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S. V. KOSTJUK^{1,2}**CATIONIC STEP-GROWTH POLYMERIZATION
OF 2-METHOXYBENZYL ALCOHOL
USING DIFFERENT LEWIS ACIDS AS CATALYSTS**¹*Belarusian State University, Minsk, Belarus*²*Research Institute for Physical Chemical Problems of the Belarusian State University,
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Исследована катионная поликонденсация 2-метоксибензилового спирта в присутствии различных кислот Льюиса (TiCl_4 , SnCl_4 и ${}^t\text{BuAlCl}_2$) и при разных температурах. Показано, что использование сильных кислот Льюиса (TiCl_4) в качестве катализатора процесса способствует протеканию побочных реакций разветвления и сшивки цепи, приводящих в конечном счете к образованию нерастворимого в органических растворителях полимера. Снижение температуры реакции также вызывает заметное увеличение доли побочных реакций. Наоборот, использование мягких кислот Льюиса в качестве катализаторов (SnCl_4 и ${}^t\text{BuAlCl}_2$) и проведение полимеризации при комнатной температуре позволяет получать линейные полимеры с низкой полидисперсностью. Так, при полимеризации 2-метоксибензилового спирта в присутствии SnCl_4 в качестве катализатора при 20 °С был получен линейный поли(2-метоксибензиловый спирт) с M_n около 2000 г · моль⁻¹ и относительно низкой полидисперсностью ($M_w/M_n < 2,0$).

The cationic step-growth polymerization of 2-methoxybenzyl alcohol in the presence of different Lewis acids (TiCl_4 , SnCl_4 and ${}^t\text{BuAlCl}_2$) at various temperatures has been investigated. It was shown that the use of strong Lewis acids (TiCl_4) leads to proceeding of side reactions such as branching and cross-linking, which results in the formation of a polymer insoluble in organic solvents. The decrease in the temperature of the reaction also intensifies the proceeding of side reactions. On the contrary, the use of soft Lewis acids as catalysts (SnCl_4 and ${}^t\text{BuAlCl}_2$) and polymerization at room temperature ensures obtaining linear polymers with low polydispersity. The SnCl_4 -catalyzed polymerization of 2-methoxybenzyl alcohol at 20 °C affords linear poly(2-methoxybenzyl alcohol) with M_n of about 2000 g · mol⁻¹ and relatively low polydispersity ($M_w/M_n < 2.0$).

Ключевые слова: катионная поликонденсация; 2-метоксибензиловый спирт; кислота Льюиса; среднечисловая молекулярная масса; полидисперсность.

Keywords: cationic step-growth polymerization; 2-methoxybenzyl alcohol; Lewis acid; number-average molecular weight; polydispersity.

Cationic polymerization of vinyl monomers, similarly to anionic and radical polymerizations, proceeds by the way of chain-growth mechanism via multiple addition of the monomer molecule to the active center with the formation of high molecular weight product even at the beginning of the reaction [1]. In contrast, step-

growth polymerization results in the formation of oligomers in conjunction with the release of small molecules (water, alcohols) as by-products at the earlier steps of reaction followed by the further condensation of these oligomers with generation of high molecular weight polymers at the later stages of polymerization [1]. However, it was shown recently that chain-growth and step-growth polymerization can proceed simultaneously under certain conditions leading to polymers of unique architectures, which are difficult to prepare by other means. For example, simultaneous chain-growth and step-growth radical copolymerization of methyl acrylate and 3-butenyl 2-chloropropionate catalyzed by $\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2$ (Cp^* is 1,2,3,4,5-pentamethylcyclopentadiene) results in copolymers possessing both C–C and C–O linkages in a main chain [2]. Moreover, chain-growth condensation polymerization [3] as well as self-condensing radical polymerization of *p*-(2-bromoisobutyloylmethyl)styrene using $\text{Cu}/\text{CuBr}_2/2,2'$ -bipyridine catalytic system [4] were also reported. In addition, coordination polymerization of *para*- and *meta*-methoxystyrenes catalyzed by half-sandwich rare-earth alkyl complexes activated by $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ proceeds simultaneously via chain-growth and step-growth mechanisms [5, 6].

In respect to cationic polymerization, only several examples of acid-catalyzed step-growth cationic polymerization are known including polymerization of specific monomers such as organic carbonates [7] or phenol/formaldehyde mixture [1]. In addition, chain-growth/step-growth polymerization for 2-vinylthiophene [8] and 2-alkenylfuranes [9] was reported, while for the latter monomer a set of side reactions (cross-linking, isomerization) was also observed [10]. Very recently, we have reported simultaneous step-growth and chain-growth cationic polymerization of 9-(4-vinylphenyl)carbazole leading with polymers with totally different photophysical properties in comparison with polymer from the same monomer obtained via conventional chain-growth radical polymerization involving only vinyl double bond into the reaction [11].

In this article, the concept of cationic step-growth polymerization was expanded to polymerization of 2-methoxybenzyl alcohol (MeBzOH), a monomer, which, in contrast to 9-(4-vinylphenyl)carbazole, does not contain the vinyl group. Particularly, the effect of Lewis acid nature and concentration as well as polymerization temperature will be investigated here in order to find optimal conditions for the preparation of linear poly(2-methoxybenzyl alcohol) via step-growth cationic polymerization.

EXPERIMENTAL PART

Materials. 2-Methoxybenzyl alcohol (Sigma-Aldrich, 99 %) was dried with CaCl_2 and then distilled under reduced pressure. CH_2Cl_2 (Reachim), 1,2-dichloroethane were treated with sulphuric acid, washed with aqueous sodium bicarbonate, dried over CaCl_2 and distilled twice from CaH_2 under an inert atmosphere. SnCl_4 (Aldrich, 98 %), TiCl_4 (Sigma-Aldrich, >99 %) were distilled under reduced pressure before the usage. AlCl_3 (Aldrich, 99.999 %), $t\text{Bu}_3\text{Al}$ (1 M solution in hexane, Aldrich), CDCl_3

(Euriso-top[®]), tetrahydrofuran (anhydrous, Merck Millipore, >99.9 %) and ethanol were used as received. Isobutylaluminium dichloride (^tBuAlCl₂) was obtained as 1 M solution in hexanes or toluene by mixing of AlCl₃ suspension and ^tBu₃Al solutions in an appropriate molar ratio at room temperature according to procedure described in [12]. The concentration and composition of synthesized ^tBuAlCl₂ solutions were controlled by back titration of Al with EDTA by ZnSO₄ with diphenylthiocarbazone as an indicator and back titration of chlorine using Volhard's method, respectively.

Methods. Size exclusion chromatography (SEC) was performed on a Agilent 1200 apparatus with Nucleogel GPC LM-5, 300/7.7 column and one precolumn (PL gel 5 mm guard) thermostated at 30 °C. The detection was achieved by differential refractometer. Tetrahydrofuran (THF) was eluted at a flow rate of 1.0 cm³/min. The calculation of molar mass and polydispersity was based on polystyrene standards (Polymer Labs, Germany). ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded in CDCl₃ at 25 °C or C₆D₆ on a Bruker AC-400 spectrometer calibrated relatively to the residual solvent resonance.

Polymerization procedures. Cationic polymerization of 2-methoxybenzyl alcohol was carried out under dry argon atmosphere in a Schlenk tube. Liquid reagents were transferred to reactor via dry syringes against a continuous argon flow. In a typical experiment, the reaction was initiated by adding of SnCl₄ (0.22 cm³) to a mixture of 2-methoxybenzyl alcohol (1 cm³) and CH₂Cl₂ (8.2 cm³) at room temperature. After a predetermined time, ~1 cm³ aliquots were withdrawn and poured into excess of ethanol. The precipitated polymers were separated from the solution by centrifugation and then dried in vacuum at 65 °C. Monomer conversions were determined gravimetrically. Then, for NMR investigations the polymers were further purified by column chromatography using silica gel 60 from Fluka and CH₂Cl₂ as eluent. The solvent was evaporated by rotary evaporator and polymer was dried in vacuum at 65 °C.

RESULTS AND DISCUSSION

In the first series of experiments, three Lewis acids of different acidity were tested as catalysts of step-growth polymerization of 2-methoxybenzyl alcohol (MeBzOH). Titanium tetrachloride (TiCl₄), which is the strongest Lewis acid among the studied acids [13, 14], induced the polymerization only at a very high concentration ([TiCl₄] : [MeBzOH] = 1 : 1) and low temperature due to the formation of strong complex between the Lewis acid and monomer [15] (samples 1 and 2, Table). Lewis acid of much lower concentration was required to initiate the polymerization at higher temperature due to the decrease in the strength of TiCl₄ complex compound with MeBzOH (Table) [15]. However, independently on the temperature and Lewis acid concentration, the TiCl₄-co-initiated polymerization of MeBzOH was accompanied by side reactions leading to the formation of cross-linked polymer, which was insoluble or only partially soluble in common organic solvents (Table). The soluble part of these polymers was characterized by multimodal molecular weight distribution that confirmed the fact of cross-linking during the polymerization (Fig. 1, a).

**Effect of the Lewis acid (LA) and temperature
on the cationic step-growth polymerization of MeBzOH**

№	LA	$T, ^\circ\text{C}$	[LA], mM	t, min	Conversion, %	M_n , g · mol	M_w/M_n
1	TiCl ₄	-80	0.2	90	0	—	—
2		-80	0.8	5	gel ¹	—	—
3		-30	0.2	200	7	2600	2.66
4		-30	0.4	300	gel ¹	2280 ²	6.43 ²
5		20	0.2	100	gel ¹	—	—
6	SnCl ₄	-80	0.6	20	10	2410	1.62
7		-30	0.6	1	gel ¹	3730 ²	3.37 ²
8		20	0.2	10	71	1300	2.04
9		20	0.2	30	99	2000	2.89
10		20	0.15	1800	92	1500	1.67
11		50 ³	0.15	360	100	1970	1.56
12	^t BuAlCl ₂	20	0.2	140	0	—	—
13		20	0.4	60	0	—	—
14		20	0.4	1020	100	870	1.30

Footnotes: Solvent – CH₂Cl₂; [MeBzOH] = 0.8 M.

¹ The formation of gel insoluble in common organic solvents is observed.

² For a part of polymer sample soluble in the THF.

³ In case of the sample reagents were agitated at higher temperature in 1,2-dichloroethane.

The use of SnCl₄ as a catalyst, which was a weaker Lewis acid than TiCl₄, resulted in the formation of well-defined polymers with relatively low polydispersity when the process of polymerization occurred at room temperature (samples 8–11, Table). At low reaction temperature (less than -30 °C), however, the side reactions leading to the formation of cross-linked polymer became predominant (samples 6, 7, Table). Further optimization of reaction conditions allowed us to prepare poly(2-methoxybenzyl alcohol), which was characterized by low polydispersity and monomodal molecular weight distribution (sample 10, Table, Fig. 1, *b*). Finally, ^tBuAlCl₂ as the weakest Lewis acid among the studied acids induced a slow cationic step-growth polymerization of MeBzOH yielding polymers of low molecular weight ($M_n = 870 \text{ g} \cdot \text{mol}^{-1}$) and quite low polydispersity (sample 14, Table, Fig. 1, *c*).

Based on the obtained results, it was decided to perform further investigations of the cationic step-growth polymerization of MeBzOH using SnCl₄ as a catalyst. Firstly, in order to validate the concept of proceeding the polymerization via step-growth mechanism, the molecular weight of poly(2-methoxybenzyl alcohol) obtained at different conversions was analyzed. Indeed, molecular weight of the polymer

appeared to be much lower at low monomer conversion that is consistent with the step-growth mechanism (samples 8, 9, Table). To validate the step-growth mechanism for SnCl_4 -catalyzed polymerization of MeBzOH, the separately prepared polymer (sample 10, Table) was treated with SnCl_4 without an addition of monomer at elevated temperature (run 11, Table). As a result, molecular weight was increased due to the formation of larger molecules via condensation of small ones (sample 11, Table). Thus, all these results indicate that Lewis acid-catalyzed cationic polymerization of MeBzOH proceeds via step-growth mechanism.

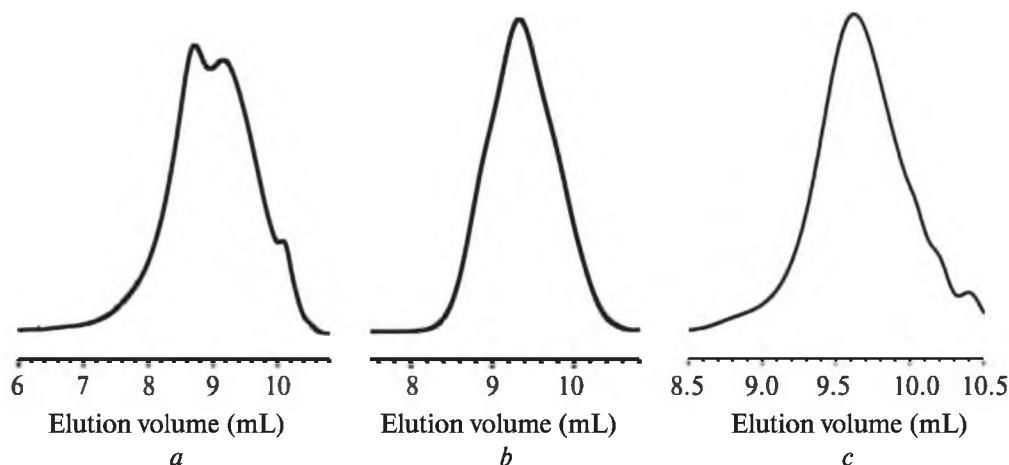


Fig. 1. SEC traces of poly(methoxybenzyl alcohol) synthesized with different Lewis acids as catalysts:
a – TiCl_4 (sample 4, Table); *b* – SnCl_4 (sample 10, Table);
c – $t\text{-BuAlCl}_2$ (sample 14, Table)

Then, the structure of synthesized poly(2-methoxybenzyl alcohol) was investigated by means of ^1H , ^{13}C and DEPT-135 NMR spectroscopy (Fig. 2, Fig. 3). In ^1H NMR spectrum of poly(2-methoxybenzyl alcohol), two groups of very broad signals were observed. The signal at 3.2–4.2 ppm in aliphatic part of spectrum corresponds to protons of methylene group located between two phenyl groups (1, 1') as well as to protons of methoxy group (2). The signal in olefinic part of spectrum corresponds to protons of aromatic ring after different binding of methoxybenzyl alcohol molecule (Fig. 2) into the polymer chain (5, 7, 8, 6', 7', 8'). It should be noted that the integration of signals of protons in aliphatic and olefinic regions of ^1H NMR spectrum gives the ratio of 5.00 to 2.95. That is very close to theoretical ratio of 5 : 3, since there are 5 aliphatic protons in methylene and methoxy group and 3 aromatic protons, respectively. These data indicate the formation of predominantly linear polymer, since the branching will lead to an increase in the ratio of aliphatic to aromatic protons due to the appearance of branching points similarly to cationic polymerization of isoprene [16].

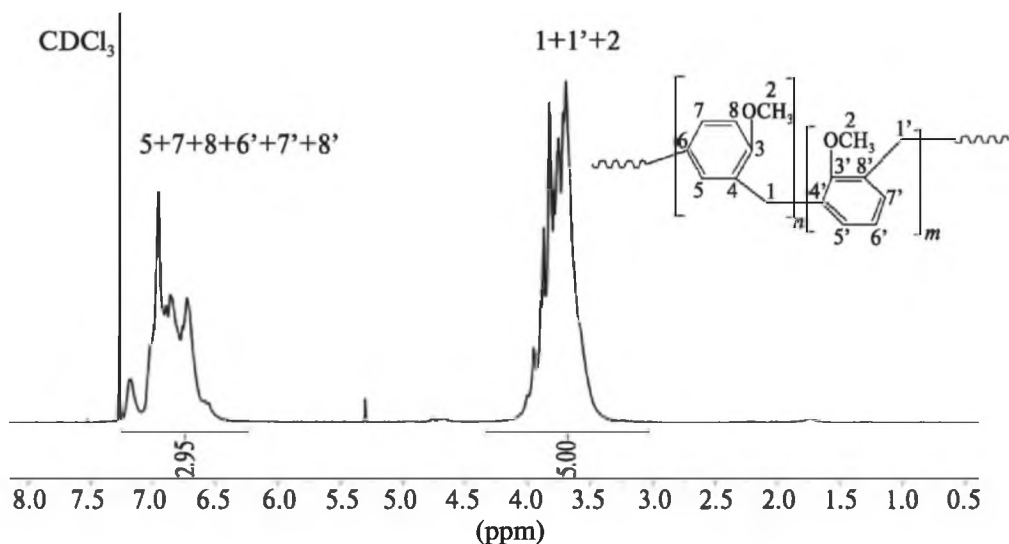


Fig. 2. ^1H NMR spectrum of poly(methoxybenzyl alcohol) ($M_n = 1300 \text{ g} \cdot \text{mol}^{-1}$; $M_w/M_n = 2.04$) synthesized using SnCl_4 as a catalyst

Further elucidation of the structure of poly(2-methoxybenzyl alcohol) was made using the combination of ^{13}C (Fig. 3, *a*) and DEPT-135 (Fig. 3, *b*) NMR spectroscopy. The signals at 30–35 ppm in ^{13}C NMR spectrum (Fig. 3, *a*) were attributed to methylene carbon atom of benzyl group after addition of benzyl cation to *para*- (1) and *ortho*- (1') position of 2-methoxybenzyl alcohol molecule (Scheme 1). The belonging of these signals to carbon atoms of the methylene group is confirmed by DEPT-135 NMR spectroscopy as these signals are located in the negative part of the spectrum (Fig. 3, *b*). According to both ^{13}C and DEPT-135 NMR spectroscopy, the signal of carbon atom of methoxy group (2) is appeared to be at 55 ppm (Fig. 3).

The signals at 155–157 ppm (3, 3') as well as a series of signals between 125–135 ppm belong to quaternary carbon atoms of benzene ring 4, 4', 5' and 6 as these signals are disappeared in DEPT-135 ppm. The rest of the signals (5, 6', 7, 7', 8, 8') belong to methine (CH) carbon atoms of benzene ring of methoxybenzyl unit in a polymer chain (Fig. 3). To summarize, it can be concluded based on NMR investigations (Fig. 2 and Fig. 3) that the polymer chain of poly(2-methoxybenzyl alcohol) consists of the methoxybenzyl units connected predominantly through *para*-position in respect to methoxy group.

Based on the obtained results, the following mechanism for the Lewis acid-catalyzed step-growth polymerization was proposed (Fig. 4). Lewis acid forms the complex with MeBzOH, the strength of which depends on the acidity of Lewis acid and temperature. The abstraction of hydroxyl group from this complex leads to the generation of stable benzyl cation, which alkylates another molecule of MeBzOH

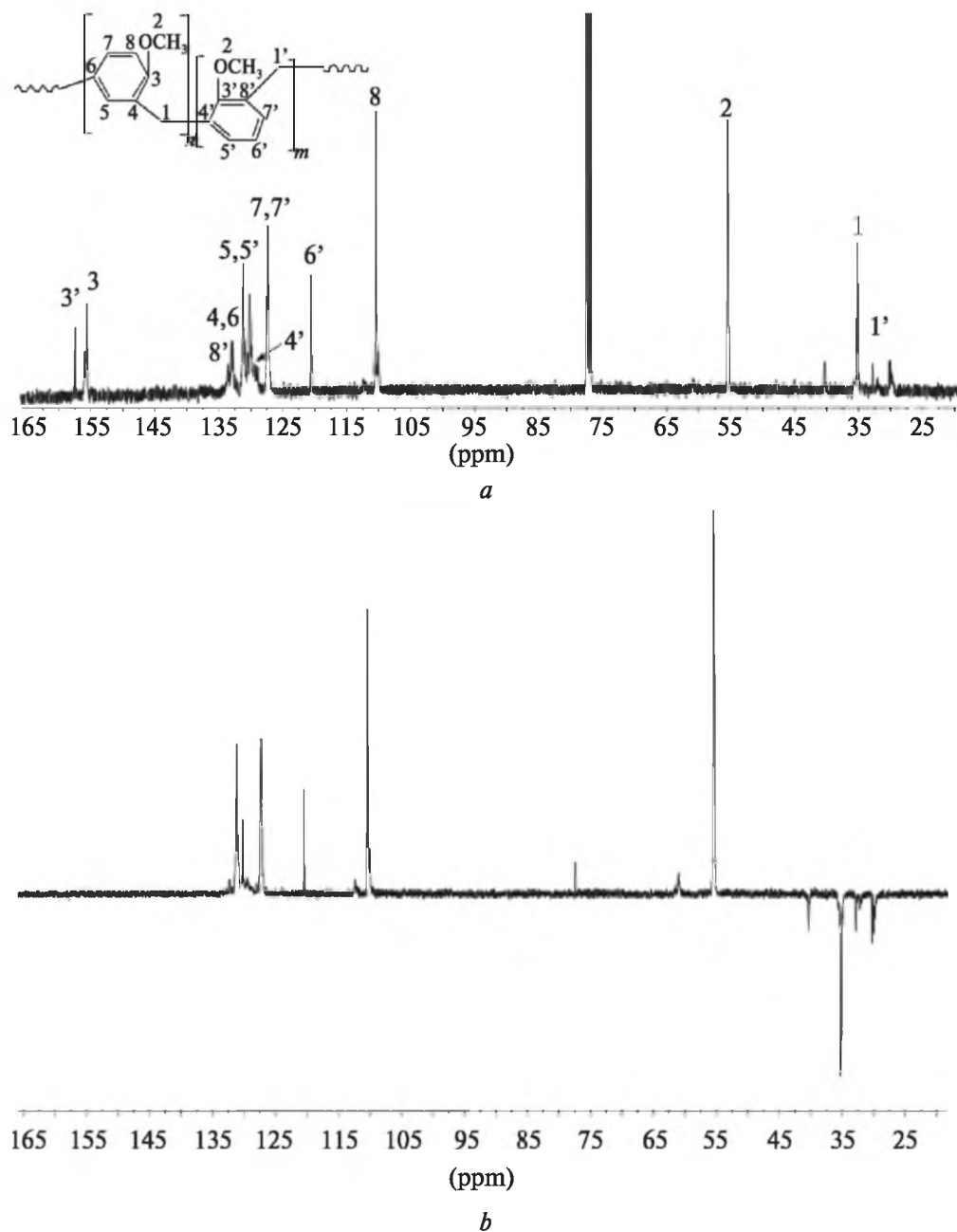


Fig. 3. NMR spectra of poly(methoxybenzyl alcohol)
 ($M_n = 1300 \text{ g} \cdot \text{mol}^{-1}$; $M_w/M_n = 2.04$) synthesized using SnCl_4 as catalyst:
a – ¹³C NMR spectrum; *b* – DEPT-135 NMR spectrum

(or complex of MeBzOH with Lewis acid) predominantly in *para*-position in respect to methoxy group with the formation of a dimer (Fig. 4). Further condensation of dimers and other low molecular weight compounds leads to the formation of desired linear polymer. The similar mechanism was also recently proposed for self-condensation of hydroxybenzyl alcohols [17] and Friedel-Crafts alkylation of multi-substituted benzyl bromide with benzene [18].

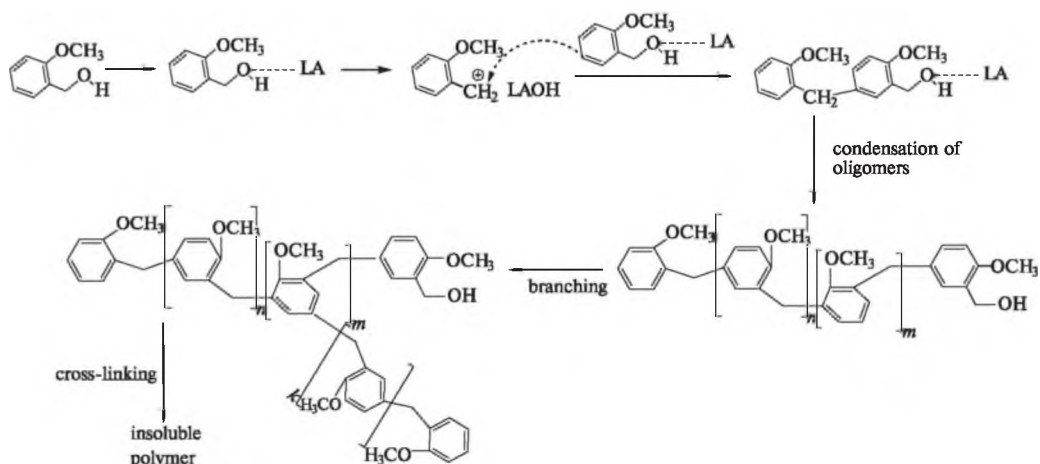


Fig. 4. The scheme illustrating a tentative mechanism of the step-growth polymerization of MeBzOH catalyzed by Lewis acids (LA)

However, along the formation of linear polymer, the branched and even cross-linked polymer can be formed via interaction of oligomeric cations with another polymer chain. It was shown that these side reactions became important at low reaction temperatures and in the presence of strong Lewis acid. Therefore, the use of such soft Lewis acid as SnCl_4 as a catalyst at room temperature allowed us to obtain predominantly linear poly(2-methoxybenzyl alcohol) via cationic step-growth pathway.

CONCLUSIONS

In this work, the Lewis acid catalyzed cationic polymerization of 2-methoxybenzyl alcohol was studied. It was shown that polymerization proceeds via step-growth pathway with the generation of oligomers at the reaction beginning followed by their condensation with the formation of relatively high molecular weight product at the later stage of the process. The linear poly(2-methoxybenzyl alcohol) with number-average molecular weight up to $M_n = 2000 \text{ g} \cdot \text{mol}^{-1}$ and rather low polydispersity ($M_w/M_n < 2.0$) could be obtained using such relatively soft Lewis acid as SnCl_4 as a catalyst and conducting the process at room temperature. In case of using stronger Lewis acid as a catalyst (TiCl_4) or low temperatures (below $-30 \text{ }^\circ\text{C}$), the polymerization is accompanied by side reactions leading to the formation of branched or even cross-linked polymer.

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