ОРГАНИКАЛЫҚ ХИМИЯ
ОРГАНИЧЕСКАЯ ХИМИЯ
ORGANIC CHEMISTRY

G.Ya. Guba[1], A.O. Gusar[1], A.A. Bakibayev[2], Ye.M. Tazhbayev[3], Ye.V. Minayeva[3]

[1]Tomsk Polytechnic University, Russia;
[2]Tomsk State University, Russia;
[3]Ye.A. Buketov Karaganda State University, Kazakhstan
(E-mail: anngsa@mail.ru)

Dehydration/polycondensation of lactic acid under microwave irradiation

In this paper the effect of microwave irradiation power (MW) on the processes of polycondensation of lactic disturbed total internal reflection acid (LA) was studied for the first time. LA polycondensation was carried out in a multimodal reactor in a vacuum while bubbling with nitrogen at powers of 80, 130, 280, 360 and 500 watts. The change in the temperature of the LA sample under conditions of MW as a function of time and irradiation power was determined. Based on the data of 1H NMR and IR spectroscopy, it was suggested that at 80 W the molecules of physically bound water are mainly removed. The formation of lactic acid oligomers (LAO) occurs at a power of 130–280 W along with the removal of water and LA. Complete removal of water from LAO occurs at 360 watts. When LA is heated at MW power of 430 W, the formation and isolation of colorless crystals is observed, which can be classified by the IR spectra as lactide molecules (νC=O is 1770 cm^{-1}, νC–O–C is 1240 cm^{-1}). The molecular weight of LAO decreases at a power of 430 W and above. The kinetic curves of LA polycondensation at 130, 280 and 360 W are presented. The process of LA polycondensation at 360 watts is optimal. It was established that the rate of LA dehydration under MW conditions increases by 15–20 times as compared with carrying out the process under normal heating conditions.

Keywords: microwave irradiation, lactic acid, polylactic acid, lactic acid oligomers, NMR spectroscopy, IR spectroscopy, specific optical rotation, molecular weight.

Introduction

Polylactic acid (PLA) occupies the most significant market share of biodegradable polymers. PLA preference is due to the fact that it is made from renewable raw materials and has the ability to decompose in the natural environment under the action of bacteria, first to lactic acid and then to H_2O and CO_2, ultimately without damaging the biosphere [1–7]. PLA is widely used in the biomedical and pharmaceutical industries as an agent for controlled drug delivery and wound healing, tissue engineering etc. The use of PLA in medicine is primarily due to the fact that it does not cause allergic, inflammatory and other harmful reactions in living organisms and is completely decomposed into non-toxic metabolizing products [2–4, 7]. Lactic acid (LA) is used as a raw material for the synthesis of PLA. Due to the high hygroscopicity of LA, its concentrated aqueous solutions, namely, syrupy colorless odorless liquids with different percentages are usually used. In general, lactic acid polymers are obtained under conditions of ordinary heating in two ways, namely, by polymerization of lactic acid dimers (lactides) with ring opening [1–3, 5] and direct LA polycondensation [1, 5].

During the last decade, significant progress has been made in the field of polymer synthesis under MW conditions, including biologically active substances [8–17]. The use of MW can significantly reduce the time of reactions from hours to minutes, increase the yield and molecular weight of the product, and develop resource-efficient and environmentally friendly methods for the synthesis of biologically active compounds [8–14, 18, 19].

At the initial stage in all methods, dehydration / polycondensation of aqueous solutions of LA is carried out. This process is energy-intensive under normal conditions, the time for removal of water is up to 5–7 hours, and complete removal of water is difficult [18]. Microwave reactors are divided into multimode and monomode depending on the type of energy distribution in the reaction space. Some chemical reactions are sensitive to the type of irradiation and occur at different rates in multimode and monomode microwave reactors [8–9, 11, 13, 18–20]. LA and its LAO are polar molecules and can absorb microwave energy [21–23]. In this regard, much attention is paid to the synthesis of PLA polymers in the MW conditions [2–3, 8–10, 21, 24–27].

The processes of direct LA polymerization in MW conditions are attractive as energy-saving processes, since they make it possible to avoid the labor-intensive and energy-intensive stage of lactide synthesis [9, 17, 18, 26, 28]. The rate of LA polycondensation processes in the MW conditions depends on the volume of the reacting substances [26] and pressure [6].

The process of water removal and the subsequent lactic acid polycondensation under microwave irradiation takes place 10–15 times faster than at conventional thermal heating [18, 28, 29]. Direct LA condensation is carried out in three stages, namely, removal of free water, polycondensation of oligomers and condensation of high molecular weight polymers in the melt. In the first and third stages, the removal of water is decisive for the reaction rate. For the second stage, the rate is determined by chemical reaction [17, 12, 24].

LAO of high-purity without impurities of metals and solvents were obtained under MW conditions [18]. The reaction was carried out in a monomode reactor at 100–250 ºC at a power of 300 W. This high-purity oligomer of LA can be used as a safe and high-purity intermediate for the synthesis of PLA for use in medicine and pharmaceuticals. In Japan [10], an industrial installation of microwave synthesis of highly pure lactic acid oligomers under MW conditions for medical purposes was created.

In [10, 26], LAO was synthesized from aqueous solutions of LA in the presence of catalysts in monomode reactors under irradiation with 300 W [10, 26, 18]. When comparing the conduct of the polycondensation reaction of LA under MW conditions at 250–300 W in multi- and monomode reactors [30], the formation of high molecular weight PLAs in the case of multimode irradiation was noted. Thus, despite the large number of publications on the synthesis of PLA under MW conditions, the data obtained are scattered, performed under unequal conditions and in different microwave reactors. Although it is definitely possible to say that the time of PLA synthesis decreases by 10–15 times under MW conditions. Systematic studies on the effect of irradiation power and time on the process of dehydration / polycondensation of LA in the literature are missing. In this work, we investigated the effect of the MW power and the time on the LA polycondensation process under MW conditions in a multimode reactor.

Experimental

80 % Aqueous solution of D(+)lactic acid of brand «PURAK 80», manufacturer the Netherlands, was used as an object of the study. Chloroform was used as a solvent to determine the molecular weight. IR spectra of starting compounds and reaction products were recorded on an Agilent Resolutions Pro IR spectrometer. ^{1}H NMR spectra of LAO and PLA synthesized were recorded using a Fourier spectrometer AVANCE AV 300 from Bruker (Germany), the operating frequency was 300 MHz, and the solvent was deuterated chloroform. The molecular weight of the samples obtained was determined by the viscometric method using an Ubbelohde viscometer. To determine the molecular weight M, a non-linear Mark — Huvink equation is used, expressing the dependence of the characteristic viscosity on the molecular weight:

$$[\eta] = KM^a ,$$

where K — is the Huggins constant; α is a constant for this polymer-solvent system. Usually, depending on the nature of the solvent, the value of α, which determines the degree of curliness of the macromolecule, ranges from 0.5 to 0.8. In this work, $K = 4.7 \times 10^{-4}$, $\alpha = 0.67$ for LAO and PLA solutions in chloroform. The molecular weights of the PLA samples obtained were also determined by gel permeation chromatography on an Agilent 1200 instrument. Chloroform was used as a solvent; the eluent rate was 1 ml/s. To determine the angle of optical rotation (degrees×ml/dm×g), an AP-300 polarimeter was used, a tube length of 1 dm, solvent — chloroform, $\lambda = 589$ nm.

Dehydration/polycondensation of LA was carried out in a multimode microwave reactor in a vacuum while bubbling with nitrogen at powers of 80, 130, 280, 360 and 500 watts. The microwave reactor was created using a Daewoo Kor-5A17W microwave oven. The temperature was measured with a thermometer through the side opening of the microwave oven.

20 g of LA were loaded into a 100 ml glass heat-resistant flask, placed in a microwave reactor and sparged with nitrogen at a pressure of 200 mmHg at various capacities.
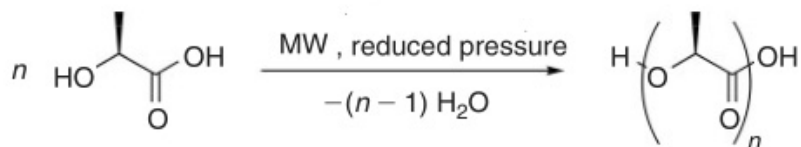
Results and discussion

Dehydration of LA in the MW conditions. Figure 1 shows the change in the temperature of the LA sample under MW conditions as a function of time and irradiation power. As MW power is increased from 130 (478 K) to 280 W, the temperature is increased only by 283 K. The temperature of LA samples in the MW conditions at a power of 280, 360, 500 W is the same and is 488 K.
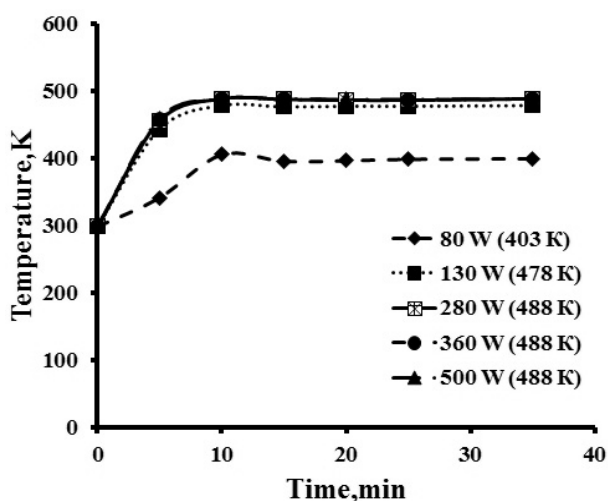
1 — 80 watts; *2* — 130 watts; *3* — 280 watts; *4* — 360 watts; *5* — 500 watts

Figure 1. Dependence of the temperature of a sample of lactic acid on time under MW conditions
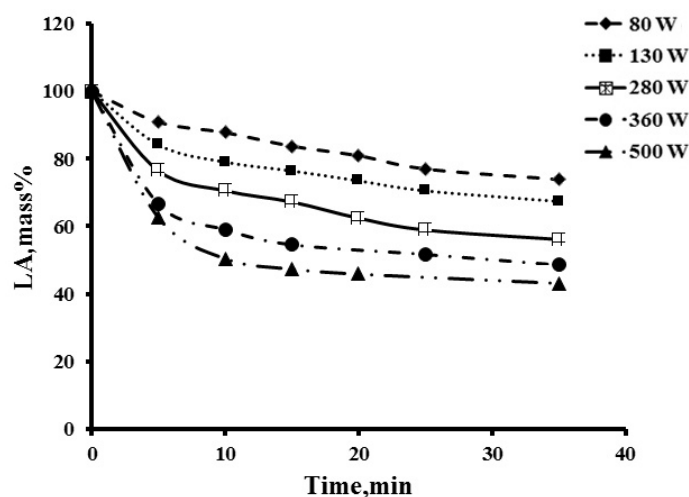
1 — 80 W; *2* — 130 W; *3* — 280 W; *4* — 360 W; *5* — 500 W

Figure 2. Weight reduction of 80 % LA solution after vacuuming under MW conditions

Figure 2 shows the decrease in the LA weight after vacuuming under MW conditions. In the first 5 minutes of LA dehydration the maximum amount of water and LA were obtained. With increasing vacuum

time, the process of water removal slows down. At 80 and 130 W, LA samples approximately lose 30 % of their weight.

The course of the dehydration/polycondensation reaction was evaluated by the change in the intensity of the absorption bands in the IR spectra (Fig. 3). The values of the troughs of the PLA IR spectra are given below (wavenumber, cm^{-1} (group): 3500–3300 (υOH), 2997 ($\upsilon_{as}CH_3$), 2947 ($\upsilon_{s}CH_3$), 2882 (υCH), 1760–1727 ($\upsilon C=O$), 1452 ($\delta_{as}CH_3$), 1388–1348 ($\delta_{s}CH_3$), 1368–1360 ($\delta1CH+\delta_{s}CH_3$), 1315–1300 ($\delta2CH$), 1270 (υCOC), 1215–1185 ($\upsilon_{as}COC$), 1130 ($r_{as}CH_3$), 1100–1090 ($\upsilon_{s}COC$), 1045 ($\upsilon C\text{-}CH_3$), 960–950 ($rCH_3 + \upsilon CC$), 875–860 ($\upsilon C–COO$).

In the IR spectrum of 80 % LA, a broad intense band with a maximum at 3400 cm^{-1} is observed, which can be attributed to the stretching vibrations of OH groups belonging to the associated water molecules. The intense band at 1727 cm^{-1} refers to the stretching vibrations of the C=O groups. The absorption band at 1650 cm^{-1} characterizes the deformation vibrations of O–H groups of water molecules. Also on this spectrum there is an intense band of 1240 cm^{-1}, which refers to the stretching vibrations of the C–O group.

After microwave irradiation at 80 W, an absorption band at 1727 cm^{-1} is observed in the IR spectra of LA, which relates to stretching vibrations of the C=O groups of LA, and a shift of the band at 1240 cm^{-1} to the low frequency region (1211 cm^{-1}) (Fig. 3, spectrum 1). It can be assumed that the molecules of physically bound water are mainly removed at 80 W.

As the MW power increases to 130 and 280 W (Fig. 3, spectra 2 and 3), the absorption bands of carbonyl groups at 1744 cm^{-1} are observed in the LA IR spectra, and the vibrations of the C–O bond shift to the low-frequency region (1188 cm^{-1}). The data obtained suggest that,, the polycondensation processes of LA and the rearrangement of the LAO obtained occur at a power of 130–280 W along with the removal of water.

The absorption band with a maximum of 1650 cm^{-1}, which characterizes the bending vibrations of water molecules, is absent in the IR spectra of LAO synthesized at MW power of 360–500 W (Fig. 3, curves 4 and 5). Consequently, the process of removing water from LA is complete.
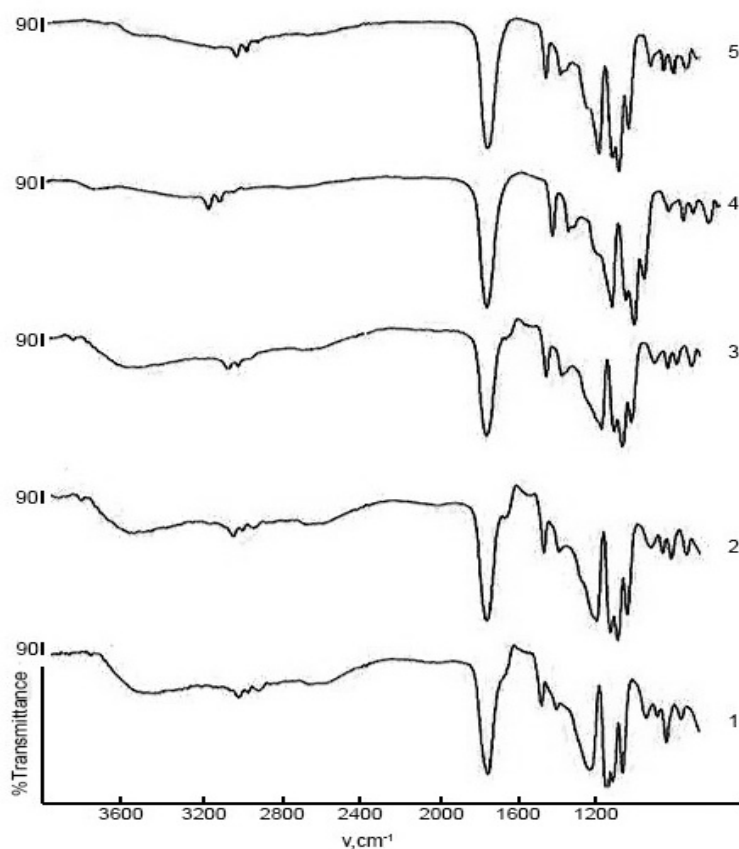
1 — 80 W; 2 —130 W; 3 — 280 W; 4 — 360 W; 5 — 500 W

Figure 3. The Disturbed Total Internal Reflection IR-spectrum of LA
after vacuuming in the MW conditions for 35 minutes at a power

At MW power of 430 W and above, the formation and release of colorless crystals is observed, which can be classified by IR spectra as lactide molecules ($vC=O$ is 1770 cm^{-1}, vC-O-C is 1240 cm^{-1}). The assumption of the process of dehydration/polycondensation of LA is confirmed by ^{1}H NMR data. The ^{1}H NMR chemical shifts are presented below.

The multiplet of the methylene group of LA is observed at 4.4 ppm, the chemical shift of the proton of the LAO methylene group multiplet is observed at 5.2 ppm. By changing the chemical shifts of the methylene groups of LA and LAO, one can judge the course of the process of oligomerization of lactic acid. The results of the ^{1}H NMR studies are presented in Figure 4 and Table.

Chemical shift, ppm	Structural fragments
5.2	1H, m, -**CH**(CH$_3$)-)
4.4	1H, m, -**CH**(CH$_3$)OH, end group)
1.6	(3H, d, -**CH$_3$**)

In the [1]NMR spectrum of an LAO sample obtained by vacuuming LA under MW conditions at 130 W (Fig. 4), there are quite intense chemical shifts of 4.4 and 5.2 ppm, characterizing the C–H group of LA and LAO, respectively. With an increase in power, the chemical shift at 5.2 ppm increases and 4.4 ppm decreases, that is, the formation of LAO.
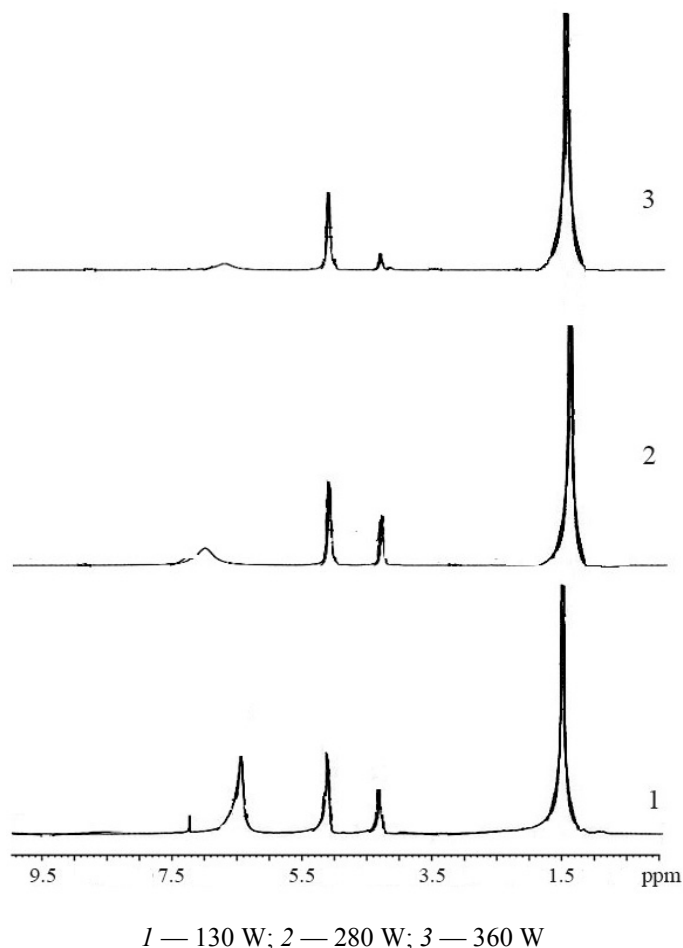

1 — 130 W; *2* — 280 W; *3* — 360 W

Figure 4. ^{1}H NMR spectrum of LA after vacuuming in MW conditions for 35 minutes

T a b l e

^{1}H NMR chemical shifts and physico-chemical properties of the LAO samples synthesized

Power (heating time) W/(min)	Chemical shifts, ppm (intensity)		The degree of conversion, %	M [Da]
	LA,δ, m(C–H)	LAO, δ, m(C–H)		
80(35)	4.3(1.18)	5.1(1)	46	-
130(35)	4.40(0.55)	5.2(1)	64	290
280(35)	4.4(0.49)	5.2(1)	67	440
360(35)	4.4(0.22)	5.2(1)	85	758
500(15)	4.3(0.51)	5.1(1)	66	420

The degree of conversion of LA into LAO was determined by the formula:

$$\frac{I(CH)_{LAO}}{I(CH)_{LA}+I(CH)_{LAO}}\times100\,\%\,.$$

Based on the ^{1}H NMR data presented in Table, it can be assumed that the molecules of physically bound water are mainly removed at 80 W and the formation of LAO does not occur. When dehydrating LA under MW conditions at 130 W, an increase in the molecular weight and an increase in the intensity of the chemical shift of 5.2 ppm, characterizing the C–H bond of the LAO, are observed. It can be assumed that, at a given power, the formation of LAO begins. In the range of 130–280 W, it appears that polycondensation of LA and LAO occurs, while in this power range the molecular weight changes slightly (Fig. 5).
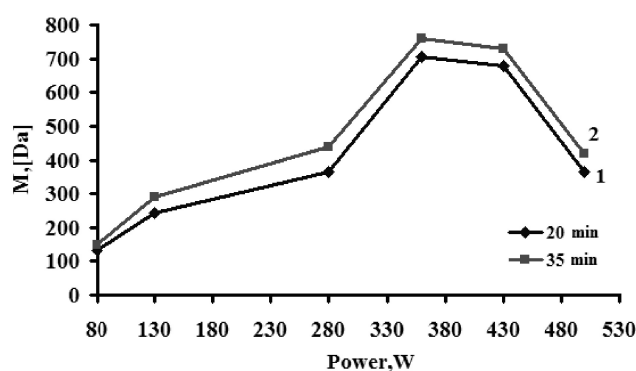
1 — 20 minutes; *2* — 35 minutes

Figure 5. Dependence of the molecular weight of LAO on the MW power
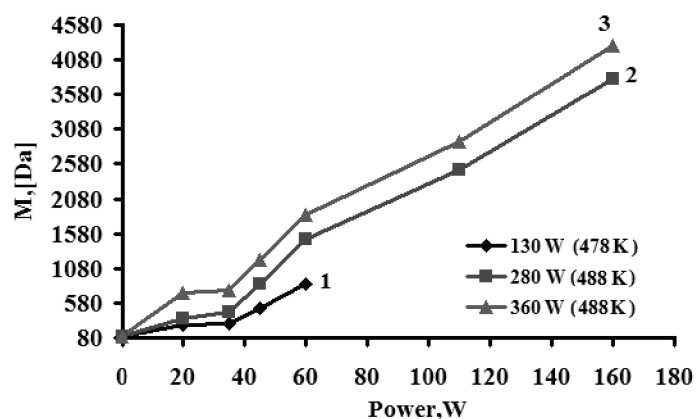
1 — 130 W (478 K); *2* — 280 W (488 K); *3* — 360 W (488 K)

Figure 6. Dependence of the molecular weight of LAO on the time of LA dehydration

When LA is heated at MW power above 360 W, the formation and release of colorless crystals is observed, which can be classified by IR spectra as lactide molecules (vC=O is 1770 cm^{-1}, vC–O–C is 1240 cm^{-1}).

With a power of 360 W, a significant increase in molecular weight occurs (Fig. 5). With an increase in the MW monosity up to 430 W and higher, the molecular weight of LAO decreases. The destruction of LAO apparently occurs with the formation of lactide.

The kinetic curves of LA polycondensation are shown in Figure 6. On the kinetic curves for up to 35 minutes, there is a slight increase in the molecular weight of LAO. Apparently, in this interval, the limiting stage is the removal of water molecules. In the range from 35 to 60 minutes, there is a sharp increase in the molecular weight of the polymer. Then the chain slows down, which may be due to the fact that the limiting stage is the release of water during the polymerization of higher molecular weight LAOs. The process of LA polycondensation at 360 watts is optimal.

Conclusions

It is established that when the MW power is increased from 130 to 280 W, the LA temperature is increased by 283 K, and at 280, 360, 500 W, the temperature of LAO samples is the same and is 488 K. Based on ^{1}H NMR and IR spectroscopy, it has been suggested that at 80 W physically bound water molecules are mainly removed. The formation of low molecular weight oligomers of lactic acid (LAO) occurs at a power of 130–280 W along with the removal of water and LA. LA polycondensation in the absence of a catalyst proceeds most effectively at 360 watts. That is, the process of polycondensation is determined not only by temperature, but primarily by the MW power. When LA is heated at MW power of 430 W, the formation and release of colorless crystals is observed, which can be classified by the IR spectra as lactide molecules (vC=O is 1770 cm^{-1}, v C–O–C is 1240 cm^{-1}). The molecular weight of LAO decreases at a power of 430 W and above. The kinetic curves of LA polycondensation at 130, 280 and 360 W are presented. The process of LA polycondensation at 360 watts is optimal. It is established that the rate of LA dehydration under MW conditions is increased by 15–20 times as compared with carrying out the process under normal heating conditions.

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Г.Я. Губа, А.О. Гусар, А.А. Бакибаев, Е.М. Тажбаев, Е.В. Минаева

Сүт қышқылының микротолқынды сәулелендіру жағдайларында дегидратациялануы/поликонденсациялануы

Мақалада алғаш рет микротолқынды сәулелендірудің (МТС) сүт қышқылының (СҚ) поликонденсациялану үрдістеріне әсері зерттелді. СҚ поликонденсациялануын мультимодалды реакторда вакуумда азотты 80, 130, 280, 360 және 500 Вт қуатында өткізу арқылы жүргізілді. СҚ үлгісінің температурасы МТС жағдайларында уақытқа және сәулелендіру қуатына байланысты өзгеретіні анықталды. ^{1}Н ЯМР және ИҚ-спектроскопия мәліметтері негізінде қуат 80 Вт болғанда негізінен физикалық байланысқан су молекулалары кетететіні туралы болжам ұсынылды. Қуат мөлшері 130–280 Вт болғанда, судың және СҚ бөлінуінен басқа, сүт қышқылының олигомерлері (СҚО) түзілетіні байқалды. Судың СҚО толық бөлінуі 360 Вт қуатында жүреді. СҚ МТС 430 Вт қуатында қыздырғанда түссіз кристалдардың түзілуі және бөлінуі байқалады. Оларды ИҚ-спектрлері бойынша лактид (v C=O 1770 см$^{-1}$, v C–O–C 1240 см$^{-1}$ құрады) молекулалары деп жіктеуге болады. СҚО молекулалық салмағы қуаты 430 Вт және одан да жоғары болғанда төмендейді. Қуат мөлшерлері 130, 280 және 360 Вт болғанда СҚ поликонденсациялануының кинетикалық қисықтары көрсетілген. Оңтайлы болып СҚ поликонденсациялануы 360 Вт қуатында табылады. СҚ дегидратациялану жылдамдығы МТС жағдайларында үрдісті әдеттегі қыздыру жағдайында өткізгенмен, салыстырғанда 15–20 есе артатыны анықталды.

Кілт сөздер: микротолқынды сәулелендіру, сүт қышқылы, полисүт қышқылы, сүт қышқылының олигомерлері, ЯМР-спектроскопия, ИҚ-спектроскопия, меншікті оптикалық айналу, молекулалық салмақ.

Г.Я. Губа, А.О. Гусар, А.А. Бакибаев, Е.М. Тажбаев, Е.В. Минаева

Дегидратация/поликонденсация молочной кислоты
в условиях микроволнового облучения

В статье впервые изучено влияние мощности микроволнового облучения (МВО) на процессы поликонденсации молочной кислоты (МК). Поликонденсацию МК проводили в мультимодальном реакторе в вакууме при барботировании азотом при мощностях 80, 130, 280, 360 и 500 Вт. Определено изменение температуры образца МК в условиях МВО в зависимости от времени и мощности излучения. На основании данных ^1H ЯМР и ИК-спектроскопии высказано предположение, что при 80 Вт в основном удаляются молекулы физически связанной воды. При мощности 130–280 Вт, наряду с удалением воды и МК, происходит образование олигомеров молочной кислоты (ОМК). Полное удаление воды из ОМК происходит при 360 Вт. При нагревании МК при мощности МВО 430 Вт наблюдается образование и выделение бесцветных кристаллов, которые можно классифицировать по ИК-спектрам как молекулы лактида (ν C=O составляет 1770 см$^{-1}$, ν C–O–C — 1240 см$^{-1}$). Молекулярный вес ОМК при мощности 430 Вт и выше уменьшается. Представлены кинетические кривые поликонденсации МК при 130, 280 и 360 Вт. Оптимальным является процесс поликонденсации МК при 360 Вт. Установлено, что скорость дегидратации МК в условиях МВО увеличивается в 15–20 раз по сравнению с проведением процесса в условиях обычного нагрева.

Ключевые слова: микроволновое облучение, молочная кислота, полимолочная кислота, олигомеры молочной кислоты, ЯМР-спектроскопия, ИК-спектроскопия, удельное оптическое вращение, молекулярный вес.