VIBRATIONAL ANALYSIS OF RING-OPENING POLYMERIZATIONS OF GLYCOLIDE, L-LACTIDE AND D,L-LACTIDE

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Abstract—The i.r. and Raman spectra of glycolide, L-lactide and D,L-lactide in the solid state have been investigated in the 4000–100 cm^{-1} range. An assignment of the fundamental vibrations is given. The Raman spectra of aqueous solutions of these cyclic diesters showed ring-opening and the beginning of polymerization, characterized by the appearance of ester group bands and acid and alcohol end-group bands.

INTRODUCTION

Aliphatic polyesters, poly(glycolic acid), poly(L-lactic acid), poly(D,L-lactic acid) and their copolymers have biomedical applications as surgical sutures, prosthetic devices, implants or drug delivery systems [1–3]. The interest in such polymers stems from their susceptibility to hydrolytic biodegradation, leading to the scission of polymer chains into non-toxic oligomers and monomers [4]. These polymers can be obtained by polycondensation of the corresponding α-hydroxycarboxylic acids to give low molecular weight compounds or by ring-opening polymerization of six-membered cyclic diesters to obtain higher molecular weight polyesters.

Glycolide is the cyclic diester mainly used to synthetize poly(glycolic acid) [5]. The principal method of polymerization is ring-opening by hydrolysis at 220° with stannous octoate as catalyst. L-lactide and D,L-lactide are mainly used for the synthesis of poly(L-lactic acid) and poly(D,L-lactic acid) [6, 7].

The ring-opening polymerization may be followed by spectroscopic methods, especially Raman spectroscopy. The behaviour of the cyclic diesters in H$_2$O may be easily studied because, unlike i.r. absorption, the Raman scattering of water is very weak in the region 200–3200 cm^{-1}. However, a preliminary study of lactonic monomers is necessary before considering the aqueous solutions. Our previous reports have shown the value of Raman spectroscopy in the study of aqueous solutions of lactic and glycolic acid [8, 9] as well as for the following of polymerization of these monomers [10].

In this paper, we present the Raman and i.r. spectra of the cyclic monomers glycolide, L-lactide, D,L-lactide and propose vibrational assignments, isolating the bands characterizing the ring vibrations. We also performed Raman spectroscopic analyses of the aqueous solutions to show the beginning of the polymerization.

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EXPERIMENTAL PROCEDURES

Glycolide, L-lactide and D,L-lactide were purchased from Phusis Society Le Versoud, France. Oligomers were prepared by dissolving the cyclic diesters in water and stirring for 3–4 hr at room temperature. Concentrations of the aqueous solutions were 10% w/w.

The Raman spectra were recorded using a Ramanor HG2S spectrometer (Jobin-Yvon) of 2–4 cm^{-1} resolution, equipped with an Argon laser (514 nm radiation) of 200 mW power for solids and 400 mW power for aqueous solutions. Infrared spectra were obtained with a Perkin–Elmer 983G spectrometer; the solid samples were pressed into KBr discs.

RESULTS AND DISCUSSION

The Raman spectra of glycolide, L-lactide, D,L-lactide and their aqueous solutions are shown in Figs 1 and 3. The i.r. spectra of the three cyclic diesters are presented in Figs 2 and 4. The frequencies of 10% aqueous solutions of glycolide and lactide are listed in Table 1. The assignments of the fundamental frequencies are given in comparison with dioxane [11] for the ring vibrations and in comparison with β-propiolactone [12], β-butyrolactone [13] and γ-valerolactone [14] for the lactone group vibrations.

Glycolide

Although the crystalline structure of glycolide (1,4-dioxane-2,5-dione) is unknown, it has been shown that the molecule exists in two conformations, viz. chain and boat forms, the former being the more stable.

Ring vibrations

The Raman and i.r. spectra show many splitting bands due to the presence of both conformers in the unit cell. The most intense Raman line at 798 cm^{-1} and its shoulder at 771 cm^{-1} are attributed to the
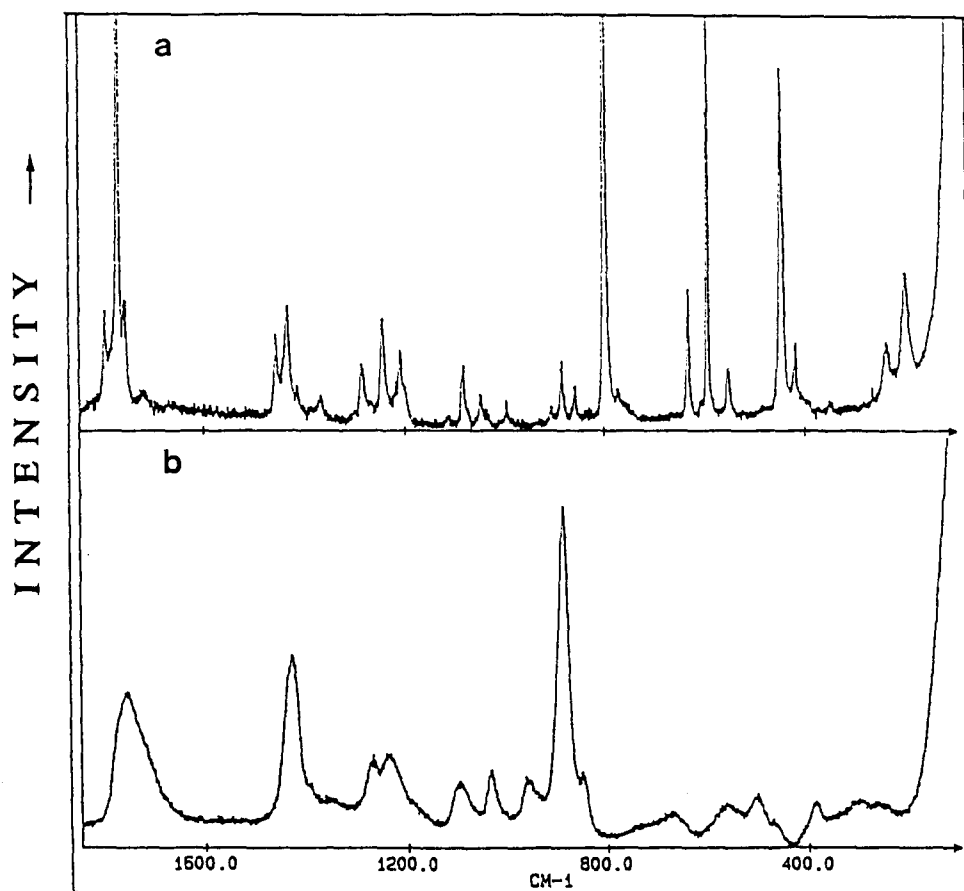
Fig. 1. Raman spectra of glycolide: (a) solid state; (b) aqueous solution.

ring-breathing vibration modes of glycolide. The modes involving $v(C\!-\!O)$ stretching vibrations are assigned to strong i.r. bands splitting as doublets at 1211–1190, 1100–1080 and 1051–1030 cm^{-1}; the Raman spectra show lines practically at the same frequencies, and a strong peak at 1245 cm^{-1} corresponding to the 1245 cm^{-1} weaker absorption band. The last $v(C\!-\!C)$ ring stretching mode is observed as a Raman doublet (886–860 cm^{-1}); a 862 cm^{-1} band and its shoulder at 880 cm^{-1} are observed in the i.r. spectrum.

Ring deformation modes are expected to be observed below the 700 cm^{-1} region. The Raman spectrum presents an intense line at 631 cm^{-1}, associated with the strong 625 cm^{-1} i.r. band. The three Raman lines at 350, 240 and 202 cm^{-1} are attributed to the γ-(ring) torsion vibrations, in agreement with previous studies on cyclohexane-1,4-dione [15].
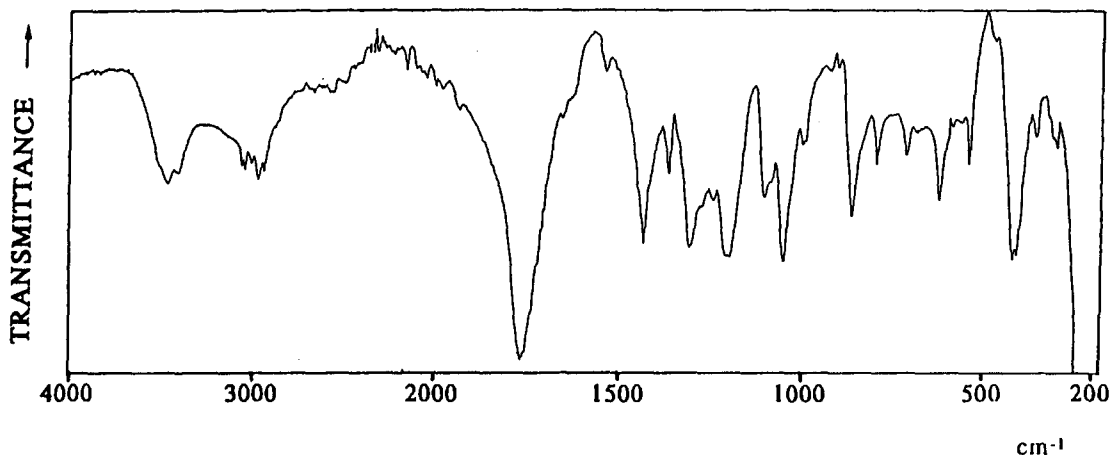

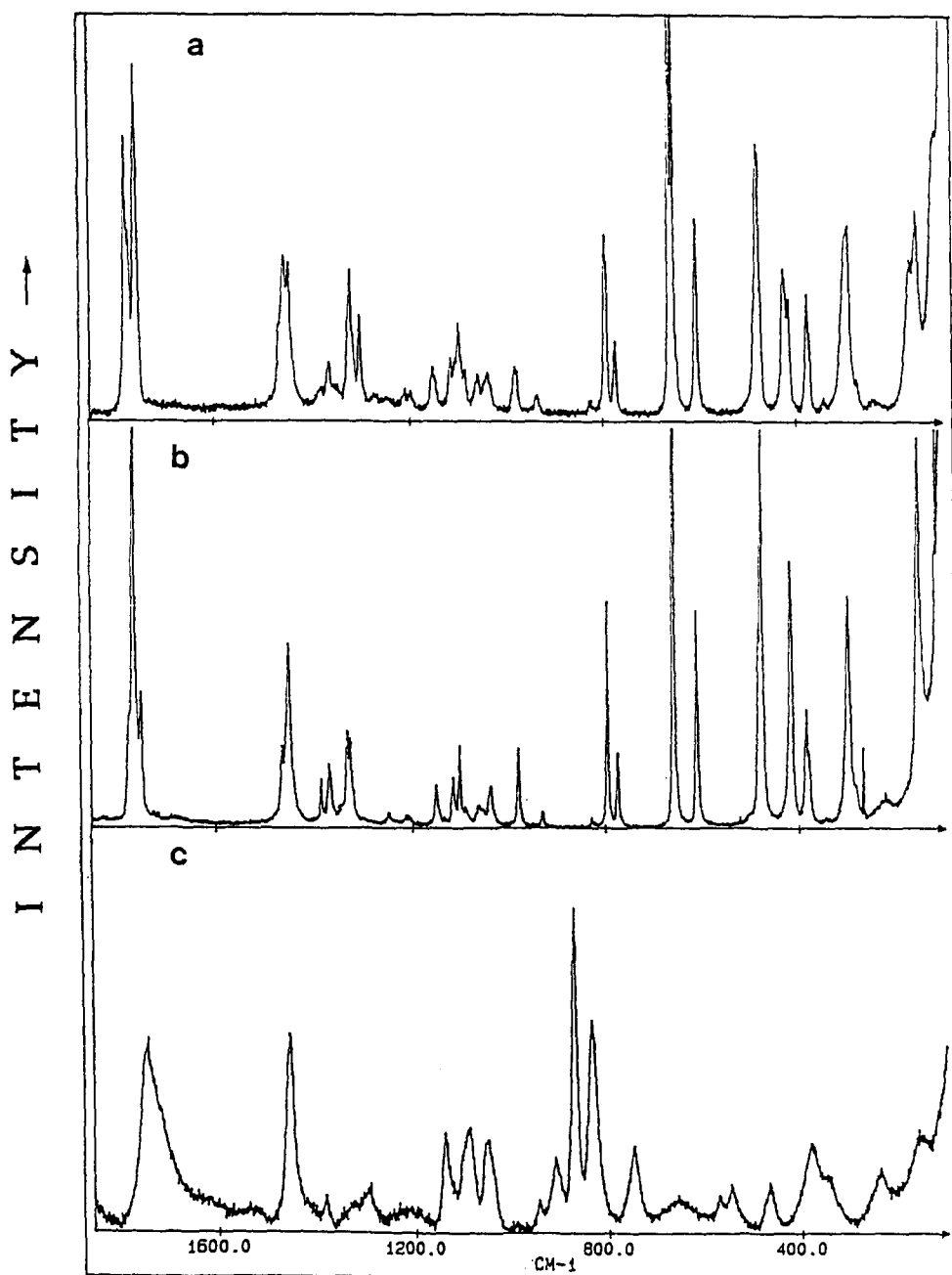Fig. 2. Infrared spectrum of glycolide in the solid state.

Fig. 3. Raman spectra: (a) L-lactide in the solid state; (b) D,L-lactide in the solid state; (c) L-lactide and D,L-lactide in aqueous solution.

Carbonyl modes

The v(C=O) stretching modes of the carbonyl groups are identified as a strong disymmetric absorption band at $1760 \, \text{cm}^{-1}$ in the i.r. spectrum and as three lines at 1798, 1770 and $1757 \, \text{cm}^{-1}$ in the Raman spectrum. The carbonyl out-of-plane γ(C=O) bendings are assigned to the Raman lines and absorption bands located at about 590, 560 and $544 \, \text{cm}^{-1}$. The in-plane δ(C=O) modes are found at lower Raman frequencies 442 and $418 \, \text{cm}^{-1}$, and at 450, 422 and $410 \, \text{cm}^{-1}$ as a large absorption band.

Lactide

There are four types of lactide: L($-$)-lactide, D($+$)-lactice, mesolactide and racemate; the two latter have no optical activity [16]. The crystalline structure of D,L-lactide was previously studied by X-ray diffraction, showing that this compound crystallizes in the monoclinic system with a $P_2 1/c$ ($Z = 4$) space group. L,L-Lactide and D,D-lactide having approximately C_2 symmetry with skew boat conformation [17].

The assignment of the fundamental frequencies was made for L-lactide. The Raman and i.r. spectra of solid L-lactide are shown in Figs 3 and 4.
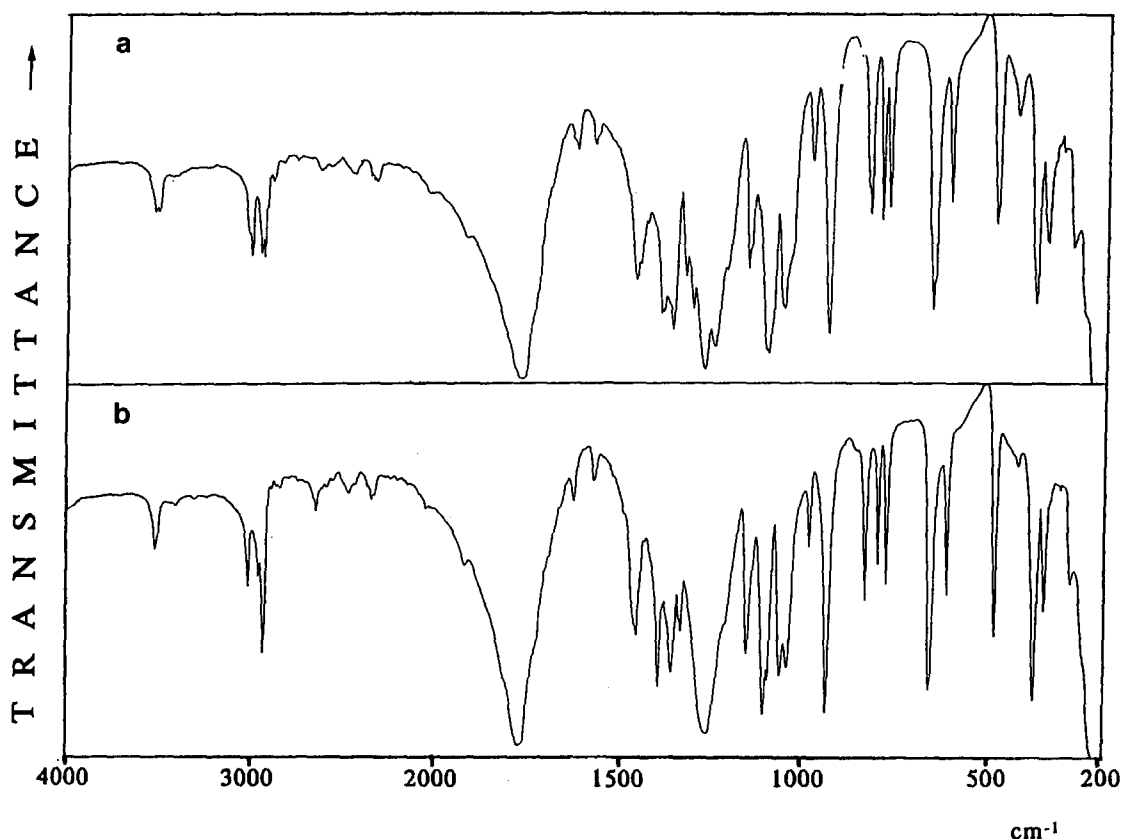
Fig. 4. Infrared spectra: (a) L-lactide in the solid state; (b) D,L-lactide in the solid state.

L-lactide

Ring vibrations. The four ring-breathing vibrations expected in the primitive cell occur in the Raman spectrum as two lines at 795 and 775 cm^{-1} and are observed in the i.r. spectrum at 795 and 775 cm^{-1}. The v(C—C) stretching vibration of the ring is attributed to the medium intensity i.r. doublet at 831–825 cm^{-1}, corresponding to the weak 827 cm^{-1} Raman line. The ring modes involving mainly v(C—O) stretching vibrations are recorded in the i.r. spectrum at 1275–1245, 1215–1200, 1105–1095 and 1060–1040 cm^{-1}, and in the Raman spectrum at 1274–1240, 1212–1200, 1097–1085 and 1058–1038 cm^{-1}. As for the glycolide, ring deformations are found below 700 cm^{-1}. The δ(ring)

Table 1. Raman frequencies characterizing ring-opening polymerization of glycolide, L-lactide and D,L-lactide

Glycolide 10% aqueous solution	L- and D,L-lactide 10% aqueous solution	
Raman (cm^{-1})		Assignment[a]
1755 m	1745 m	v_E C=O
1735 sh	1720 sh	v_{AC} C=O
1237 m	1240 w	v_{AC} CO + δ_{AC} OH
1270 m	1210 w	v_E OCO
1030 m	1137 m	v_E OCO
1092 m	1084 m	v_{AL} CO
890 s ⎱	870 s	v_E C—COO
890 s ⎰	830 m	vC—COOH

[a]AC, acid group; AL, alcohol group; E, ester group; m, medium; sh, shoulder; s, strong.

bending modes are assigned to the 662–654, 425–415 and 377 cm^{-1} lines of the Raman spectrum. The γ(ring) torsion vibrations are observed in the 350–250 cm^{-1} spectral range.

Carbonyl vibrations. In the 1800–1700 cm^{-1} range of the Raman spectrum, the three strong lines at 1779, 1770 and 1758 cm^{-1} are due to the v(C=O) stretching modes of the carbonyl groups, also recorded in the i.r. spectrum as a wide band centred at 1763 cm^{-1}.

The two γ(C=O) out-of-plane bending modes give rise in Raman diffusion to an intense line at 606 cm^{-1} and its 590 cm^{-1} shoulder; the i.r. spectrum shows a strong absorption band at 607 cm^{-1} and a 590 cm^{-1} shoulder. The relatively strong absorption band at 481 cm^{-1} is probably due to δ(C=O) in-plane bending vibration, found in the Raman spectrum at 479 and 470 cm^{-1}.

Analysis of the i.r. and Raman spectra of L-lactide in the solid state shows the existence of many splittings and the non-coincidence of the absorption and diffusion bands. These results, in agreement with Van Hummel [17], show the presence of four molecules in the crystal cell and a symmetry centre.

D,L-lactide

The Raman and i.r. spectra of D,L-lactide in the solid state are reproduced in Figs 3 and 4. The Raman and i.r. spectra of L-lactide and D,L-lactide show little differences. For L-lactide, the splitting of some lines is more important, due to the higher symmetry of the unit cell.

Hydrolysis of the Cyclic Diesters

The method used to synthetize commercial preparations of poly(glycolic acid) and poly(lactic acid) is cyclic diester opening induced by hydrolysis in the presence of catalyst [6–8].

Glycolide in aqueous solution

The Raman spectrum of the aqueous solution is simpler than that of glycolide in the solid state. The spectrum of the 10% aqueous solution is presented in Fig. 1. Three principal regions are indicative of ring-opening:

1800–1700 cm^{-1} range. The doublet (1770/1757 cm^{-1}) in the Raman spectrum of glycolide in the solid state, characteristic of the $v(C=O)$ stretching vibrations of the cyclic diester, is not observed in the spectrum of the aqueous solution. The appearances of a wide non-symmetrical band with a maximum at 1755 cm^{-1} and of a shoulder at 1735 cm^{-1} are respectively due to the $v(C=O)$ stretching vibration of the COO ester group and of the COOH acid group of an oligomer of glycolic acid, showing the opening of the lactonic ring and the beginning of polymerization.

1300–1000 cm^{-1} range. Five lines (1270, 1237, 1194, 1092 and 1030 cm^{-1}) are observed in the Raman spectrum of the aqueous solution. By comparison with the glycolic acid spectrum [8], the 1237 cm^{-1} band is attributed to the coupled motions $[v_{AC}(CO) + \delta_{AC}(OH)]$ of the oligomer acid group and the $v_{AL}(CO)$ stretching of the alcohol group appears at 1092 cm^{-1}. The new lines (1270 and 1030 cm^{-1}) are due to $v(COC)$ stretching of the ester group; the 1194 cm^{-1} band is assigned to the tw(CH$_2$) twisting.

900–700 cm^{-1} range. The two ring-breathing vibration modes which give rise to the very intense 798 and 771 cm^{-1} lines of the Raman spectrum of glycolide in the solid state disappeared in the aqueous solution spectrum. A new intense line occurred at 890 cm^{-1}. Compared with the glycolic acid Raman spectrum, this line is attributed to the $v(C-COOH)$ stretching vibration, characteristic of glycolide ring-opening.

L-lactide and D,L-lactide in aqueous solution

The opening of the lactide ring gave rise to lactoyl-lactic acid, the dimer of lactic acid [16]. The Raman spectra of the 20% aqueous solution of L-lactide and D,L-lactide are presented in Fig. 3.

1800–1700 cm^{-1} range. As for glycolide in aqueous solution, the triplet at 1775, 1765 and 1750 cm^{-1}, observed in the D,L-lactide spectrum and at related frequencies in L-lactide, and attributed to the $v(C=O)$ stretching modes of carbonyl groups, disappears from the spectrum of the aqueous solution. A broad non-symmetrical line with a maximum at 1745 cm^{-1} and its shoulder about 1720 cm^{-1} are characteristic of polymerization and are respectively attributed to the $v(C=O)$ stretching vibration of the COO ester group, and to the $v(C=O)$ vibration of the COOH group of lactoyllactic acid. These bands indicate ring-opening.

1300–1000 cm^{-1} range. Comparison with the lactic acid spectrum [9] shows the increased intensity of the 1137 cm^{-1} line, due to the $v(COC)$ stretching mode of the ester group. The widening of the band centred

at 1240 cm^{-1} argues in favour of the presence of the coupled motions $[v_{AC}(CO) + \delta_{AC}(OH)]$ and the $v(COC)$ stretching vibration of the ester group.

900–700 cm^{-1} range. As for the glycolide, the two intense lines at 795 and 775 cm^{-1} and due to the ring-breathing modes of lactide are not observed in the aqueous solution spectrum which shows two new lines at 870 and 830 cm^{-1}: the latter is attributed to the $v(C-COOH)$ stretching vibration as in lactic acid, whereas the former, situated at a higher frequency, characterizes the $v(C-COO)$ stretching of the ester group.

In conclusion, Raman spectroscopy has displayed the ring-opening of glycolide, L-lactide and D,L-lactide in aqueous solution, in particular by the disappearance of lines attributed to breathing modes of the lactonic ring. The appearance of lines characterizing the vibrations of ester groups [$v(COC)$ and $v(C-C)$] and the vibrations of the acid and alcohol end-groups of the oligomer produced shows the beginning of polyesterification, and consequently the beginning of the process for the synthesis of high molecular weight poly(glycolic acid) and poly(lactic acid). It should be noted that the Raman spectra of the cyclic diesters in aqueous solution are identical with those of glycolic and lactic acid at a concentration of 90% in aqueous solution, for which the presence of oligomers has been shown [10].

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