system of corrosion and ageing protection. Polymer materials and their components. Methods of laboratory tests for mould resistance. Moscow: Izd. Standartov; 1992.

Table 1. Scale of fungi growth in scores

Score	Score characteristic
0	Mold growth is not visible when viewed under a microscope
1	When viewed under a microscope, germinated spores and slightly developed mycelium in the form of unbranched hyphae are visible
2	When viewed under a microscope, mycelium is visible in the form of branching hyphae, sporulation is possible
3	When viewed with the naked eye, fungal growth is barely visible, but clearly visible under a microscope
4	When viewed with the naked eye, the growth of fungi is clearly visible, covering less than 25% of the tested surface
5	When viewed with the naked eye, the growth of fungi is clearly visible, covering more than 25% of the tested surface

(27 g, 0.28 mol) were sequentially loaded into a flask and stirred for 48 h at 40°C. The filtered acetate and potassium chloride solution was then poured into 300 mL of water, and VBAc was extracted with ethyl acetate. The extract was rinsed with a 3% sodium bicarbonate aqueous solution and dried over sodium sulfate. After removal at a reduced pressure of ethyl acetate, an oily brown product was obtained. The precipitate of 4-*tert*-butylpyrocatechin released from the product was removed from the filter after it was diluted with hexane. The resulting VBAc was separated from the unreacted VBC on a chromatographic column (silica gel, hexane–ethyl acetate 5:1 mixture). Hexane and ethyl acetate were removed on a rotary evaporator. The VBAc had a 65% yield. Elemental analysis, thin-layer chromatography, and IR spectroscopy all confirmed the absence of VBC in the product. In the IR spectrum, there are no bands of valence vibrations of the C–Cl bond at ν = 683 cm^{-1} and fan deformation vibrations of the CH_2Cl group δ = 1266 cm^{-1}. In turn, the appearance in the IR spectrum of the product of valence vibrations of the ester group ν = 1745 cm^{-1} confirms the presence of acetate groups in the reaction products.

VBAc polymerization and its copolymerization with styrene were carried out at 70°C in benzene in nitrogen-purged ampoules with a total concentration of monomers of 1.75 mol/L. AIBN (3.00 mol % relative to the total concentration of monomers) was employed as the initiator. Polymers from the solution were precipitated with isopropyl alcohol at the end of copolymerization and re-precipitated from the solution in benzene with isopropyl alcohol. The resulting white polymers were vacuum dried to a constant mass at 50°C.

Saponification of the obtained VBAc copolymers with styrene and polyvinyl benzyl acetate (PVBAc) was carried out with sodium hydroxide in a mixture of 1,4-dioxane with water (2/1 by volume) at 80°C for 20 h while stirring the solution with a magnetic stirrer. At the end of the process, the polymers were precipitated from the solution with a weak hydrochloric acid solution, repeatedly washed with this solution, vacuum dried at room temperature to a constant mass.

RESULTS AND DISCUSSION

The copolymerization constants of styrene and VBAc were calculated using the Feineman–Ross method for the compositions of copolymers determined by ^{1}H NMR spectroscopy at low (up to 10%) conversion of monomers.

In the ^{1}H NMR spectrum, the signals of proton-containing PVBAc groups (Fig. 1) represent broadened signals that is characteristic for polymers. The signals of the methylene (CH_2) and methine (CH) groups of the macromolecule's main chain are manifested in the region δ = 1.58–2.04 ppm. The signals of acetate groups (CH_3) δ = 1.87 ppm fall into the same region, which makes it possible to determine the ratio of phenyl and phenyl acetate units in the copolymer using the ^{1}H NMR method. The signals of –CH_2– groups of benzyl acetate fragments are significantly shifted to the low-field region and manifest themselves at $\delta = 5.1$ ppm. Additionally, the ratio of units in the copolymer was checked analyzing the material balance using the signals of the aromatic ring protons in the region $\delta = 6.71–7.57$ ppm.

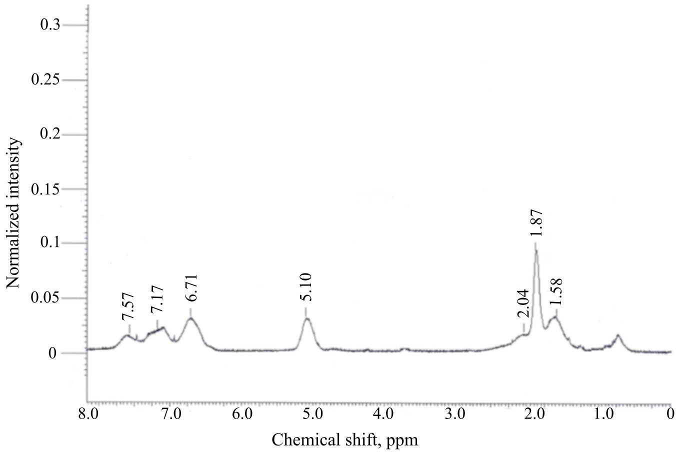


Fig. 1. ^{1}H NMR spectrum of PVBAc in C_6D_6.

The values of copolymerization constants found were $r_1 = 0.9$ and $r_2 = 1.0$, and they were close to the values of these constants previously determined using the Kelen–Tudosh method [17]: $r_1 = 0.78$ and $r_2 = 1.33$. In this study, polymerization was conducted in toluene at 60°C.

The close reactivity of these monomers under the copolymerization conditions adopted in this study made it possible to synthesize copolymers whose macromolecules differ little in composition regardless of the degree of monomer conversion. These copolymers dissolve in the same solvents as polystyrene: in benzene, toluene, 1,4-dioxane, tetrahydrofuran, chloroform, acetone, and *N,N*-dimethylformamide (DMFA), and do not dissolve in lower alcohols and water. Unlike polystyrene, copolymers containing from 28 to 84 mol % of VBAc units are dissolved in DMSO.

IR spectroscopy of PVBAc and VBAc copolymers with styrene of various compositions confirmed the data obtained using ^{1}H NMR spectroscopy.

The analysis of the IR spectra of these polymers showed that the position of the valence vibration band of the carbonyl group ν(C=O) in the VBAc units varied depending on the content of these units in the copolymer. Thus, in the IR spectra of PVBAc and a copolymer containing 84 mol % of VBAc units, there was one band at 1737 cm^{-1} (Fig. 2a and 2b). With a decrease in the content of VBAc units in the copolymer to 52 mol %, this band split into two bands with maxima at 1746 and 1728 cm^{-1} (Fig. 2c).

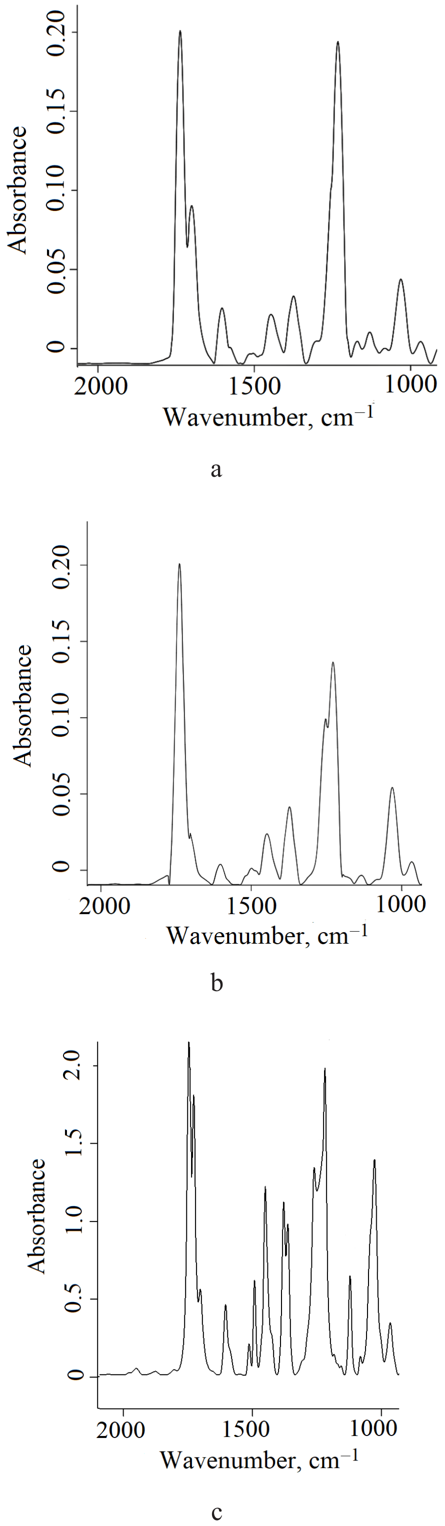


Fig. 2. IR spectrum of (a) PVBAc, (b) styrene copolymers with VBAc containing 84 mol % and (c) 52 mol % of VBAc units.

The position of the valence vibration band of the ether group also changed. In PVBAc and a copolymer containing 84 mol % of VBAc units, this band had a maximum at 1031 cm^{-1} (Figs. 2a and 2b). In the IR spectrum of a copolymer containing 52 mol % of VBA units, this maximum shifted to 1027 cm^{-1} (Fig. 2c).

It is possible that this shift and splitting of the vibration band of the carbonyl group are associated with a change in the macromolecule conformation caused by a change in the balance of hydrophobic (styrene) and hydrophilic (VBAc) units in it.

As described in Experimental, the saponification of ester groups in the synthesized VBAc copolymers with styrene and PVBAc was conducted with sodium hydroxide in a solution of an 1,4-dioxane/water mixture at 80°C for 20 h with a significant excess of alkali in relation to the number of acetate groups. Table 2 shows the ratios of the concentrations of copolymers and alkali solution and the yields of the saponified copolymers obtained.

The solubility of saponified copolymers in various solvents depends on their composition (Table 3). They do not dissolve in water and dissolve in such highly polar organic solvents as DMFA and DMSO. Saponified copolymers containing less than 60 mol % of styrene units do not dissolve in benzene and toluene. All unsaponified copolymers do not dissolve in lower alcohols. On the contrary, copolymers with a high content of VBA units (more than 62 mol %) acquire solubility in them after saponification.

In ^{1}H NMR spectra in DMSO-d_6 (Fig. 3) obtained by saponification of copolymers, positions of the CH_2 and CH groups' signals in the main chain of the macromolecule changed little compared to unsaponified samples and were manifested in the region δ = 1.42–2.04 ppm. The chemical shifts of protons of the phenyl groups were observed in the region δ = 6.54–7.56 ppm. The most significant change was observed for the signal $–CH_2–$ group benzyl acetate fragment, the chemical shift of which moved from δ = 5.10 to 4.40 ppm due to the lower polarity of the hydroxyl group in comparison with the acetate group.

IR spectra of saponified copolymers confirmed the data of ^{1}H NMR spectroscopy. In the IR spectra of saponified copolymers (Fig. 4), compared with the considered spectra of unsaponified copolymers (Fig. 2), there were a wide valence vibration band (3442–3355 cm^{-1}) and an in-plane deformation vibration band (1374–1368 cm^{-1}) of the benzyl alcohol hydroxyl group. In the spectrum, a band of 1122 cm^{-1} corresponding to valence vibrations of the C–O bond in alcohols appeared, whereas the bands of 1746–1728 cm^{-1} related to vibrations of the carbonyl group practically disappeared. This allows concluding that there is a high degree of saponification in all the copolymers obtained and a low concentration of residual acetate groups in them.

The appearance of a band with a maximum of ~1700–1691 cm^{-1} in the spectra of saponified copolymers suggests the presence of intermolecular and intramolecular hydrogen bonds between the carbonyl group of unsaponified chain units with the hydroxyl group of VBA units. Moskala [20] observed such a low-frequency shift of the carbonyl group band in the IR spectra of a mixture of polyvinylphenol (PVP) with polyvinyl acetate (PVA). The valence vibration band of the PVA carbonyl group had a maximum of 1739 cm^{-1}. When mixing PVA with PVP, a shift of this band to 1714 cm^{-1} was observed. The intensity of this band increased with an increase in the content of PVP. This band refers to the valence vibrations of the carbonyl group bound via a hydrogen bond with the hydroxyl group of phenol.

Table 2. Conditions for the saponification of PVBAc and VBAc copolymers with styrene and the yields of saponified copolymers

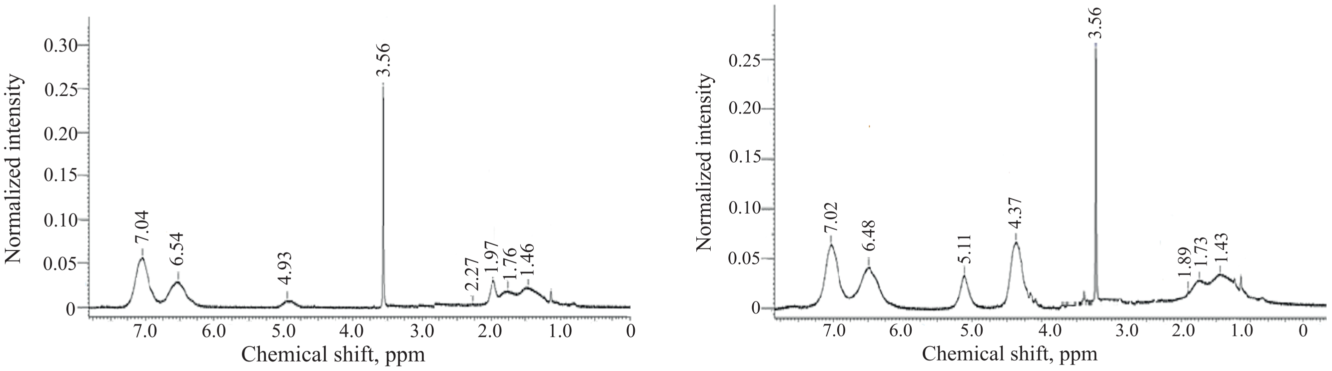
Copolymers' composition, mol % of units		Number of VBAc units, mmol of units	NaOH quantity, mmol	[NaOH]/[VBAc], mmol/mmol of units	H_2O volume, mL	1,4-Dioxane volume, mL	Yield, %
Styrene	VBAc						
82	18	1.5	15.1	10.1	9.3	18.6	81
60	40	3.0	30.0	10.0	60.0	120.0	52
48	52	2.4	24.3	10.1	5.5	11.0	79
38	62	4.2	20.9	4.9	8.3	16.6	80
16	84	5.2	25.8	5.0	8.3	16.6	99
0	100	1.1	5.6	5.1	1.7	3.4	49

Table 3. Solubility of styrene copolymers with VBAc and with VBA in solvents of various nature (“+” is soluble, “–” is insoluble)

Copolymer form	Copolymer composition, mol % of units			Solvents											
	Styrene	VBAc	VBA	1,4-Dioxane	Benzene	Toluene	Chloroform	Tetrahydrofuran	Isopropanol	Acetone	Ethanol	Methanol	DMFA	DMSO	Water
–	100	0	0	+	+	+	+	+	–	+	–	–	+	–	–
Acetate	82	18	–	+	+	+	+	+	–	+	–	–	+	–	–
Saponified		2	16	+	+	+	+	+	–	+	–	–	+	+	–
Acetate	60	40	–	+	+	+	+	+	–	+	–	–	+	+	–
Saponified		2	38	–	–	–	–	–	–	–	–	–	+	+	–
Acetate	48	52	–	+	+	+	+	+	–	+	–	–	+	+	–
Saponified		7	45	+	–	–	+	+	–	+	–	–	+	+	–
Acetate	38	62	–	+	+	+	+	+	–	+	–	–	+	+	–
Saponified		3	59	+	–	–	+	+	+	+	+	+	+	+	–
Acetate	16	84	–	+	+	+	+	+	–	+	–	–	+	+	–
Saponified		3	81	+	–	–	–	+	+	+	+	+	+	+	–
Acetate	0	100	–	+	+	–	+	+	–	+	–	–	+	–	–
Saponified		3	97	+	–	–	–	+	–	–	+	+	+	+	–
Dielectric constant				2.2	2.3	2.4	4.7	7.6	18.3	20.9	24.3	32.6	36.7	45.0	81.0

Comparison of the IR spectra of saponified copolymers showed that with increasing the saponified units’ content in the copolymer, the maximum friequency of the valence vibration band of the –OH group in the region $\nu = 3500–3100$ cm^{-1} shifted to lower frequencies (Fig. 5), indicating the formation of more strong hydrogen bonds involving hydroxyl groups. The reduction in the width of this band in its half-height indicates an increase in the exchange rate between free and associated hydroxyl groups.

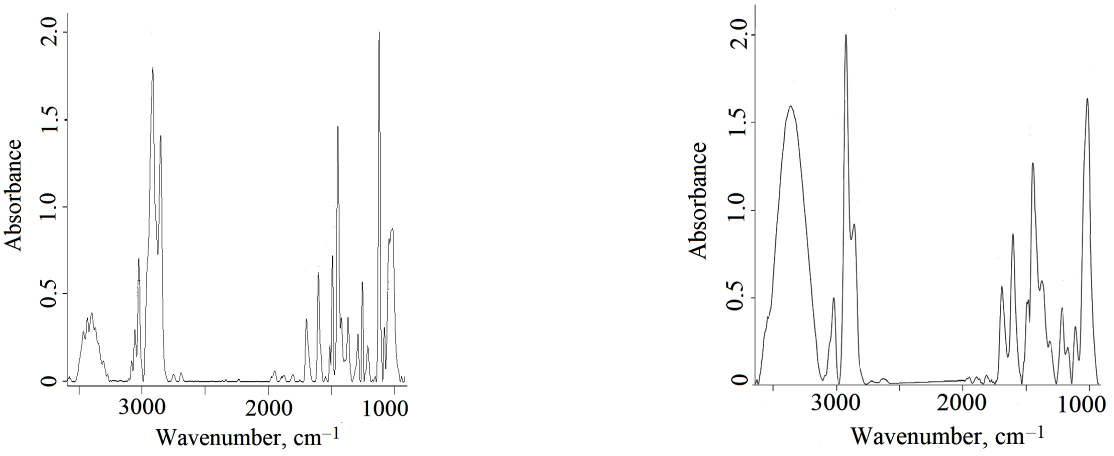
In the IR spectra of saponified copolymers with a low (16 mol %) content of VBA units, there is a band of 3583 cm^{-1} (Fig. 6) related to vibrations in free nonhydrogen-bonded –OH groups, whereas is no this band in the spectra of copolymers with a high (81 mol %) content of these units (Fig. 4b).



a

b

Fig. 3. ^{1}H NMR spectra of dissolved in DMSO-d_6 (a) styrene copolymers (82 mol %) containing VBAc (2 mol %) and VBA (16 mol %) units and (b) VBAc copolymers (3 mol %) containing VBA (97 mol %) units.



a

b

Fig. 4. IR spectra of (a) styrene copolymers (48 mol %) containing VBAc (7 mol %) and VBA (45 mol %) units and (b) styrene copolymers (16 mol %) containing VBAc (3 mol %) and VBA (81 mol %) units.

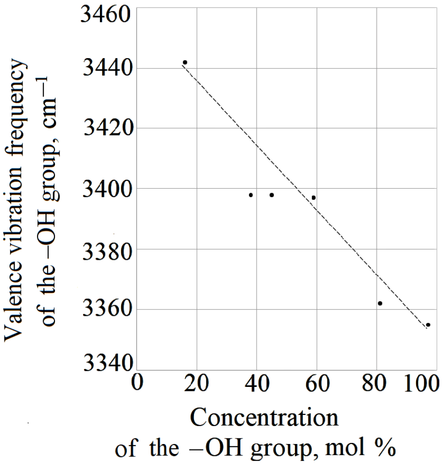


Fig. 5. Dependence of the maximum of the 3442–3355 cm^{-1} band in the IR spectra of saponified VBAc copolymers with styrene on the content of VBA units in them.

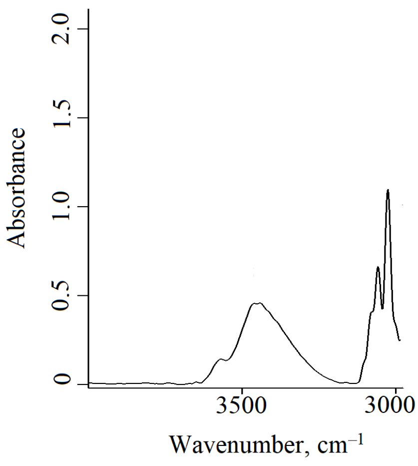


Fig. 6. IR spectrum of the styrene copolymers (82 mol %) containing VBAc (2 mol %) and VBA (16 mol %) units.

The formation of hydrogen bonds between the hydroxyl and carbonyl groups in these copolymers was confirmed using IR spectroscopy of a mixture of saponified (60%) and unsaponified (40%) copolymers with a low (16 mol %) content of styrene units (Fig. 7). In comparison with the IR spectrum of the saponified copolymer, the maximum of the valence vibration band was strongly shifted to the low-frequency region in the spectrum of the mixture: from 3442 cm^{-1} in the spectrum of the saponified copolymer to 3387 cm^{-1} in the spectrum of the polymer mixture.

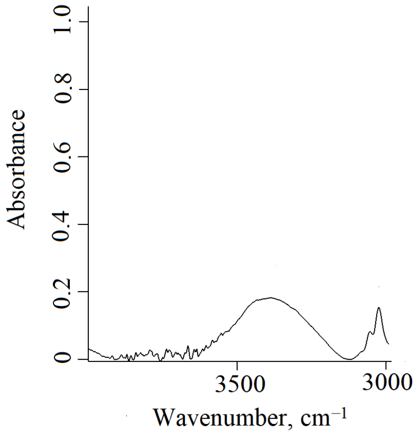


Fig. 7. IR spectrum of the mixture of saponified (60%) and unsaponified (40%) VBAc copolymers containing 16 mol % of styrene units.

A similar low-frequency shift of this band was observed in the IR spectrum of a saponified copolymer and PVA mixture (Fig. 8). These conclusions are consistent with the results of the study [20] on inter and intramolecular interactions in a mixture of PVP–PVA.

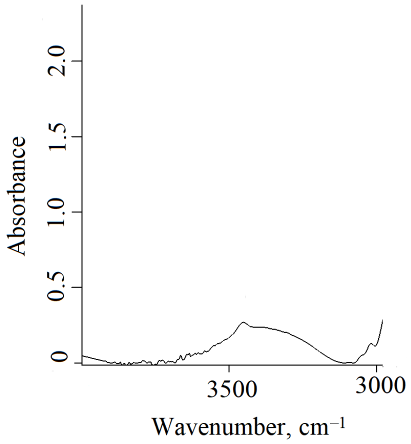
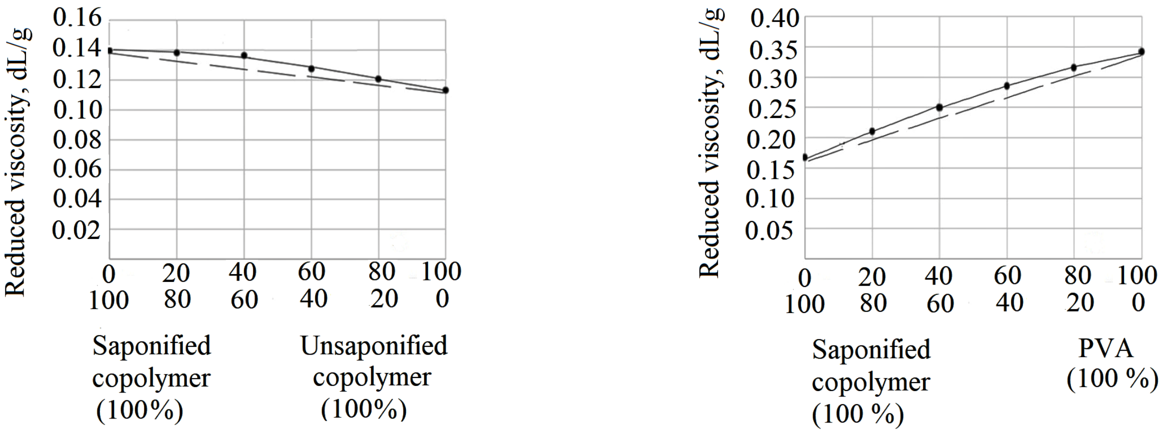


Fig. 8. IR spectrum of the mixture of saponified VBAc copolymers containing 16 mol % of styrene (40%) with PVA (60%) units.

The conclusion about the formation of intermolecular hydrogen bonds was confirmed using the viscometry of the copolymer mixtures' solutions before and after saponification and by the dependence of the reduced viscosity on the concentration of copolymer solutions with a high content of VBA units.

Figure 9 shows the dependence of the reduced viscosity of the solutions of saponified and unsaponified copolymer mixtures (containing 16 mol % of styrene units) on the composition of these mixtures and a similar dependence for mixtures of the same saponified copolymer with PVA. The deviation of these graphs upwards from additivity indicates clearly the formation of intermolecular bonds in the solutions of these polymer mixtures.



a

b

Fig. 9. Dependence of the reduced viscosity of the solutions on the composition of (a) saponified and unsaponified copolymer mixtures containing 16 mol % of styrene units, and (b) saponified copolymer mixtures containing 16 mol % of styrene units with PVA. The solvent is 1,4-dioxane, 30°C. The concentration of the polymer mixture, g/dL: (a) 1 and (b) 2.

The viscometry of saponified copolymer solutions in various solvents also indicated the formation of intermolecular hydrogen bonds in them (Fig. 10). The dependencies of the reduced viscosity on the concentration of the solutions of polystyrene and copolymers with a high content of styrene units in benzene are linear (Fig. 10a). In a nonpolar solvent, such as benzene, macromolecules of copolymers have a conformation in which the VBA units are located inside the tangle of the macromolecule. These dependencies are also linear for the solutions of polystyrene and copolymer with a high (48 mol %) content of styrene units in 1,4-dioxane (Fig. 10b). However, for the solutions of copolymers with a low (16 mol %) content of styrene units and a copolymer that does not contain styrene units, these dependencies are nonlinear. There is an increase in the reduced viscosity associated with the formation of intermolecular hydrogen bonds. These dependencies for the solutions of copolymers with a high content of VBA units in isopropanol have similar forms (Fig. 10c).

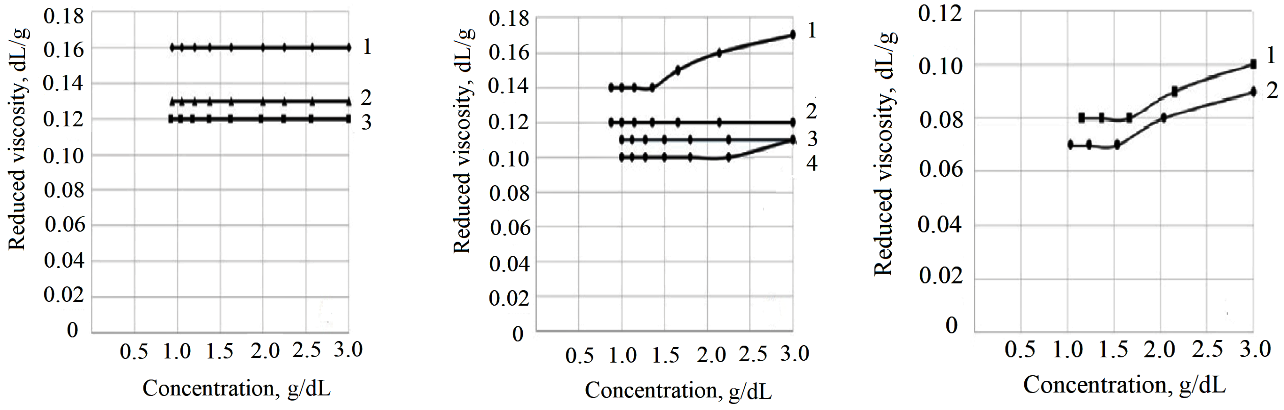
As the result, hydrogen bonds between both hydroxyl and hydroxyl and carbonyl groups are realized in the VBA copolymers. The concentration of these bonds depends on the composition of the copolymer and can be regulated by the solvent from which the films of these copolymers are formed.

Solutions of VBA and styrene copolymers form smooth rigid transparent colorless film coatings with high adhesion to metal and silicate glass surfaces.

Table 4 shows that the films' wetting contact angles characterizing the hydrophobicity of their surface decrease with increasing the concentration of VBA units in the polymers. The wettability of the films depends on the solvent from which the films were formed. The contact angles of the films with a high content of VBA hydrophilic units and a low (16 mol %) content of styrene units were higher when forming films from a solution in 1,4-dioxane (dielectric constant is 2.2) than when forming from solutions in a more polar solvent—isopropyl alcohol (dielectric constant is 18.3). Such a change in the contact angle is due to the dependence of the macromolecule conformation on the solvent, which leads to a change in the concentration of VBA hydrophilic groups on the surface of the macromolecule tangle, i.e., their concentration is higher when the formation of films from a solution in isopropyl alcohol.

Such a change in the conformation of macromolecules is reflected in the hardness of the formed films too. Table 4 shows that the film formed from a solution in isopropanol had a lower hardness than the film formed from a solution in 1,4-dioxane. As expected, for films formed from the same solvent (1,4-dioxane), the polystyrene film has the highest hardness. The hardness decreases wth an increase in the VBA units' concentration in the polymer.

Table 5 shows the results of microbiological tests of the saponified VBAc copolymers with styrene. Polystyrene had low fungicidal activity (fungi growth is 3 points). The introduction of even a small concentration



a b c

Fig. 10. Dependence of the reduced viscosity on the concentration of solutions of styrene copolymer with VBA at 30°C in (a) benzene, (b) 1,4-dioxane, and (c) isopropanol.
(a): 1–polystyrene; 2–styrene copolymer (48 mol %) with VBAc (7 mol %) and VBA (45 mol %) units; 3–styrene copolymer (82 mol %) with VBAc (2 mol %) and VBA (16 mol %) units.
(b): 1–VBAc copolymer (3 mol %) with VBA (97 mol %) units; 2–styrene copolymer (48 mol %) with VBAc (7 mol %) and VBA (45 mol %) units; 3–polystyrene; 4–styrene copolymer (16 mol %) with VBAc (3 mol %) and VBA (81 mol %) units.
(c): 1–styrene copolymer (16 mol %) with VBAc (3 mol %) and VBA (81 mol %) units; 2–styrene copolymer (38 mol %) with VBAc (3 mol %) and VBA (59 mol %) units.

Table 4. Contact angles and the hardness of saponified VBA c copolymers' films with styrene

Content of styrene units in the copolymer, mol %	Solvent	Contact angle of wetting, degree	Hardness
100	1,4-dioxane	90	H
82		85	
48		80	
38		77	
16			HB
0			
16	Isopropanol	62	B

Table 5. Fungi growth on film coatings of the styrene copolymers with VBA of various compositions, in scores

Styrene copolymers with VBAc and VBA units, mol %			Fungi growth, scores
Styrene	VBAc	VBA	
100	0	0	3
82	2	16	1
48	7	45	0
38	3	59	
16	3	81	
0	3	97	

of VBA units (16 mol %) into the composition of a macromolecule led to an increase in the copolymer biocidal activity. A further increase in the VBA units' concentration in the copolymer (45 mol % or more) led to complete suppression of the microorganisms' growth.

Thus, the styrene copolymers with VBA units are effective biocides that inhibit the growth of mold fungi.

CONCLUSIONS

It has been demonstrated that copolymerization of VBAc followed by saponification of ester groups in these copolymers yields soluble VBA copolymers in a wide range of compositions. Saponification occurs quantitatively in mild conditions. ^{1}H NMR and IR spectroscopy established the structure of styrene copolymers with VBAc and these copolymers, after saponification of the ester groups of the VBAc units with the formation of the VBA units.

IR spectroscopy of copolymers and the viscometry of the solutions of saponified and unsaponified copolymers mixtures, solutions of mixtures of saponified copolymer with PVA, and viscometry of saponified copolymers in different solvents reveal that the hydroxyl groups in these saponified polymers form inter and intramolecular hydrogen bonds when interacting with each other and carbonyl groups of ester groups of unreacted VBA units.

It is shown that all saponified copolymers form smooth, transparent film coatings on metals and silicate glass. The hardness and edge angle of wetting of these films decreases with increasing concentration in the copolymer of the VBA units and depends on the solvent's polarity from which the films are formed. In terms of mold fungi, these coatings have high biocidal activity.

Authors' contribution

M.V. Gusarov– design and conducting the experiments, discussion of the results;

A.V. Krylov – NMR spectrometry studies, data processing;

E.A. Deshevaya – evaluation of the microbiological properties of compounds according to GOST 9.049-91;

V.A. Tverskoy – development of a research concept, consultation during individual stages of the research, data processing.

The authors declare no conflicts of interest.

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The article was submitted: September 30, 2021; approved after reviewing: October 04, 2021; accepted for publication: October 30, 2021.

Translated from Russian into English by N. Isaeva
Edited for English language and spelling by Enago, an editing brand of Crimson Interactive Inc.