Pure Appl. Chem., Vol. 84, No. 10, pp. 2081–2088, 2012.
http://dx.doi.org/10.1351/PAC-CON-11-10-19

Activated monomer mechanism in the cationic polymerization of L,L-lactide*

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Abstract: Cationic polymerization of L,L-lactide (LA) in the presence of trifluoromethanesulfonic acid (TfA) has been studied. It was found that propagation proceeds mainly according to the activated monomer (AM) mechanism. Hydroxyl groups required for this type of propagation are formed as a result of the ring opening of protonated lactide. Thus, part of the acid (acting as an initiator) is consumed for the generation of hydroxyl groups, and part (acting as a catalyst) is involved in the protonation of monomer molecules forming secondary oxonium ions which are then able to react with the hydroxyl groups. A dual role of the protic acid is reflected in the kinetic results and in the dependence of experimental degree of polymerization on theoretical values. The structure of active species responsible for polymer chain growth was determined by phosphorus ion-trapping method.

The evidence that in the cationic ring-opening polymerization (ROP) of LA initiated by protic acids, both hydroxyl groups and secondary oxonium ions are present throughout the polymerization (as required for polymerization proceeding by the AM mechanism) was found on the basis of changes of the averaged proton chemical shift in ^{1}H NMR spectra of LA polymerizing mixture.

Keywords: heterocyclic chemistry; polymerization; ring-opening reactions.

INTRODUCTION

The most common mechanism of cationic ring-opening polymerization (ROP) of oxygen-containing heterocyclic monomers is an active chain-end (ACE) mechanism in which the propagation involves a nucleophilic attack of the oxygen atom from monomer molecule on the α-carbon atom in tertiary oxonium ion-growing species located at the chain end (Fig. 1) [1].

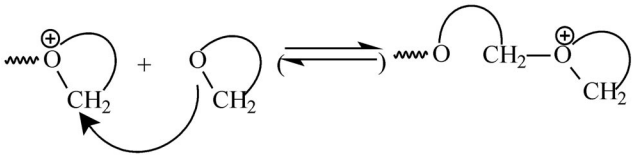

Fig. 1 Mechanism of growth in the ACE mechanism.

The nucleophilic site (oxygen atom) is preserved in the polymer chain. Reactions similar to propagation, involving the oxygen of the own or foreign chain, lead to undesirable side-reactions (chain

Pure Appl. Chem.* **84, 2065–2133 (2012). A collection of invited papers based on presentations at the International Symposium on Ionic Polymerization (IP 2011), Akron, OH, USA, 10–15 July 2011.

transfer to polymer). Intramolecular chain transfer to polymer leads to the formation of a cyclic fraction while segmental exchange results from intermolecular reaction (so-called scrambling).

It has been found, however, that if the polymerization is conducted in the presence of hydroxyl group-containing compounds and a protic acid as the catalyst, another mechanism of propagation competes with the ACE mechanism (Fig. 2).

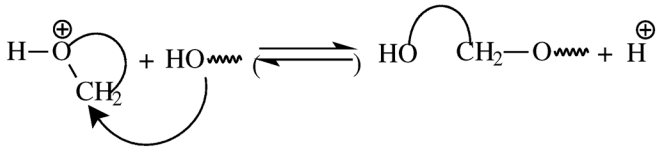

Fig. 2 Mechanism of growth in the AM mechanism.

The protic acid protonates all nucleophilic sites, including the monomer. Nucleophilic attack of the oxygen atom in a hydroxyl group on α-carbon atom in a protonated monomer molecule leads to the incorporation of monomer into the polymer chain. Protons, exchanging fast between all basic sites, protonate other monomer molecules, and the process is repeated. Propagation proceeds, therefore, by the nucleophilic attack of the oxygen atom in a hydroxyl group on α-carbon atom in a protonated monomer molecule [so-called activated monomer (AM) mechanism]. In such a system, the hydroxyl group-containing compound acts as an initiator while the protic acid is a catalyst.

In the AM mechanism, there is no charged species at the end of the growing polymer chain, thus the undesired side-reaction typical for the ACE mechanism can be avoided.

The presence of hydroxyl groups does not preclude polymerization proceeding by the ACE mechanism. To conduct polymerization predominantly by the AM mechanism, conditions should be created at which propagation via AM mechanism is much faster than via ACE mechanism. The ratio of rates depends on relative nucleophilicities of the oxygen atom in the monomer molecule and in the hydroxyl group, respectively, and on the instantaneous [HO–]/[monomer] ratio. Typically, to ensure a high contribution of the AM mechanism, the polymerization should be carried out at low instantaneous monomer concentration, i.e., with constant feeding of the monomer into the reaction system.

Competition between AM and ACE mechanism in the polymerization of oxiranes was studied in a series of articles from our group, as presented in review papers [2–5]. Subsequently, cationic polymerization of various groups of oxygen-containing heterocyclic monomers, including cyclic ethers, cyclic acetals, and cyclic esters (lactones) in the presence of hydroxyl group-containing compounds has been reported, and although the authors did not always explain the results in terms of AM mechanism, it seems that this mechanism operates in all those systems [6–8].

In recent years polymerization of cyclic dimer of lactic acid: L,L-lactide (LA) has been studied extensively because the corresponding polymer is a promising biodegradable material that may be obtained from renewable resources [9]. Although the coordination polymerization has mostly been studied and applied for the synthesis of polylactide, cationic mechanism is also considered.

The cationic polymerization of LA was studied by Kricheldorf et al. more than 20 years ago, but the mechanism of polymerization was not fully elaborated [10]. Various acidic compounds were tested as potential initiators, and it was found that only strong protic acids were efficient initiators, while alkylating agents or Lewis acids were essentially inactive. It is interesting that in the subsequent studies of cationic ROP of lactones, reactions were conducted in the presence of alcohols or diols and the AM mechanism was postulated [11,12]. Thus, it seems that a proton source (either a protic acid or a hydroxyl group) was needed for conducting those processes. This may suggest that cationic ROP of lactones proceeds preferentially via the AM mechanism.

Recently, in a paper from our group it was postulated that cationic polymerization of LA proceeds by the AM mechanism even in the absence of intentionally added hydroxyl group-containing compound

and that hydroxyl groups required for the AM mechanism are formed by reaction of the catalyst (triflic acid, TfA) with LA, thus TfA acts as both an initiator precursor and a catalyst [13]. In this paper, results are presented, providing additional indication of the dual role of TfA.

DISCUSSION

Homopolymerization of LA was studied in CH_2Cl_2 at room temperature. Initiators typical for cationic polymerization, including strong protic acids and Lewis acids, were applied. Conversion of LA was monitored by recording the changes of optical rotation of the solution. Results were plotted as $\ln([M]_0 - [M]_e)/([M]_t - [M]_e) = f(t)$. Rate of polymerization (R_p) was determined as the initial tangent of the plot. The results are shown in Table 1.

Table 1 Polymerization of LA with different cationic initiators [13].

Initiator	$[I]_0$ (mol/L)	Conversion of LA	R_p (s^{-1})
CF_3SO_3H	0.14	~99 % in 17 h	4.4×10^{-3}
$CF_3SO_3CH_3$	0.1	~99 % in 30 days	7.5×10^{-7}
$CF_3SO_3CH_3$ + PS	0.1	0 % in 2 days	0
$(CF_3SO_2)_2O$	0.1	0 % in 2 days	0
CF_3COOH	0.1	0 % in 2 days	0
BF_3Et_2O	0.1	0 % in 2 days	0

Conditions: $[M]_0$ = 2.0 mol/L, CH_2Cl_2, 25 °C.

It was found that at given conditions only CF_3SO_3H (TfA) initiated relatively fast polymerization (~99 % in 17 h). Polymerization proceeded also (although much more slowly) with $CF_3SO_3CH_3$ (~99 % in 30 days) but was completely inhibited in the presence of proton sponge [(PS), (1,8-bis(dimethylamino)naphthalene] which indicates that polymerization was initiated by residual TfA present as an impurity in the triflate ester. A weaker protonic acid, triflic anhydride, or BF_3 etherate were inactive (0 % in 2 days).

Further studies of the cationic polymerization of LA initiated with TfA revealed a deflection from linearity in the kinetic plots. It was also found that R_p is not simply proportional to the acid concentration and that degrees of polymerization are significantly higher than the theoretical values calculated as the ratio of monomer to initiator concentrations.

In all three plots shown in Fig. 3, deviations from the simple scheme, in which one molecule of acid would initiate growth of one and only one polymer chain, are observed. The kinetic plots in semilogarithmic anamorphoses are not linear, R_p is not simply proportional to the concentration of TfA and the polymerization degrees are considerably higher than the $[LA]_0/[TfA]_0$ ratio, which indicates that only a fraction of TfA molecules is involved in the initiation.

In order to clarify the mechanism of acid action, polymerization initiated with TfA was conducted in the presence of PS. When added at ~50 % conversion of LA, PS stopped the polymerization completely [13].

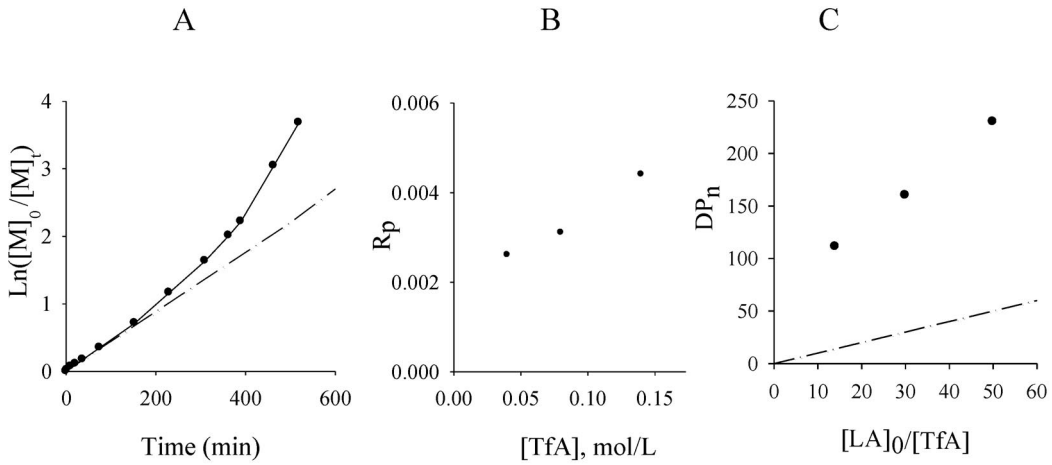

Fig. 3 Dependences of $\ln([M]_0/[M]_t)$ on time (A), polymerization rate on TfA concentration (B) and experimental degree of polymerization on theoretical degree (C) in polymerization of LA initiated with TfA.

PS binds protons but should not interact with oxonium ions. Thus, observation that PS added at a relatively late stage completely stops the polymerization indicates that at this stage of polymerization the growing propagation species are secondary oxonium ions (protonated monomer molecules) as required by the AM mechanism rather than tertiary oxonium ions as in the ACE mechanism.

To identify the active species present in the course of cationic polymerization of LA, a phosphorus ion-trapping method was used [14]. The principle of this method is outlined in Fig. 4 (counterions omitted).

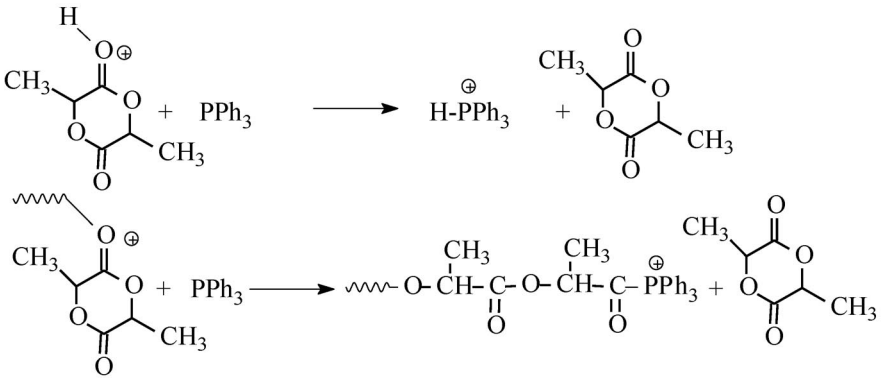

Fig. 4 Determination of the structure of active species present in cationic polymerization of LA on the basis of phosphorus ion-trapping method.

The method is based on fast, quantitative, and irreversible transformation of active species into stable end groups containing a phosphorus atom. Thus, secondary oxonium ions (protonated species) in reaction with tertiary phosphines are converted into tertiary phosphonium ions while tertiary oxonium ions are transformed into quaternary phosphonium ions. Both types of ions can be separately observed in ^{31}P NMR spectra.

Table 2 Chemical shifts of signals present at ^{31}P NMR spectrum of cationic LA polymerization terminated with excess of Ph_3P.

Structure	Chemical shift of model compounds	Signals observed in polymerization mixture
Ph_3P	–9 ppm	present
Ph_3P^+H	7 ppm	present
Ph_3P^+R	10 ppm	absent

^{31}P NMR spectrum of the polymerization mixture terminated at ~50 % conversion with a known excess of triphenylphosphine exhibited exclusively signals from protonated and free triphenylphosphine.

This observation shows that in the cationic polymerization of LA the protonated monomer participates in the propagation. This result, coupled with the observed effect of PS, leads to the conclusion that even in the absence of intentionally added alcohol or diol, the chain growth proceeds exclusively (or at least predominantly) via the AM mechanism.

In this mechanism, the presence of a hydroxyl group at the chain end is required. It was postulated that in the studied system hydroxyl end groups are formed by opening of the ring of protonated LA [13]. Simultaneously, in order for the AM mechanism to proceed, an acid has to be present throughout the polymerization to protonate the monomer, which is then able to react with the terminal hydroxyl.

Thus, part of the acid should be involved in the formation of hydroxyl groups (playing the initiator role) while the other part of it should protonate (activate) the monomer (acting as a catalyst) (Fig. 5).

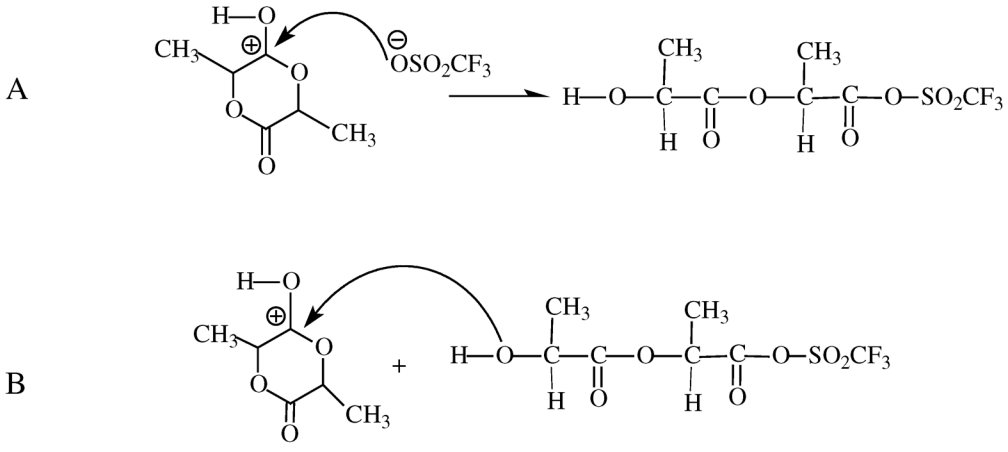

Fig. 5 The dual role of acid in cationic polymerization of LA: A - as an initiator (formation of hydroxyl groups) and B - as a catalyst (protonation of LA).

Reaction of TfA with LA leads to the linear dimer of lactic acid having a hydroxyl group at one chain end and a mixed anhydride group at the other. These two groups can react forming back TfA and the ester bond as shown in Fig. 6.

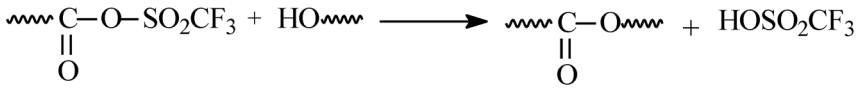

Fig. 6 Formation of protic acid by reaction of mixed anhydride end group with hydroxyl end group.

Thus, the interconversion of protonated species into hydroxyl groups is a reversible process. In the course of polymerization with the changing composition of reaction mixture, the fractions of protons involved in the formation of secondary oxonium ions and hydroxyl groups, respectively, may be expected to change. Thus, the concentration of neither protonated species nor hydroxyl groups will remain constant (although the sum of their concentrations is constant and equal to the initial concentration of TfA). This can explain the nonlinearity of kinetic plots in semilogarithmic coordinates (as shown in Fig. 3A).

Evolution of the proton chemical shift in the homopolymerization of LA provides an indication that the interconversions shown in Figs. 5 and 6 indeed proceed in the system and fractions of both involved species change with changing composition of the reaction mixture.

In ^{1}H NMR spectra of polymerizing mixture of LA, the signal of acidic protons could be clearly identified. In the samples analyzed at different stages of polymerization, the chemical shift of acidic protons underwent characteristic changes (Fig. 7).

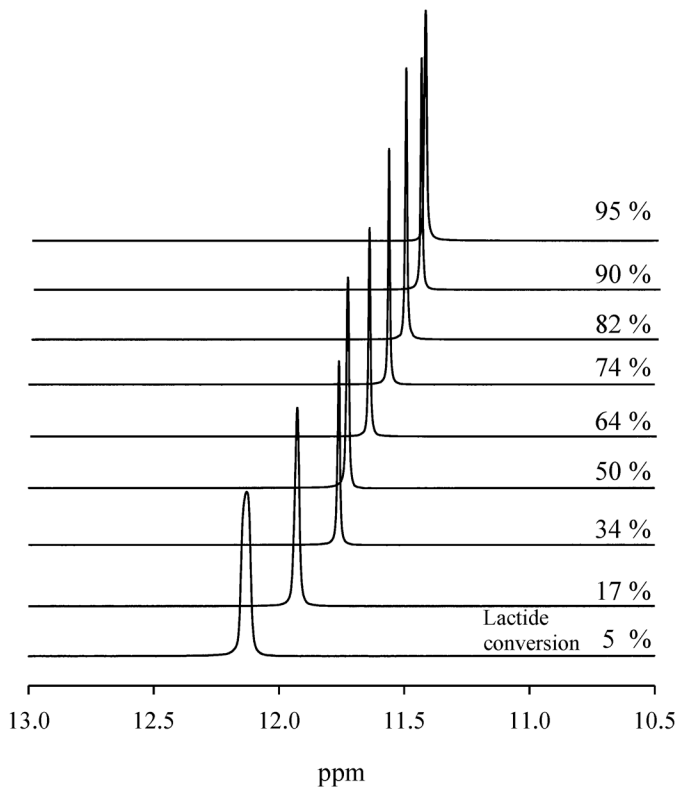

Fig. 7 Changes of the chemical shift of acidic proton in ^{1}H NMR spectra in the cationic homopolymerization of LA.

If, as proposed, both protonated species and hydroxyl groups are present in the system, fast exchange should result in one proton signal with a chemical shift intermediate between that of a proton in H–$^+$O< group and of a hydroxyl group proton. Chemical shift of the proton in the hydroxyl group of isopropanol [CH_3–$CH(CH_3)$–OH] taken as a model of polymer terminal group [–C(O)–$CH(CH_3)$–OH] in CH_2Cl_2 solution is close to 2 ppm. To estimate the chemical shift of a proton in H–$^+$O< group, non-polymerizing γ-butyrolactone (γ-BL) was added to the solution of TfA in CH_2Cl_2. For the solution of TfA in CH_2Cl_2, a signal at 9.8 ppm was observed (in CH_2Cl_2 solution TfA should be only weakly ionized). Upon addition of γ-BL, a shift toward higher chemical shift values was observed up to 14.4 ppm for [γ-BL]/[TfA] ratio = 1/1. Further increasing of γ-BL concentration did not cause any chemical shift changes. Thus, the value of ~14.4 ppm should correspond to the chemical shift of a proton in H–$^+$O< species.

As shown in Fig. 7, in the course of polymerization the averaged chemical shift changes from ~12.15 ppm at 5 % conversion to ~11.4 ppm at 95 % conversion of LA.

The following conclusions may be drawn from these observations:

- The observed averaged proton chemical shift is between the values expected for H–$^+$O< and a hydroxyl group, which indicates that both species are present in the course of polymerization.
- The observed averaged proton chemical shift is drifting toward lower values with increasing conversion, which may indicate that the fractions of H–$^+$O< and hydroxyl groups change slightly in the course of polymerization in favor of the latter. The change of the chemical shift of the ^{1}H NMR resonance signal for the acidic proton due to the different basicity of the ester moieties in LA and poly-LA can, however, also contribute to the observed drift.
- If it is assumed that when a single resonance is observed, chemical shift is the weight average of the chemical shifts of the two individual states ($\delta_{obs} = f_A\delta_A + f_B\delta_B$), then on the basis of the observed chemical shift and chemical shifts of model compounds it may be estimated that the fractions of H–$^+$O< and HO–groups at the end of the polymerization correspond to 0.75/0.25. $11.4 = f_{(H–^+O<)} \times 14.4 + f_{(HO–)} \times 2.0; f_{(H–^+O<)} = 0.75, f_{(HO–)} = 0.25$
- Interestingly, this estimation is in full agreement with the results shown in Fig. 3C. Observed DP_n values are ~4 times higher than calculated values. Because each macromolecule contains one hydroxyl end group, it means that the number of hydroxyl groups is about 4 times lower than the concentration of TfA used. This corresponds very well with the fraction of hydroxyl groups estimated on the basis of averaged chemical shift values ($f = 0.25$). Such an agreement indicates that in spite of a possible effect of changing basicity upon conversion of LA into poly-LA, the fraction of TfA acting as an initiator can reliably be estimated on the basis of averaged chemical shift of the acidic proton.

CONCLUSIONS

Although the results presented in this paper do not permit a precise analysis of polymerization kinetics, they provide a convincing indication that in the cationic ROP of LA initiated by protic acids, both secondary oxonium ions and hydroxyl groups are present throughout the polymerization as required for polymerization proceeding by the AM mechanism. Determination of the averaged proton chemical shift allows the estimation of fractions of both species. About 75 % of the acid acts as a catalyst protonating monomer molecules, while about 25 % acts as an initiator precursor, generating hydroxyl groups. Those estimations are in full agreement with the observation that DP_n is about 4 times lower than the $[LA]_0/[TfA]_0$ ratio, indicating that only about 25 % of the acid acts as an initiator.

ACKNOWLEDGMENTS

Special acknowledgment is addressed to Prof. Przemyslaw Kubisa who has guided the described studies and inspired this manuscript.

Financial support by the project entitled "Technology of biodegradable polyesters production from renewable resources – BIOPOL", realized by Contract No. POIG.01.01.02-10-025/09 and cofinanced by the European Union in the framework of the Operational Program–Innovative Economy (IE OP) is gratefully acknowledged.

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