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Polymerization of lactic acid oligomers under microwave irradiation

The kinetics of the polymerization of lactic acid oligomers (LAO) was studied for the first time at various microwave irradiation powers (MW) in the presence of Sn(Oct)₂/benzyl alcohol (C₆H₅CH₂OH) catalyst and toluenesulfonic acid (TSA). LAO was polymerized in a multimodal reactor in a vacuum while sparging with nitrogen at powers of 130, 280, 360 W. The optimal concentrations of catalysts and initiator were determined, which represent 0.03 % Sn(Oct)₂/C₆H₅CH₂OH and 0.3–0.4 % TSA by weight of LAO. It was established that the polymerization of LAO in the presence of TSA proceeds already at 130 W. As the MW power increases, the rate of LAO polymerization increases. When Sn(Oct)₂/C₆H₅CH₂OH was used as a catalyst, the LAO polymerization process proceeds at a noticeable rate at 280 W, and after 25 min the molecular weight was about 20,000 Da. During the polymerization of LAO in the presence of catalysts at 360 W, lactide forms along with the formation of polylactic acid (PLA). Using the methods of IR and NMR spectroscopy, the structure of the obtained substances was studied. The synthesized PLA samples are optically pure; the optical rotation angle is 156–158 degrees×ml/dm×g. It has been suggested that during LAO polymerization under MW conditions, the so-called «non-thermal microwave effect» is observed, that is, at the same temperature (215 °C), but at different powers (280 W and 360 W), the LAO polymerization proceeds at different rates.

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

Introduction

PLA is one of the most promising biodegradable polymers used for various biomedical applications because of its biocompatibility and biodegradation in the human body into non-toxic metabolites [1–5].

Tin octanoate is recognized as the most effective catalyst for the synthesis of PLA. In this case, compounds containing hydroxyl groups, such as alcohols [2, 6, 7], initiate the ring opening polymerization process.

With traditional methods for the synthesis of PLA stringent conditions are necessary: high vacuum, long polymerization time and the consumption of large amounts of energy.

MW is able to accelerate chemical reactions 10–100 times. The wide possibilities offered by MW in chemistry are of great interest in the study and application of the effects of exposure to microwave radiation. It is believed that MW has firstly, the ability to cause rapid and significant heating of organic compounds and secondly, to activate reagent molecules and especially, cause their dissociation into ions and free radicals. The MW photon at a frequency of 2.45 GHz has the energy equal to 9.6×10^{-4} eV. This is not enough even to break the hydrogen bond [8, 9].

To date considerable experience has been accumulated on the use of MW to accelerate the synthesis of PLA [10–19].

The works [3, 6, 17–18, 20–23] show the results of studies of the synthesis of PLA under MW conditions by polymerization of lactides. The rate of polycondensation of lactic acid (LA) under MW conditions depends on the volume of reacting substances [24], pressure [19–20], and the monomer/catalyst ratio [25].

The polymerization of PLA with the opening of the lactide ring was successfully carried out using the conventional and microwave methods in [26]. The lactide polymerization reaction time under MW conditions was reduced from 6 hours to 20 minutes, the molecular weight (Mw) of the PLA was 11000 Da and under ordinary conditions the Mw of the PLA was 2000 Da.

The processes of direct polymerization of LA under MW conditions are attractive as energy-saving processes, since they avoid the labor-consuming and energy-consuming stage of lactide synthesis [3, 12, 14, 26, 27].

Direct condensation of LA is carried out in three stages: removal of free water, polycondensation with the formation of oligomers and condensation of oligomers to high molecular weight polymers in the melt. On the first and third stages, water removal is critical to the reaction rate. For the second stage, the rate is determined by the chemical reaction [12, 28].

The authors of [12, 26] studied the polycondensation of 85 % LA in the presence of a SnCl₂/TSA binary catalyst under MW conditions in a monomode reactor. MW with Mw 16000 Da was obtained by carrying out the reaction for 30 min at a pressure of 30 mmHg. When only TSA is used as a catalyst, LAO with Mw less than 1000 Da is formed. This polymer can also be converted to high molecular weight PLA by melt polycondensation [12].

The effect of MW is currently debatable [6, 11, 25, 27, 29–31]. No data were found on increasing the reaction rate due to an increase in activation energy in the MW field in the literature.

The authors of [25], while studying the polymerization of lactide in a toluene solution, expressed the opinion that microwave irradiation did not cause any changes in the polymerization kinetics, which made it possible to consider the absence of a specific «non-thermal» effect during microwave synthesis.

Authors [30] studied the kinetics of caprolactam polymerization under MW conditions. As a result, a specific «non-thermal» effect was suggested.

Authors [31] investigated the polycondensation of LA under MW conditions in xylene in the presence of catalysts at a power of 100–400 W and pointed to the existence of a specific «non-thermal» effect induced by an electric field.

In [32], a lactide-pullulan copolymer was synthesized in a monomode microwave reactor and it was found that at the same reaction temperature (80 °C) with increasing irradiation power from 50 to 200 W, the yield of the final product increased. The authors suggested the existence of a specific «non-thermal» effect.

An analysis of the literature data showed that, despite the large number of publications on the synthesis of PLA under MW conditions, the results obtained are disparate, performed under different conditions and in various microwave reactors [29]. Although it can be said unequivocally that under MW conditions, the time for the synthesis of PLA decreases by 10–15 times.

In this work, the influence of the MW power, the time and nature of the catalysts on the polymerization of LAO under the MW conditions in a multimode reactor was investigated.

Experimental

LAO obtained according to the method described in [33] by evacuation for 25 min at 280 W of an 80 % aqueous solution of D(+)-acid of the PURAK 80 brand (country of origin is the Netherlands) was used as the object of study. Sn(Oct)₂, TSA applied qualifications chemically pure, C₆H₅CH₂OH analytical grade was used as initiator.

The IR spectra of the starting compounds and reaction products were recorded on an Agilent Resolutions Pro IR spectrometer.

The ¹H NMR spectra of the synthesized LAO and PLA were recorded using a Bruker AVANCE AV 300 Fourier spectrometer (Germany), an operating frequency of 300 MHz, and a deuterated CDCl₃ solvent.

The molecular weights of the obtained samples were determined by the viscometric method using a Ubbelode viscometer. Chloroform was used as a solvent. The molecular weights of PLA were also determined by gel permeation chromatography on an Agilent 1200 instrument. Chloroform was used as a solvent, the eluent velocity was 1 ml/s.

To determine the angle of optical rotation (degrees×ml/dm×g), an AR-300 polarimeter was used, the tube length was 1 dm, and the solvent was chloroform, λ = 589 nm.

Thermal studies of PLA samples were performed on an SDT Q600 V20.9 Build 20 instrument. LAO was polymerized under microwave irradiation according to the general scheme shown in Figure 1.

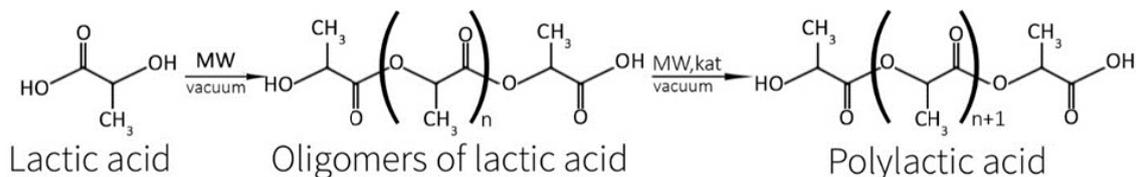


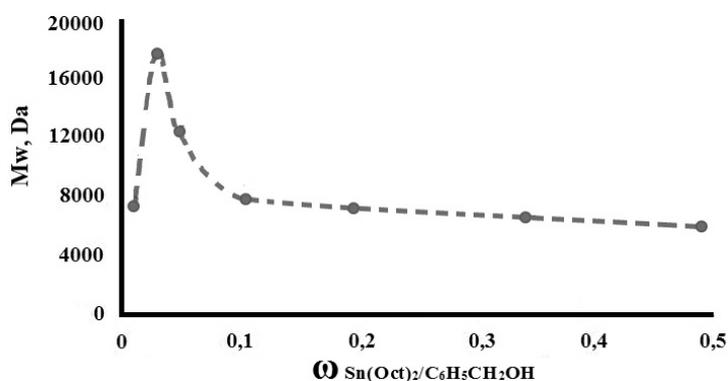
Figure 1. Scheme for the synthesis of PLA (catalyst — $\text{Sn}(\text{Oct})_2$, TSA)

The resulting 10 g LAO was loaded into a 100 ml glass heat-resistant flask and catalysts ($\text{Sn}(\text{Oct})_2$, TSA) were added in an amount of 0.03–0.3 %, together with the initiator ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, in the ratio of catalyst/initiator 1:1). They were placed in a microwave reactor and sparged with nitrogen at a pressure of 200 mmHg at various powers 130–360 W.

Results and Discussion

It is known that Mw of PLA depends on a number of factors: the nature and amount of the catalyst, the ratio of catalyst:cocatalyst, temperature and polymerization time. Figure 2 shows the curves of the dependence of the molecular weight of PLA on the concentration of the catalyst. The polymerization was carried out at 280 W for 25 min. The highest Mw of PLA was achieved at a catalyst concentration (ω) of 0.03 mass.%.

The increasing of catalyst concentration to $\omega = 0.03$ mass.% leads to molecular weight growth. However, further catalyst concentration increase provokes the reverse process of molecular weight decreasing. Moreover, samples changed the color to darker one. Taking into account these facts, it could be suggested that catalyst concentration increase stimulates polymer destruction process.



$\text{Sn}(\text{Oct})_2/\text{C}_6\text{H}_5\text{CH}_2\text{OH} = 1:1$; Power = 280 W; $\tau = 25$ min

Figure 2. Dependence of Mw PLA on ω of the catalyst during LAO polymerization under MW

$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ is an effective initiator of $\text{Sn}(\text{Oct})_2$ in the synthesis of PLA. Upon addition of $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ Mw to $\text{Sn}(\text{Oct})_2$, the PLA increases and reaches a maximum at a ratio of 1:1, and then decreases (Fig. 3). In the absence of $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, the polymerization process is practically not observed. When the ratio of catalyst: initiator is 1:2 and the reaction takes more than 15 minutes, the polymer is degraded and the reaction mass becomes black-brown. The mechanism of PLA at $\text{Sn}(\text{Oct})_2$ and alcohols are described in [15, 17]. It is known that alcohols presence increases the reaction rate of cyclic LAO polymerization at the presence of $\text{Sn}(\text{Oct})_2$.

It could be suggested that $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ forms intermediate complex. The optimal ratio is 1:1.

The kinetic curves of LAO polymerization in the presence of $\text{Sn}(\text{Oct})_2/\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ are shown in Figure 4. The dependence of Mw at an irradiation power of 130 W (205 °C), Mw LAO slowly increases. So, during the course of the reaction for 30 min, the Mw LAO is only 1500 Da.

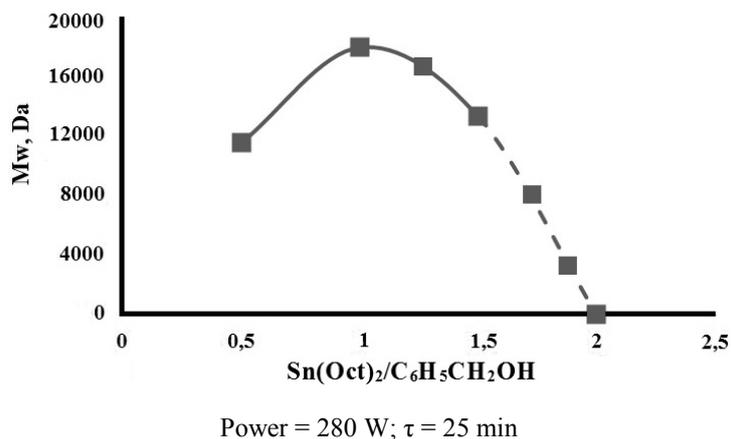
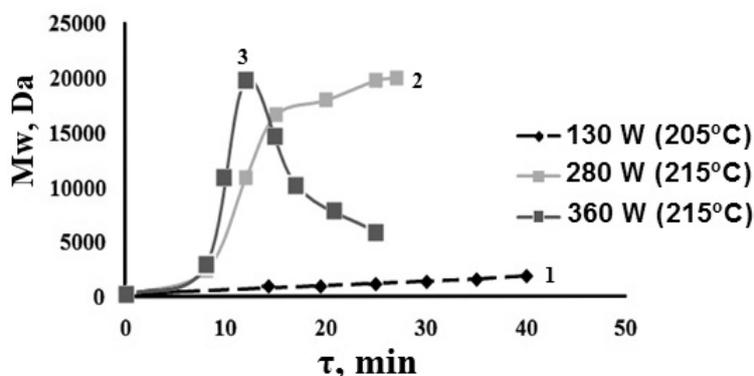


Figure 3. Dependence of Mw of PLA on the molar ratio of Sn(Oct)₂/C₆H₅CH₂OH during LAO polymerization under MW conditions



Catalyst — Sn(Oct)₂/C₆H₅CH₂OH; Power: 1 — 130 W; 2 — 280 W; 3 — 360 W
Ratio catalyst/initiator/LAO = 3/3/10000 (mass.%)

Figure 4. Kinetic curves of LAO polymerization in the presence of a catalyst

At an MW power of 280 W, the sample heats up during the first 10 minutes and the process of polycondensation of low molecular weight LAO occurs with the removal of water. With an increase in the process time, the molecular weight of LAO sharply increases. Presumably, at this period of the process, the LAO polymerization stage is limiting with the opening of the cycle after 15 minutes the polymerization process slows down, which is apparently due to the fact that the diffusion stage of the process becomes limiting.

It should be noted separately that the temperature of the LAO reaction mass reaches 215 °C both at 280 W and 360 W [33].

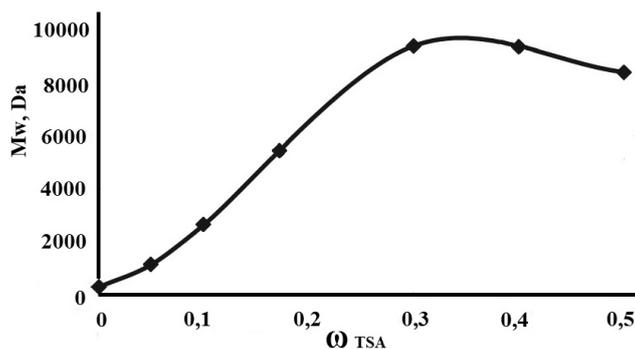
At a power of 360 W, the molecular weight of the polymer increases sharply and reaches its maximum value of about 20000 Da in 12 minutes.

With an increase in the process time, the resulting polymer is degraded and Mw LAO sharply decreases, and a white crystalline compound is formed at the outlet of the reactor, which was identified as lactide using IR spectroscopy.

Thus, we can assume that in this case the so-called «non-thermal microwave effect» is observed, that is, under the same conditions at the same temperature (215 °C), but with different capacities (280 W and 360 W), the LAO polymerization proceeds at different rates.

LAO polymerization in the presence of TSA was performed at powers of 130 W, 280 W, and 360 W. The dependence of Mw of PLA on ω TSA is presented in Figure 5.

This dependence shows that with an increase in the catalyst concentration from 0.05 to 0.3 %, an increase in Mw is observed. The optimal ω TSA is in the range of 0.3–0.4 mass.%.

Power = 280 W; τ = 30 minFigure 5. Dependence of Mw of PLA on ω TSA upon polymerization of LAO under MW conditions

The kinetic curves of LAO polymerization in the presence of TSA are presented in Figure 6. With an increase in reaction time, an increase in Mw of LAO is observed. However, Mw PLA grows unevenly at 280 W. When carrying out the reaction up to 15 minutes, a weak growth of the LAO chain is observed, low molecular weight oligomers are formed. In the range from 15 to 30 minutes, a sharp increase in the Mw of the polymer occurs, and then the chain grows in a linear relationship.

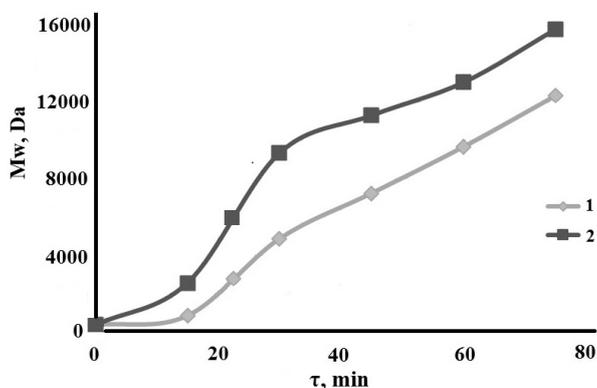
1 — 130 W; 2 — 280 W (ω TSA 0.3 mass.%)

Figure 6. Dependence of Mw of the PLA sample on time in the conditions of MW

During the polymerization of LAO at a power of 360 W, volatile cyclic lactides are formed in parallel with the formation of PLA, which are white crystals deposited on the walls of the flask and the condenser. Physicochemical properties of the synthesized samples and experimental conditions are presented in Table.

Table

Synthesis conditions and physicochemical properties of synthesized LAO samples

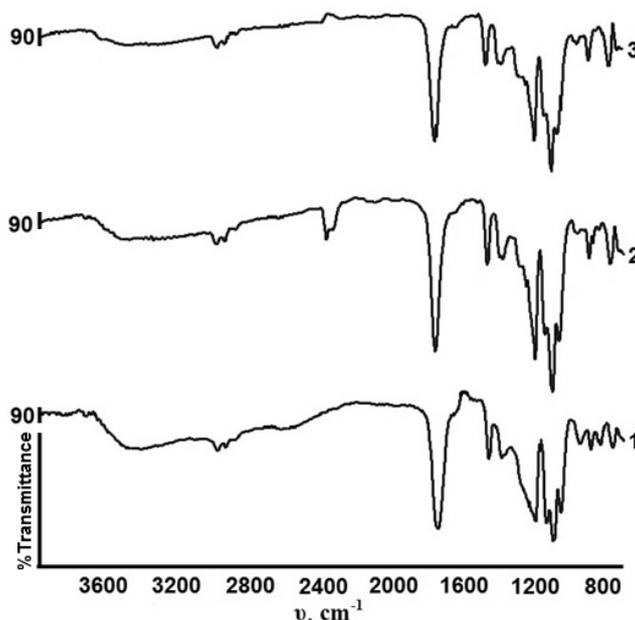
Catalyst	Power, W	t , °C	τ , min	Mw ^a , Da	Mw ^b , Da	Mn ^b , Da	PD	$[\alpha]_{589}^{25}$ degrees×ml/ dm×g
Sn(Oct) ₂ / C ₆ H ₅ CH ₂ OH	130	205	35	1700	—	—	—	—
Sn(Oct) ₂ / C ₆ H ₅ CH ₂ OH	280	215	25	19900	19230	12820	1,50	-156
TSA	280	215	35	9350	9940	5402	1,84	-157
Sn(Oct) ₂ / C ₆ H ₅ CH ₂ OH	360	215	8	3000				—
			12	19500				-158
			17	10300				-152
			25	6000	The sample darkened, lactide formed			
TSA	360	215	10	Lactide formed				

Note. t , °C — temperature; τ — reaction time, min; Mw^a, Da — calculated using a viscometric method; Mw^b, Da — determined by NMR spectroscopy; Mn^b, Da — determined by gel permeation chromatography; $[\alpha]_{589}^{25}$ — optical rotation angle.

Therefore, it could be suggested that MW power determines the kinetics of LAO polymerization in the presence of TSA.

The data obtained confirm the presence of a «non-thermal microwave effect» during LAO polymerization under MW conditions, since at the same temperature but diverse capacities, LAO polymerization proceeds at different rates by various mechanisms at 280 W and 360 W.

The optical rotation angle of the synthesized samples is 156–158 degrees \times ml/dm \times g, i.e., the synthesized samples are optically pure. Figure 7 shows the IR spectra of PLA samples synthesized under MW conditions.



1 — $\tau = 20$ min after polymerization;
 2 — $\tau = 30$ min at 280 W in the presence of 0.3 mass.% TSA;
 3 — $\tau = 30$ min at 280 W in the presence of 0.03 mass.% Sn(Oct)₂/C₆H₅CH₂OH

Figure 7. IR spectra of LAO obtained at a power of 280 W

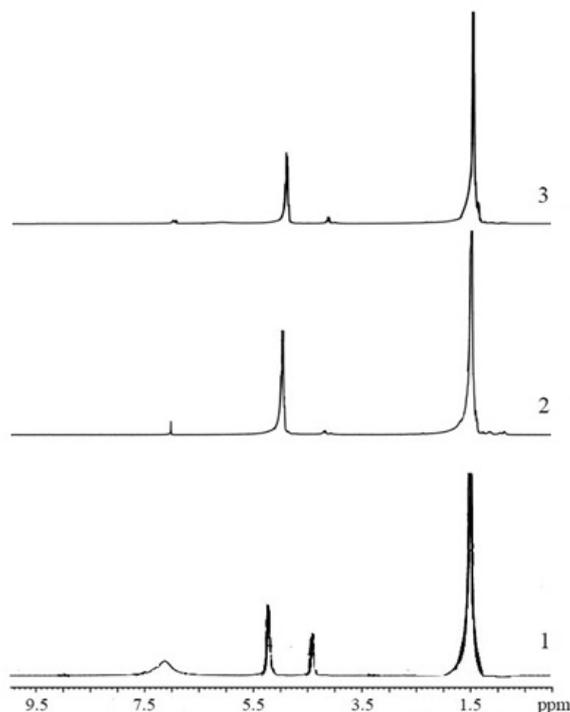
The interpretation of the absorption bands of the IR spectra is given below: 3500–3300 (ν OH), 2997 (ν_{as} CH₃), 2947 (ν_s CH₃), 2882 (ν CH), 1760–1727 (ν C=O), 1452 (δ_{as} CH₃), 1388–1348 (δ_s CH₃), 1368–1360 (δ_1 CH+ δ_s CH₃), 1315–1300 (δ_2 CH), 1270 (ν COC), 1215–1185 (ν_{as} COC), 1130 (ν_{as} CH₃), 1100–1090 (ν_s COC), 1045 (ν C-CH₃), 960–950 (ν CH₃ + ν CC), 875–860 (ν C-COO), 760–740 (δ C=O).

In the IR spectra, intense absorption bands of carbonyl groups C=O (1757 cm⁻¹) and absorption bands of C-O-C bonds of 1188 cm⁻¹, PLA characteristic are observed.

On curves 2 and 3 (Fig. 7), belonging to the samples of synthesized PLA, the intensity of the absorption bands in the region of 3600–3500 cm⁻¹, characterizing the vibrations of the OH groups, significantly decreased. The peaks in the region of 1759 cm⁻¹, which belong to the stretching vibrations of the C=O bond, become more symmetrical. The band in the region of 1188 cm⁻¹, related to the stretching vibrations of the –C–O– bond, becomes more pronounced. Figure 8 shows the ¹H NMR data of PLA samples synthesized under MW conditions.

Chemical shifts ¹H NMR LAO and PLA are presented below:

Chemical shift in ppm	Structural assignments
5.2	1H, m, – <u>CH</u> (CH ₃)–
4.4	1H, m, – <u>CH</u> (CH ₃)OH, end group)
1.6	(3H, d, – <u>CH</u> ₃)



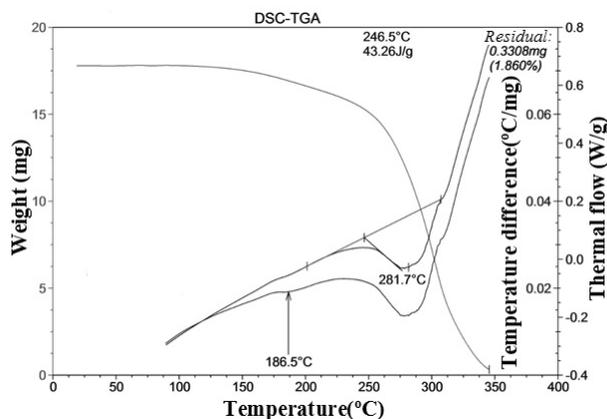
- 1 — OLA obtained by irradiating MW in vacuum for 20 minutes;
 2 — PLA, obtained from OLA in the presence of TSA for 30 minutes at a power of 280 W;
 3 — PLA obtained from OLA in the presence of $\text{Sn}(\text{Oct})_2$ for 25 minutes at a power of 280 W

Figure 8. ^1H NMR spectra

The proton signal of the multiplet of the methine group of the terminal group $-\text{CH}(\text{CH}_3)\text{OH}$ LAO is 4.4 ppm, the chemical shift of the proton of the multiplet of the methylene group of the PLA is 5.2 ppm. By the ratio of signal intensities of methine groups in the region of 4.4 and 5.2 ppm we can judge the depth of the polymerization process of LAO to PLA.

Intensive chemical shifts of 4.4 ppm are observed on curve 1 (Fig. 8), which suggests the presence of a significant number of terminal hydroxyl (and, accordingly, carboxyl) groups in LAO. In the spectra of PLA samples obtained by the polymerization of LAO in the presence of TSA and $\text{Sn}(\text{Oct})_2$ (see Fig. 8). Chemical shifts at 4.4 ppm are observed. Other shifts are absent.

Figure 9 shows the DSC thermogram of a PLA sample synthesized at 280 W for 25 min in the presence of 0.09 mass.% $\text{Sn}(\text{Oct})_2$. The absence of a pronounced melting peak at 180–190°C suggests that the polymer mainly has an amorphous structure.



$\tau = 20$ min in the presence of $\text{Sn}(\text{Oct})_2$

Figure 9. DSC-TGA spectra of PLA synthesized under MW conditions

Conclusions

The optimal concentrations of catalysts and initiator for the synthesis of PLA were determined, which are 0.03 % Sn (Oct)₂/C₆H₅CH₂OH and 0.3–0.4 % TSA by weight of LAO.

It was found that with an increase in the power of MW, the rate of LAO polymerization in the presence of catalysts increases. When Sn(Oct)₂/C₆H₅CH₂OH is used as a catalyst, the LAO polymerization process proceeds at a noticeable rate at 280 W, and after 25 min Mw is about 20000 Da. The synthesized PLA samples are optically pure; the optical rotation angle of the synthesized samples is 156–158 degrees×ml/dm×g. It has been suggested that during LAO polymerization under MW conditions, the so-called «non-thermal microwave effect» is observed, that is, at the same temperature (215 °C), but with various capacities (280 W and 360 W), the LAO polymerization proceeds at different rates by diverse mechanisms. During the polymerization of LAO in the presence of catalysts at 360 W, a small amount of lactide is formed along with the formation of PLA.

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Қысқа толқынды сәулелендіру жағдайында сүт қышқылы олигомерлерін полимерлеу

Сүт қышқылының олигомерлерінің (СҚО) полимерленуінің кинетикасы алғаш рет микротолқынды сәулеленудің (МТС) әртүрлі қуаттарында, Sn(Oct)₂ / бензил спирті (C₆H₅CH₂OH) катализаторы және толуолсульфоқышқылы (ТСК) қатысуымен зерттелді. СҚО полимеризациясы мультимодальды реактордағы вакуумда азотпен барботаждау және 130, 280, 360 Вт қуаттылықтарда жүргізілді. 0.03 % Sn(Oct)₂/C₆H₅CH₂OH және СҚО салмағы бойынша 0,3–0,4 % ТСК болатын катализаторлар мен сокатализаторлардың оңтайлы концентрациясы анықталды. СҚО салмағынан 0,03 % Sn(Oct)₂/C₆H₅CH₂OH және 0,3–0,4 % ТСК тұратын катализаторлар мен сокатализаторлардың оптималды концентрациясы табылды. ТСК қатысуымен СҚО-ны полимерлеу 130 Вт-тан басталатындығы анықталды. МТС қуатының жоғарылауымен СҚО полимерлену жылдамдығы артады. Sn(Oct)₂/C₆H₅CH₂OH катализатор ретінде қолданғанда, СҚО полимеризациясы 280 Вт жылдамдықпен жүреді, ал 25 минуттан кейін молекулалық массасы шамамен 20000 Да болды. СҚО полимерлеу процесі кезінде катализаторлардың қатысуымен 360 Вт қуаттылықта полисүт қышқылдың (ПСК) түзілуімен бірге лактид түзіледі. ИҚ және ЯМР спектроскопия әдістерінің көмегімен алынған полимерлердің құрылымы зерттелді. Синтезделген ПСК үлгілері оптикалық таза, оптикалық бұрылу бұрышы 156–158 градус×мл/дм×г тең. Болжам бойынша, МТС жағдайында СҚО полимеризациясы кезінде «жылусыз микротолқынды эффект» деп аталатын, яғни бірдей жағдайларда, бірдей температурада (215 °C), бірақ әртүрлі қуаттылықта (280 және 360 Вт) СҚО полимерленуі әр түрлі жылдамдықпен жүреді.

Кілт сөздер: микротолқынды сәулелендіру, сүт қышқылы, полисүт қышқылы, сүт қышқылы олигомерлері, ЯМР спектроскопиясы, ИҚ спектроскопиясы, меншікті оптикалық айналу, катализатор.

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Полимеризация олигомеров молочной кислоты в условиях микроволнового облучения

Впервые изучена кинетика полимеризации олигомеров молочной кислоты (ОМК) при различных мощностях микроволнового облучения (МВО) в присутствии катализатора/сокатализатора Sn(Oct)₂/бензиловый спирт (C₆H₅CH₂OH) и толуолсульфокислоты (ТСК). Полимеризацию ОМК проводили в мультимодальном реакторе в вакууме при барботировании азотом при мощностях 130, 280,

360 Вт. Определены оптимальные концентрации катализаторов и сокатализаторов, которые составляют 0,03 % $\text{Sn}(\text{Oct})_2/\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ и 0,3–0,4 % ТСК от массы ОМК. Установлено, что полимеризация ОМК в присутствии ТСК протекает уже при 130 Вт. С повышением мощности МВО скорость процесса полимеризации ОМК увеличивается. При использовании в качестве катализатора $\text{Sn}(\text{Oct})_2/\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ процесс полимеризации ОМК с заметной скоростью протекает при 280 Вт, и через 25 мин молекулярный вес составлял около 20000 Да. При проведении процесса полимеризации ОМК в присутствии катализаторов при 360 Вт, наряду с образованием полимолочной кислоты (ПМК), происходит образование лактида. С применением методов ИК- и ЯМР-спектроскопии изучено строение полученных полимеров. Синтезированные образцы ПМК являются оптически чистыми, угол оптического вращения равен 156–158 градусам \times мл/дм \times г. Высказано предположение, что при полимеризации ОМК в условиях МВО наблюдается так называемый «нетепловой микроволновой эффект», т.е. в одинаковых условиях при одинаковой температуре (215 °С), но разных мощностях (280 и 360 Вт) процесс полимеризации ОМК протекает с различной скоростью.

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