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Polymer-Analog Reactions of Polyvinyl Alcohol under the Action of Microwave Radiation

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Abstract—Effect of microwave radiation on the polymer-analog reaction of polyvinyl alcohol with low molecular ketone, cyclohexanone, was studied. It is shown that using the energy of this radiation permits to increase considerably the rate of formation of polyketal as compared to the thermal action. It is found that the process of formation of final product may be governed by the nature of solvent. In this case not only the change in solubility must be considered, but the competing absorption of microwave energy by the solvent as well.

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Effect of microwave radiation on chemical processes is determined in the first turn by the quick and uniform heating of all the reaction volume. Besides the thermal effect there exists also the non-thermal action, the so-called special effect, arising from the dependence of chemical activity of polar compound on the changes in the solvate shell of ion or the electronic density of dipole caused by electromagnetic field [1–10].

An especially clear effect of microwave radiation may be demonstrated by an example of high molecular compounds. A macromolecule is an informative model for investigation of the influence of the microwave irradiation on the chemical activity as well as supramolecular structure and phase state of such compound. We have shown previously [11–15] that the dehydration of polyvinyl alcohol proceeds according to different mechanisms under the convectional and the microwave heating. Thermal action causes the intramolecular reaction leading to unsaturated structure, but microwave irradiation under the same temperatures leads to intermolecular etherification, the structurization of polymer, and the formation of the water-stable form of polyvinyl alcohol which was used for preparing the compositional adsorbents working in water media.

Besides, it was shown that the degree of crystallinity of polyvinyl alcohol under the action of microwave radiation is higher than under thermal treatment, and thermooxidative destruction leads to the formation of different reaction products under the conditions equal in all other respects. The high effecttiveness of the microwave radiation was shown also in the polymer-analog reaction of polyvinyl alcohol with formaldehyde leading to polyacetals [16]. The reaction rate and the yield of the product are much higher under the action of microwave radiation as compared to the thermal activation.

Continuing these studies we have investigated thoroughly the reaction of polymer-analog transformation of polyvinyl alcohol in the presence of low molecular ketone under the action of microwave radiation. The choice of the object was caused not only by the desire to broaden the sphere of application of microwave radiation in organic synthesis, but also by the possibility to consider the specific features of synthesis under the microwave activation, the more so that the conditions of formation of polyacetals and polyketals differ considerably.

As is known [17], the acetalization of low molecular aldehydes and ketones with alcohols is reversible and proceeds according to the following scheme:

$$RR^1C{=}O + 2\,R^2OH \rightleftarrows RR^1C(OR^2)_2 + H_2O.$$

The addition to a carbonyl group proceeds by the nucleophilic attack an the carbon atom of this group, and on the rates of the direct and the reverse reactions are different depending on the nature of substituents.

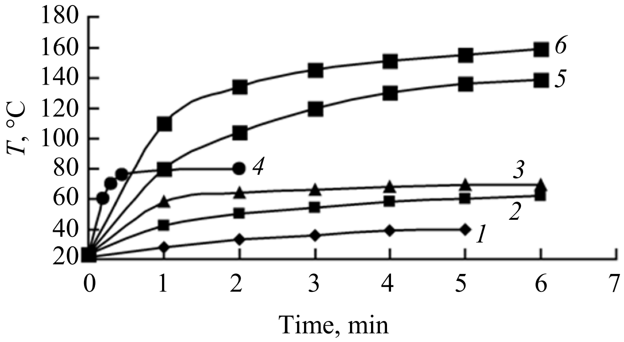

Fig. 1. Dependence of temperature of the reaction mixture (*V* = 50 ml) on the time of microwave irradiation: 450 W, [HCl] 1% vol/vol: (*1*) benzene, (*2*) dioxane, (*3*) benzene + ethanol (1:1), (*4*) ethanol, (*5*) DMF, and (*6*) DMA.

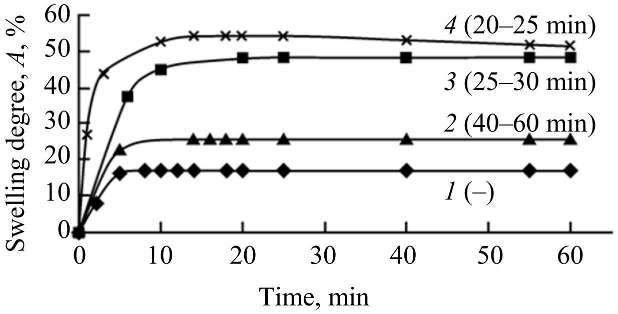

Fig. 2. Swelling degree of polyvinyl alcohol film in different solvents (time of complete dissolution of the film in the reaction with cyclohexanone under the microwave irradiation is given in brackets); (*1*) dioxane, (*2*) ethanol + benzene (1:1), (*3*) DMF, and (*4*) DMA.

The equilibrium is shifted to the side of acetalization for aldehydes and to the side of carbonyl compound in the case of ketones. The decrease in the temperature and the introduction of electronegative substituents in α-position to the keto group impedes the hydrolysis of ketals.

The reaction of high molecular alcohols with aldehydes and ketones also has specific features [18]. Polyvinyl alcohol easily forms acetals with the majority of aldehydes, but direct ketalization of this polymer takes place only in the case of cyclic ketones (cyclohexanone, methylcyclohexanone, etc.,) while aliphatic and aromatic ketones practically do not react. The thermal synthesis of polyketals on the basis of polyvinyl al;cohol and cyclohexanone proceeds in the ethanol-benzene mixture under the sufficiently rigid conditions: 50–60°C, reaction time from 2–3 to 40 h, yield 30–70%, degree of substitution 50–80% [18].

The aim of this work was the investigation of ketalization of cyclohexanone with polyvinyl alcohol under the microwave irradiation in different solvents. The solvents used by us differed in the ability to absorb microwave radiation. From Fig. 1 it is seen that DMF and DMA are active microwave absorbers while benzene and dioxane are “transparent”. Besides, in these solvents the polyvinyl alcohol film has different swelling degree (Fig. 2): DMA > DMF > ethanol + benzene + dioxane. Hence, it can be suggested that using the amide solvents would be more favorable for the synthesis of polyketals. Moreover, our studies showed that in the course of the reaction of polyvinyl alcohol with cyclohexanone under the microwave irradiation the time of formation of homogenic system, that is, the complete dissolution of the polyvinyl alcohol film in the amide solvents is the shortest. It is 20–25 min for DMA, 25–30 min for DMF, 40–60 min for the ethanol-benzene mixture, while in dioxane the film does not dissolve even after 50–80 min.

Table 1. Synthesis of polyketals in different solvents, [$C_6H_{10}O$] 30% vol/vol, [HCl] 1% vol/vol, 450 W, reaction time 27 min, *T* 30–40°C

Solvent	Yield, %	Substitution degree, %
Ethanol + benzene	35–40	33
DMF	24–30	25
DMA	26–31	25
Dioxane	2–5	–

Experimental data showed (see Table 1) that the yield of polyketals in polar solvents was lower than in ethanol-benzene mixtures, while in dioxane they practically do not form. It was found that the reaction products synthesized under different conditions have the same chemical composition. In the IR spectra absorption bands at 950–1200 cm^{-1} characteristic of this class of compounds were observed [12]. Besides, as the reaction goes on the decrease in the intensity of the absorption bands of hydroxy groups (3300–3500 cm^{-1}) and the increase in the intensity of CH-groups band (2700–2950 cm^{-1}) take place. The elemental analysis of polyketal synthesized permitted to calculate the substitution degree.

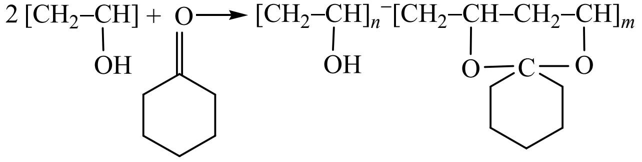

Table 2. Comparison of methods for preparing of polyketals

Reaction conditions	*T*, °C	Ethanol + benzene		DMF	
		Yield, %	%/h	Yield, %	%/h
Thermo 72 h	30–40	35–40	0.5–0.6	7–9	0.1
	50–60	55–75	0.8–1.1	41–44	0.6
Thermo 0.5 h	30–40	≈0	0	≈0	0
	50–60	≈0	0	≈0	0
Microwave radiation 450 W, 0.5 h	30–40	35–40	70–80	24–30	48–60
	50–60	43–51	86–102	30–40	60–80

Table 3. Dependence of yield of polyketals on time, ethanol + benzene, [HCl] 1vol %, *T* 30–40°C

Reaction conditions		Yield, %	Substitution degree, %
exp. no.	τ, min		
1	16	25–30	25–33
2	27	35–40	25–33
3	36	36–45	50–60
4	42	45–60	55–70

We analyzed in the course of the work not only the soluble product, but also the remaining insoluble part of polyvinyl alcohol. It was found that the polyol macromolecule in this case also contained the ketal functional groups, but their amount did not reach the value necessary for dissolution. This means that the polyvinyl alcohol macromolecules with various degree of substitution are present in the reaction mixture.

Hence, the swelling and solubility of polyvinyl alcohol and polyketal obtained in the amide solvent does not provide high yield of the product. The result obtained may be evidently interpreted taking into account that the absorption of the microwave radiation by polar DMF and DMA decreases the possibility of absorption of the energy by the less polar components of the reaction mixture. On the other hand, dioxane by itself is the solvent most inert with respect to the microwave radiation, but low swelling of the film of polyvinyl alcohol as well as of polyketal formed does not favor the increase in the yield of the product. Polyketal layer formed on the surface prevents penetration of reagents in the volume of polyvinyl alcohol film, and hence hampers further proceeding of the reaction.

For comparison we have studied formation of polyketal without the microwave radiation. From Table 2 it is seen that the reaction rate under thermal heating is much lower, the other conditions being equal, which shows the high efficiency of the microwave activation. It is also seen that the yield of polyketal in DMF in this case is lower than in the ethanol–benzene mixture, which may demonstrate the specific effect of the solvent on the chemical activity of functional groups as well as on the supramolecular structure of polyvinyl alcohol macromolecules.

On the basis of the results obtained it can be concluded that the optimal solvent for preparing polyketal from polyvinyl alcohol and cyclohexanone is the ethanol–benzene mixture. For this system kinetics of the reaction under investigation was studied more thoroughly. The results obtained are presented in Table 3. They show that the yield of polyketal increases with the dose of microwave radiation together with the degree of substitution. The obtained linear dependence (Fig. 3) permits to conclude that the ketalization occurs with a front movement, meaning that the macromolecule of polyvinyl alcohol at the achievement of the limiting substitution degree goes over to the solution and the reaction moves further into the volume of the film. At the same time the increase in the degree of substitution at the increase of time of the microwave radiation indicates the probable participation in ketalization of macromolecules in the solution.

The dependence of the yield of polyketals on the reaction temperature was also studied. As is known, the decrease in temperature of the reaction between the low molecular alcohols and ketones may favor the shift of equilibrium to the side of formation of ketals. For the decrease of the reaction temperature a procedure

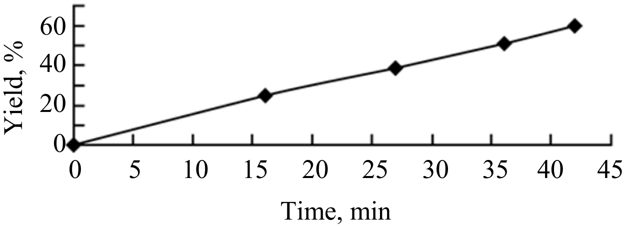

Fig. 3. Dependence of yield of polyketals on time of the microwave irradiation; 1:1 ethanol–benzene, [PVA] 1 vol %; *T* 30–40°C, 450 W.

was developed according to which the reaction vessel was placed in the cooled or frozen dioxane which does not absorb microwave radiation. It is seen that decrease in temperature does not improve the yield of polyketals as well as the increase of temperature.

T, °C	10–15	30–40	45–55
Yield, %	25–30	35–40	45–50

Hence, 30–40°C is the optimum temperature value for this reaction. Under these conditions the rates of direct and reverse reactions as well as the rate of diffusion of solvent, the rate of swelling, and the rates of dissolution of the polyvinyl alcohol film and polyketal come to the equilibrium which is most important for the heterogenic reaction with participation of macro-molecules.

Thus, in the work presented it was shown that using microwave irradiation permits to increase significantly the rate of formation of polyketal from the polyvinyl alcohol and cyclohexanone as compared to thermal activation. It was found that the effect of microwave radiation may be governed by the nature of the solvent used. At the same time it is necessary to consider not only the change in the solubility of the film of starting polyvinyl alcohol and the obtained polyketal under the action of radiation, but also the ability of polar solvent to decrease the effectiveness of formation of polyketal due to the strong competing absorption of the radiation energy.

EXPERIMENTAL

Sandiol polyvinyl alcohol (Netherlands) with the molecular mass 100 000 and the amount of acetate groups no more than 2% was used. The films were formed by casting the 8% solution of polyvinyl alcohol, their thickness varied in the range 100–200 μm. The ketone and solvents were purified according to the standard procedures. Samsung GP90 (China, 450W, 2.45 GHz) and Mars-5 CEM Corp. (USA, 350 W, 2.45 GHz) microwave ovens were used.

The ketalization of polyvinyl alcohol was carried out in the excess of ketone (1:10). For the identification of the products formed IR spectroscopy (Bruker EGUINOX-55, Germany) and elemental analysis were used.

The polyvinyl alcohol film was placed in the reaction vessel, and the ketone, the solvent, and the catalyst (concentrated hydrochloric acid) were added. Ethanol–benzene mixture, 1:1, dioxane, DMF, and DMA were used as solvents. In all cases reaction began under the heterogenic conditions, but in the course of the process at the achievement of the definite degree of substitution the polyvinyl alcohol dissolved. Yield of polyketal was estimated considering only this soluble part. The degree of substitution was calculated on the basis of the Flory statistic theory indicating that in this reaction due to formation of the isolated hydroxy groups the yield of polyketal cannot be more than 86%. Polyketal was precipitated with water, thoroughly washed until neutral reaction, residual ketone and solvent were distilled off, and the residue was dried until the constant weight. The degree of swelling of the samples was calculated according to the formula:

$$(P - P_0)/P_0 \times 100\%,$$

where P and P_0 is the mass of the swelled film and of the starting sample respectively, g.

REFERENCES

1. Malik, M.I., Trathnigg, B., and Kappe, C.O., *European Polymer J.,* 2000, vol. 45, no. 3, p. 899.
2. Kappe, C.O., *IUPAC Inter. Conf. On Biodiversity and Natural Products: Chemistry and Medical Appl*., New Delhi, India, 2004, p.33.
3. Kubrakova, I.V., *Usp. Khim*., 2002, vol. 71, no. 4, p. 327.
4. Zhang, P., Li, G.C., and Yang, L.C., *Electrochemistry Communications*, 2009, vol. 11, no. 1, p. 161.
5. Luo, Y. and Sun, X, *Material Lett*., 2007, vol. 61, p. 1622.
6. Costa, C., Santos, A.F., and Fortuny, M., *Material Science and Engineering: C*, 2009, vol. 29, no. 2, p. 415.
7. Pawluezuk, R.T., McClain, J.M., Denicola, C., Mulhearn, J.J., Rudd, D.J., and Lindsley, C.W., *Tetrahedron Lett.,* 2007, vol. 48, p. 1497.
8. Seehra, M.S., Kalra, A., and Manivannan, A., *Fuel*, 2007, vol. 86, p. 829.
9. Ono, F., Giao, K., Tomida, D., and Yokoyama, C., *J. Food Engineering*, 2006, vol. 78, p. 1382.
10. Palav, A. and Seetharaman, K., *Carbohydrate Polymers*, 2007, vol. 67, p. 596.
11. Alekseeva, N.V., Evtushenko, A.M., Chikhacheva, I.P., Zubov, V.P., and Kubrakova, I.V., *Mendeleev Commun*., 2005, p. 170.
12. Petrova, N.V., Evtushenko, A.M., Chikhacheva, I.P., Zubov, V.P., and Kubrakova, I.V., *Zh. Prikl. Khim*., 2005, vol. 78, no. 7, p. 1178.

13. Chikhacheva, I.P., Zubov, V.P., Kubrakova, I.V., Nikolaeva, E.I., Kapustin, D.V., and Yagudaeva, E.Yu., *Zh. Obshch. Khim*., 2009, no. 4, p. 203.
14. Zubov, V.P., Chikhacheva, I.P., and Kubrakova, I.V., *ICAS, Intern. Congress on Analytic Sciences*, Moscow, 2006, p. 119.
15. Chikhacheva, I.P., Abstract of Papers, *International Scientific Conference*, Ivanovo, 2008, p. 306.
16. Chikhacheva, I.P., Zubov, V.P., Kubrakova, I.V., and Maslova, E.A., *Zh. Prikl. Khim*., 2008, no. 11, p. 1721.
17. Yanovskaya, L.A., Yuffit, S.S., and Kucherov, V.F., *Khimiya atsetalei* (Acetal Chemistry), Moscow: Nauka, 1975.
18. Ushakov, S.N., *Polivinilovyi spirt i ego proizvodnye* (Polyvinyl Alcohol and Its Derivatives), Moscow: Akad. Nauk SSSR, 1960.