L(+) LACTIC ACID POLYMERS AND COPOLYMERS : STRUCTURE –PROPERTY RELATIONSHIPS

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PLLA : MAJOR PROPERTY DEFICITS

- **Slow rate of crystallization**
- **Very brittle material ; Elongation : 3-4 %,**
- **Poor heat stability**
- **Poor chain entanglement in melt state leading to poor melt viscosities**

PLLA PROPERTY IMPROVEMENTS : APPROACHES

Poor rate of crystallization

- ***Annealing and cold crystallization***
- ***Nucleation***

Poor Elongation

- ***Plasticization***
- ***Copolymerization***

Increase Tm

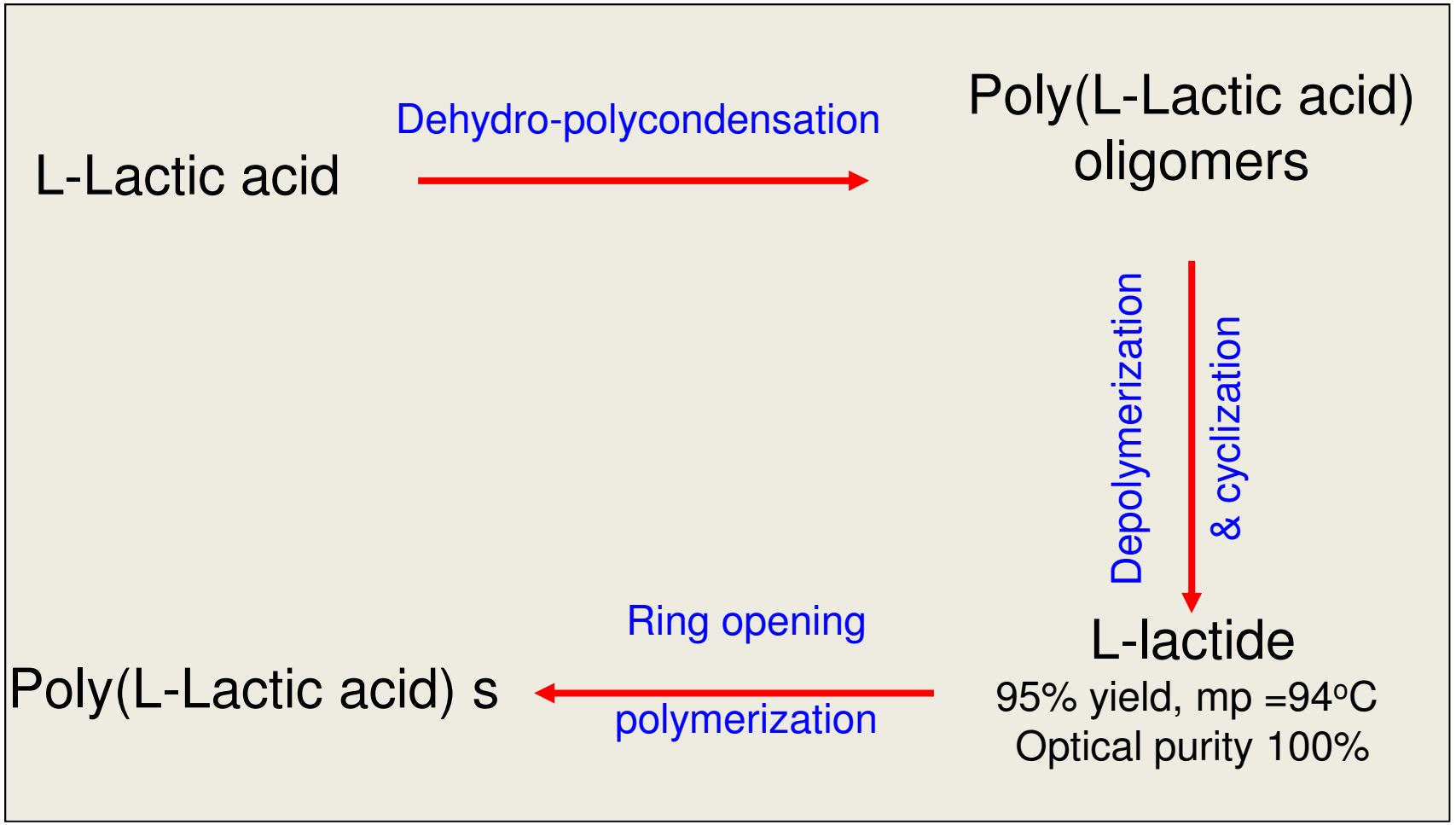
- ***Stereocomplexation***
- ***Copolymerization***
- ***Nanocomposites and blends***

Increase melt viscosity

- ***Crosslinking***
- ***Branching***

SYNTHESIS OF POLY (L+) LACTIC ACID)S FROM L(+) LACTIC ACID

POLY(L+) (LACTIC ACID)S (PLLA) : PREPARATION



SUGAR CANE

FERMENTATION OF SUGAR CANE JUICE TO L(+) LA

CRUDE L(+) LACTIDE FORMATION

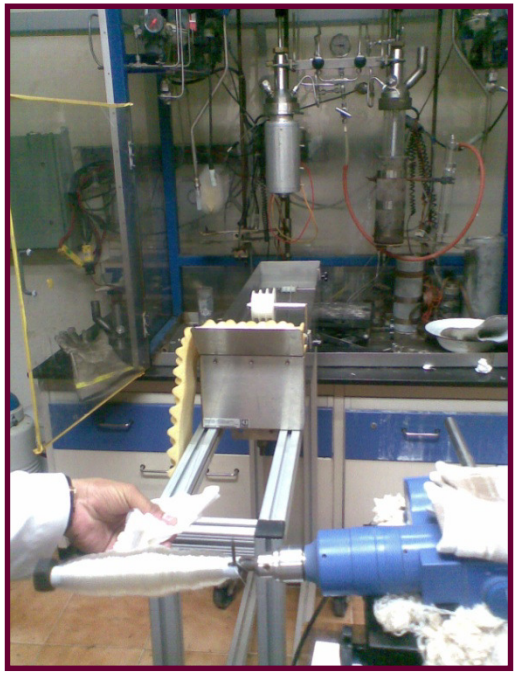
L(+) LACTIDE CRYSTALLIZATION

L(+) LACTIDE CRYSTALS

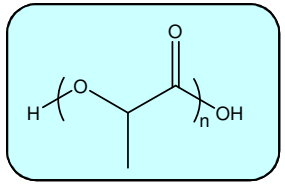
ROP

LABORATORY POLYMERIZATION SET -UP

- Polycondensation set up doubled up to do distillation.
- SS reactor of 200mL / 800 mL.
- Electrical heating and overhead stirring.
- Ability to purge, pull vacuum, add additives.
- Nozzle at bottom to extrude polymer melt coupled with a pelletizer.



PREPARATION OF L(+) LA OLIGOMER VIA DEHYDRO-POLYCONDENSATION



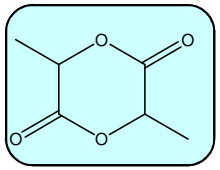
Lactic acid : 600 g (90% aqueous solution)
Conditions : 150°C/N_2/2h, 150°C/100 mm, Hg/1.5h,
150°C/30 mm, Hg/1.5h, 150°C/0.005 mm, Hg/1h

Source	Yield (%)	Mn* (g/mol)	Mw* (g/mol)	PDI
PURAC	98	3100	7100	2.29
NCL-1	98	3000	7000	2.33

* Determined by GPC in chloroform

Under these conditions only linear oligomers are obtained with no cyclic oligomers (MALDI-TOF)

PREPARATION OF DILACTIDE VIA DEPOLYMERIZATION AND CYCLIZATION)



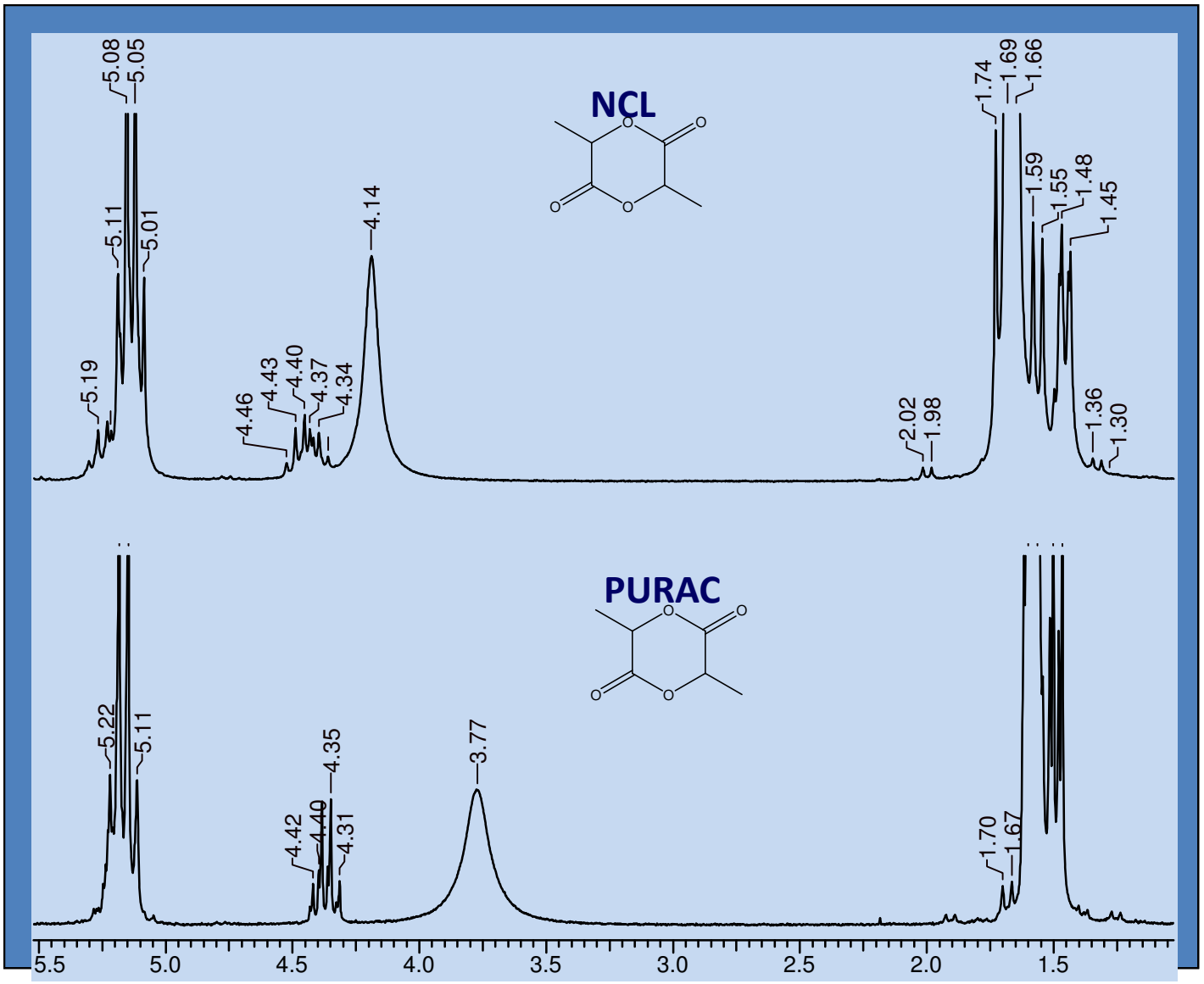
Lactic acid oligomer : 493 g; Catalyst : Tin powder (<150 μm)
Conditions : 160°C/N_2/1h, 180°C/100 mm, Hg/1h,
190°C/10 mm, Hg/1h, 200°C/0.01 mm, Hg/2h

Expt. No.	Tin Powder (wt%)	Lactide Yield (%)	Optical Purity (L+) (%)
1 (>150 μm)	0.5	70	95
6 (>150 μm)	0.5	99	100

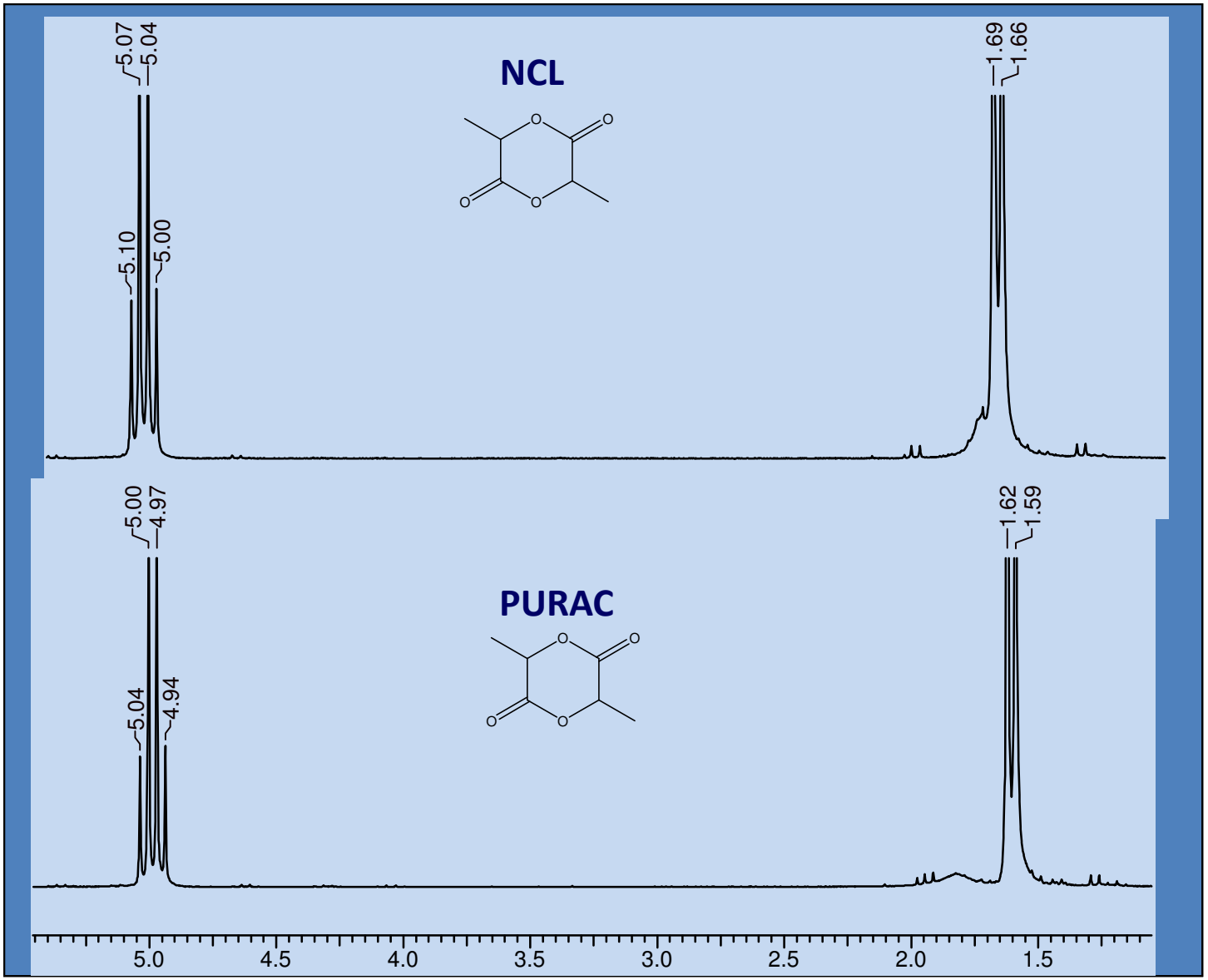
L(+) LACTIDE AS FORMED UNSUITABLE FOR POLYMERIZATION: PURIFIED BY CRYSTALLIZATION FROM MELT

:

PROTON NMR OF CRUDE L(+)LACTIDE PURIFICATION



PROTON NMR OF CRYSTALLIZED L(+) LACTIDE



PREPARATION OF POLY(LACTIC ACID)S via RING OPENING POLYMERIZATION

- Catalyst concentration: 0.03% to 0.05 wt%
- Chain stopper : Lauryl alcohol
- Temperature: 180°C

Expt. No.	Chain Stopper (wt%)	Time (min)	Mn[a] (g/mol)	Mw[a] (g/mol)	PDI
1	0	35	176000	412000	2.34
2	0.50	40	55100	92000	1.67
3	0.25	40	102000	156000	1.53

ISOSORBIDE AS A COMONOMER

ISOSORBIDE MONOMER

Dihydrohexitols - byproducts of biomass

- *prepared from starch, chiral in nature*
- *thermally stable*

Monomer for biodegradable polymers

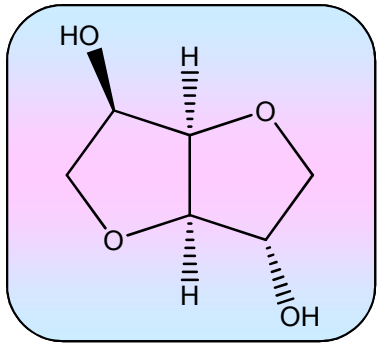
- *improved accessibility of two -OH groups*
- *exo substituent increases ring thermal stability*

Polymers presented promising properties

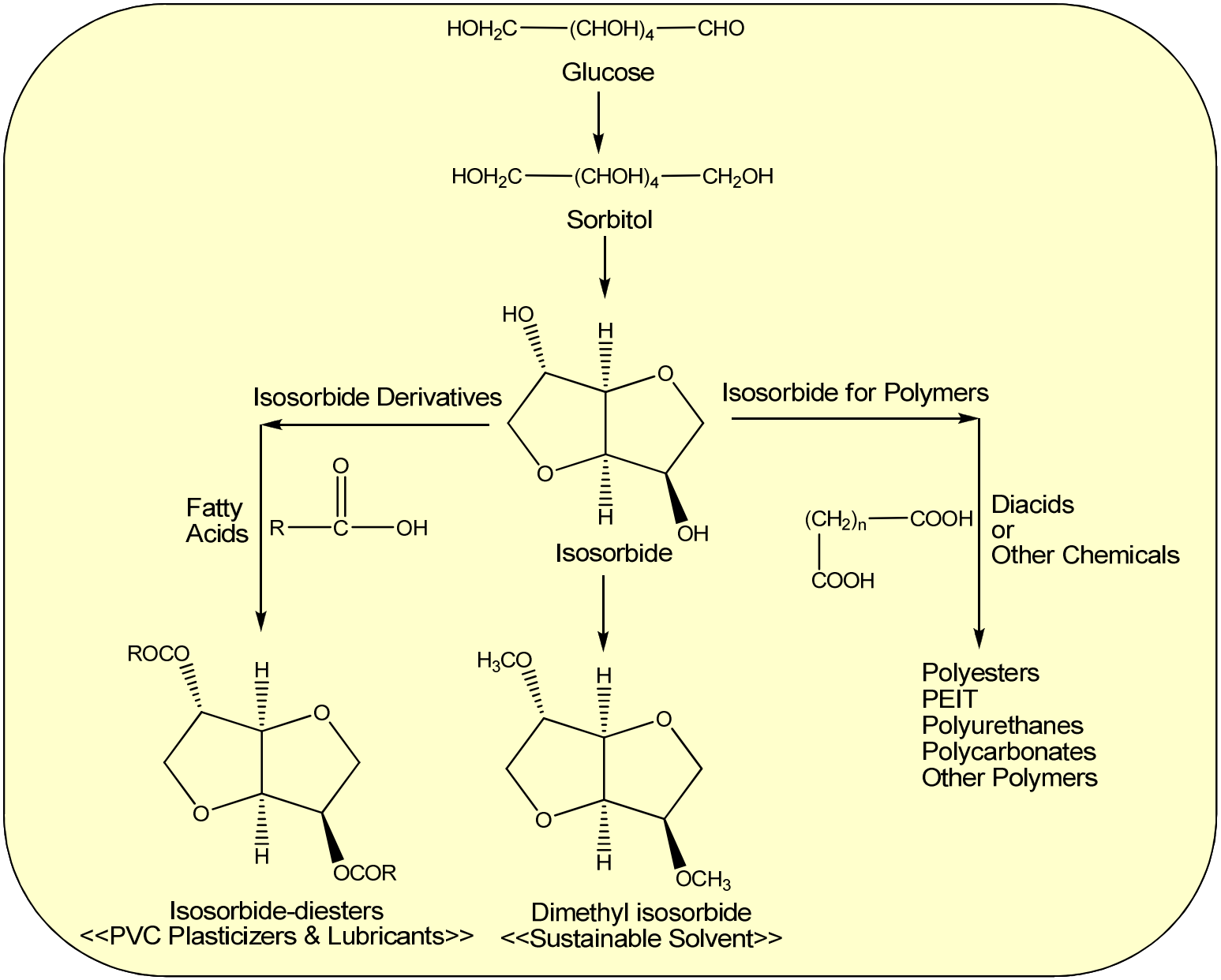
- *high glass transitions*
- *excellent thermal stabilities*
- *interesting physical properties*

Isosorbide copolyesters

- *relatively high Tg's*
- *cholesteric phase formation*



ISOSORBIDE: A PLATFORM CHEMICAL



L(+) LA- ISOSORBIDE COPOLYMER

Incorporation of isosorbide into PLLA by melt/solution disproportionation followed by solid state polymerization

L(+) LA-ISOSORBIDE COPOLYMER VIA MELT DISPROPORTIONATION

PLLA : 10 g (IV : 1.6 dL/g; Mw: 160,000 g/mol)
Catalyst : Titanium isopropoxide
Catalyst conc.: 0.5 wt% (based on PLA)

PLLA (wt%)	Isosorbide (wt%)	Temp. (°C)	Time (h)	IV* (dL/g)
98	2	200	1	0.38
94	6	200	1	0.25
90	10	200	1	0.16

* Determined in chloroform at 30°C by Ubbelhode viscometer.

DISPROPORTIONATED L(+)LA-ISOSORBIDE COPOLYMER

Sample ID	PLA:ISB Ratio	IV (dL/g)	T_m (°C)	T_c (°C)	T_g (°C)	ΔH_f (J/g)	ΔH_c (J/g)
PLAISB1	**98:02**	**0.38**	**161**	**100**	**52**	**42**	**35**
PLAISB2	**94:06**	**0.25**	**168**	**99**	**59**	**41**	**28**
PLAISB3	**90:10**	**0.16**	**174**	**85**	**64**	**36**	**21**

IV was determined in Chloroform at 30°C by Ubbelhode viscometer
Tg, Tm, Tc were determined by Q10 DSC (TA Instruments).

L(+) LA-ISOSORBIDE COPOLYMER VIA SOLUTION DISPROPORTIONATION

PLLA : 10 g (IV : 1.6 dL/g; Mw: 160, 000 g/mol)
Solvent : Chloroform
Catalyst : Titanium isopropoxide
Catalyst conc.: 0.5 wt% (based on PLA)

PLLA (wt%)	ISB (wt%)	Temp. (°C)	Time (h)	Incorp. (%)	Yield (%)	IV* (dL/g)
90	10	65	1	6	97	1.12
90	10	65	5	8	96	1.03
80	20	65	5	13	97	0.98
70	30	65	5	15	94	0.81

* Determined in chloroform at 30°C by Ubbelhode viscometer.

DISPROPORTIONATED L(+)LA-ISOSORBIDE COPOLYMER

Sample ID	PLA:ISB Ratio	IV (dL/g)	T_m (°C)	T_c (°C)	T_g (°C)	ΔH_f (J/g)
PLAISB4	**90:10**	**1.03**	**152**	**100**	**48**	**31**
PLAISB6	**70:30**	**0.81**	**141**	**101**	**40**	**17**

IV was determined in Chloroform at 30°C by Ubbelhode viscometer
Tg, Tm, Tc were determined by Q10 DSC (TA Instruments).

^1H NMR SPECTRA OF ISOSORBIDE IN $CDCL_3$

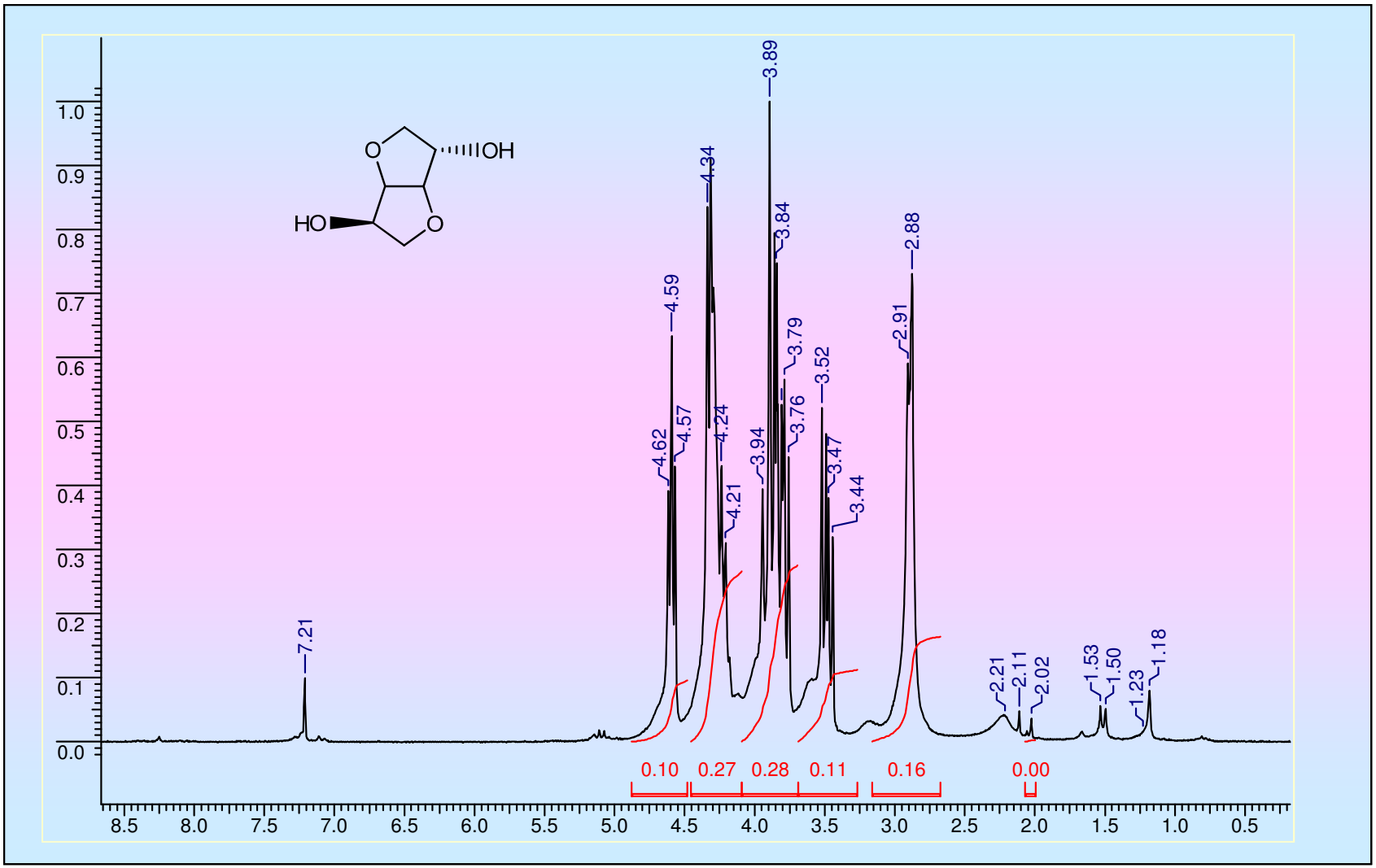
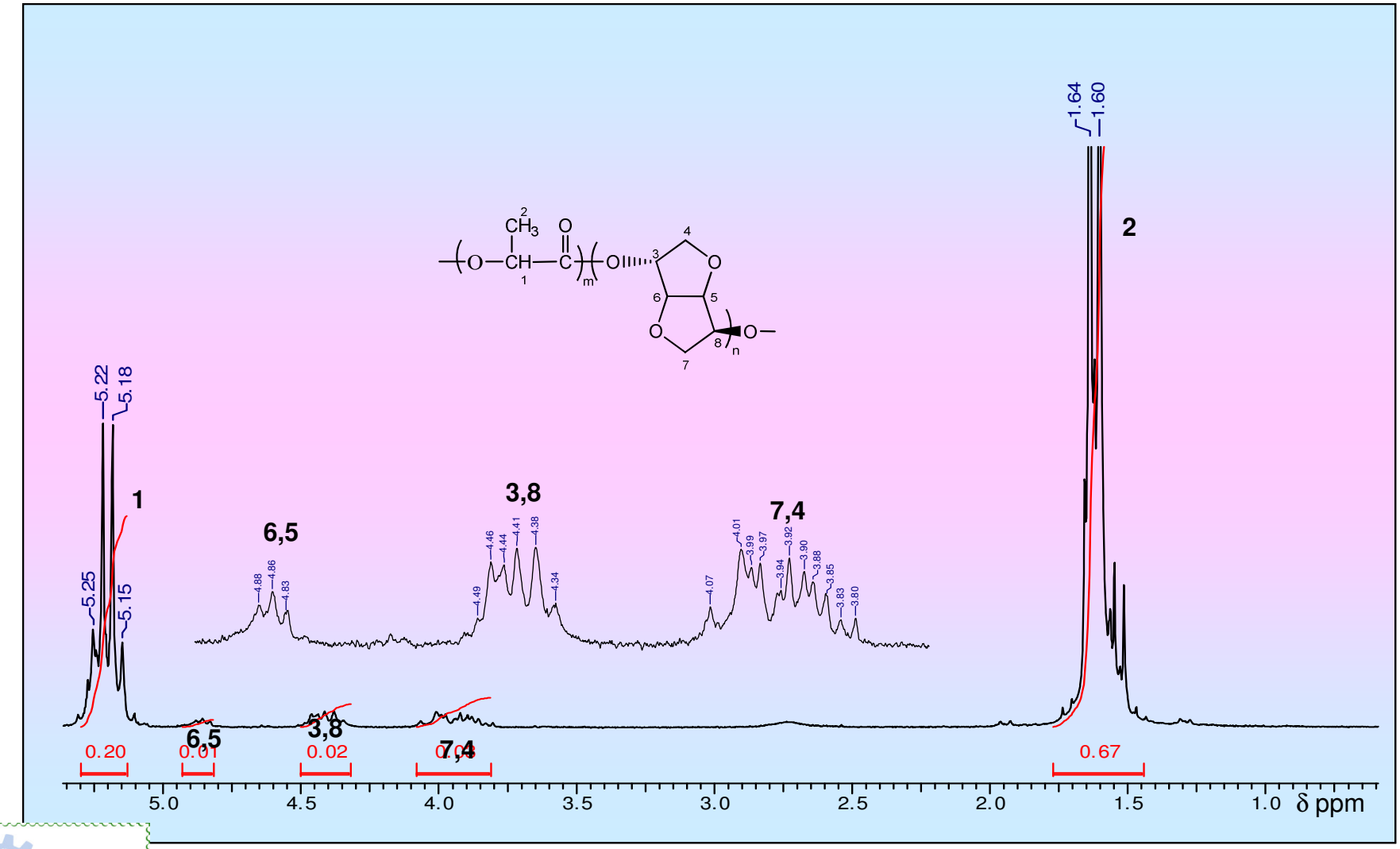
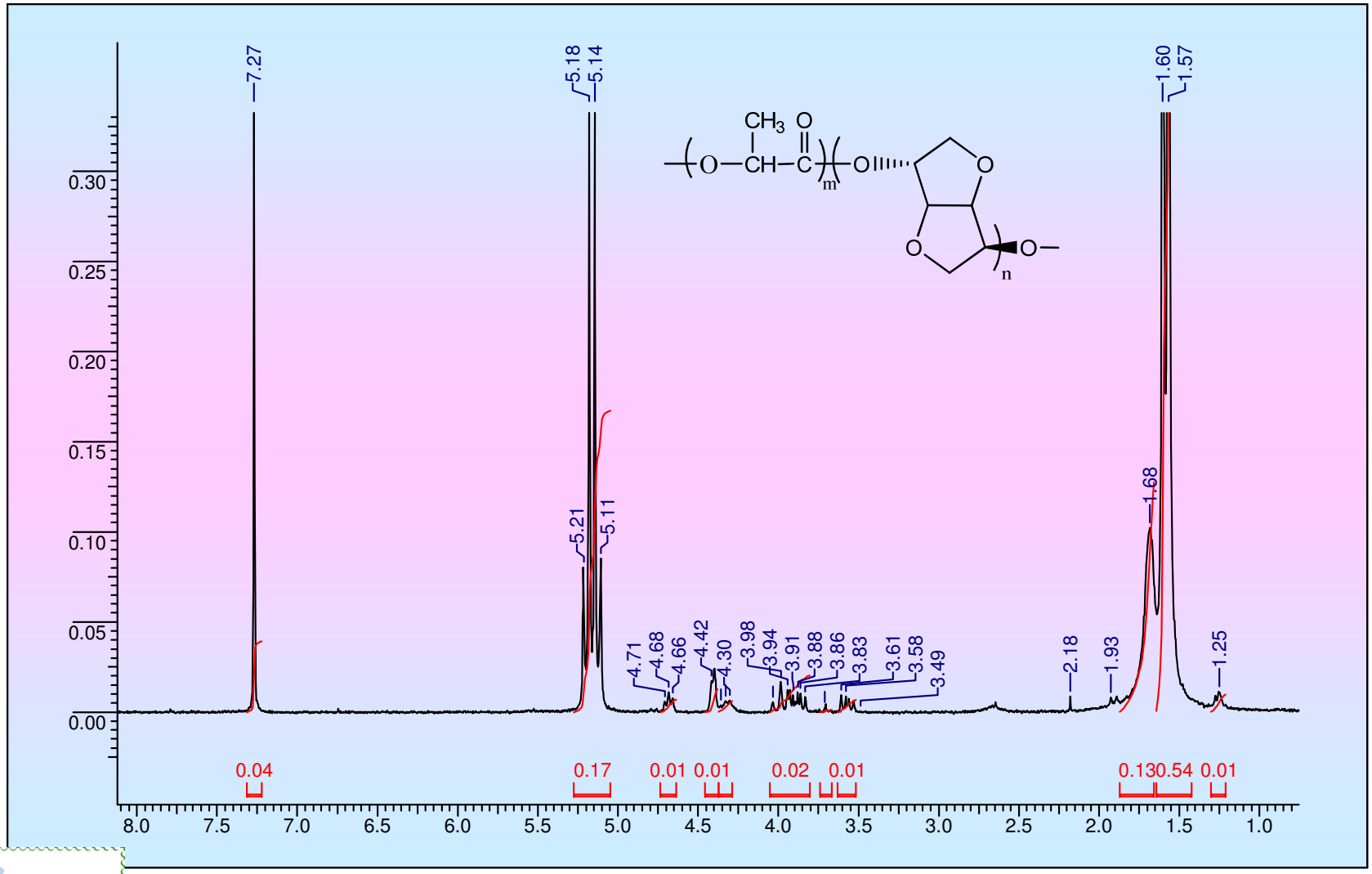


Fig. 2

^{1}H NMR SPECTRA OF PLA-ISOSORBIDE COPOLYMER IN $CDCL_3$



^{1}H NMR SPECTRA OF PLA-ISOSORBIDE COPOLYMER IN $CDCL_3$



SOLID STATE POLYMERIZATION OF DISPROPORTIONATED L(+) LA-ISOSORBIDE COPOLYMER

Polymn Steps	Sample ID	IV (dL/g)	T_g (°C)	T_m (°C)	T_c (°C)	ΔH_f (W/g)	ΔH_c (W/g)
1	PLAISB6	0.81	40	141	101	17	22
2	BSSP 100°C/1h	-	-	165	-	-	-
3	ASSP 120°C/2h	-	61	174	106	48	36
4	ASSP 135°C/3h	-	59	173	107	54	45
5	ASSP 145°C/2h	-	61	183	109	78	37
6	ASSP 155°C/2h	0.96	60	185	110	85	40

IV was determined in Chloroform at 30°C by Ubbelhode viscometer
Tg, Tm, Tc were determined by Q10 DSC (TA Instruments).

:DSC THERMOGRAMS OF PLA-ISOSORBIDE COPOLYMER DURING SSP

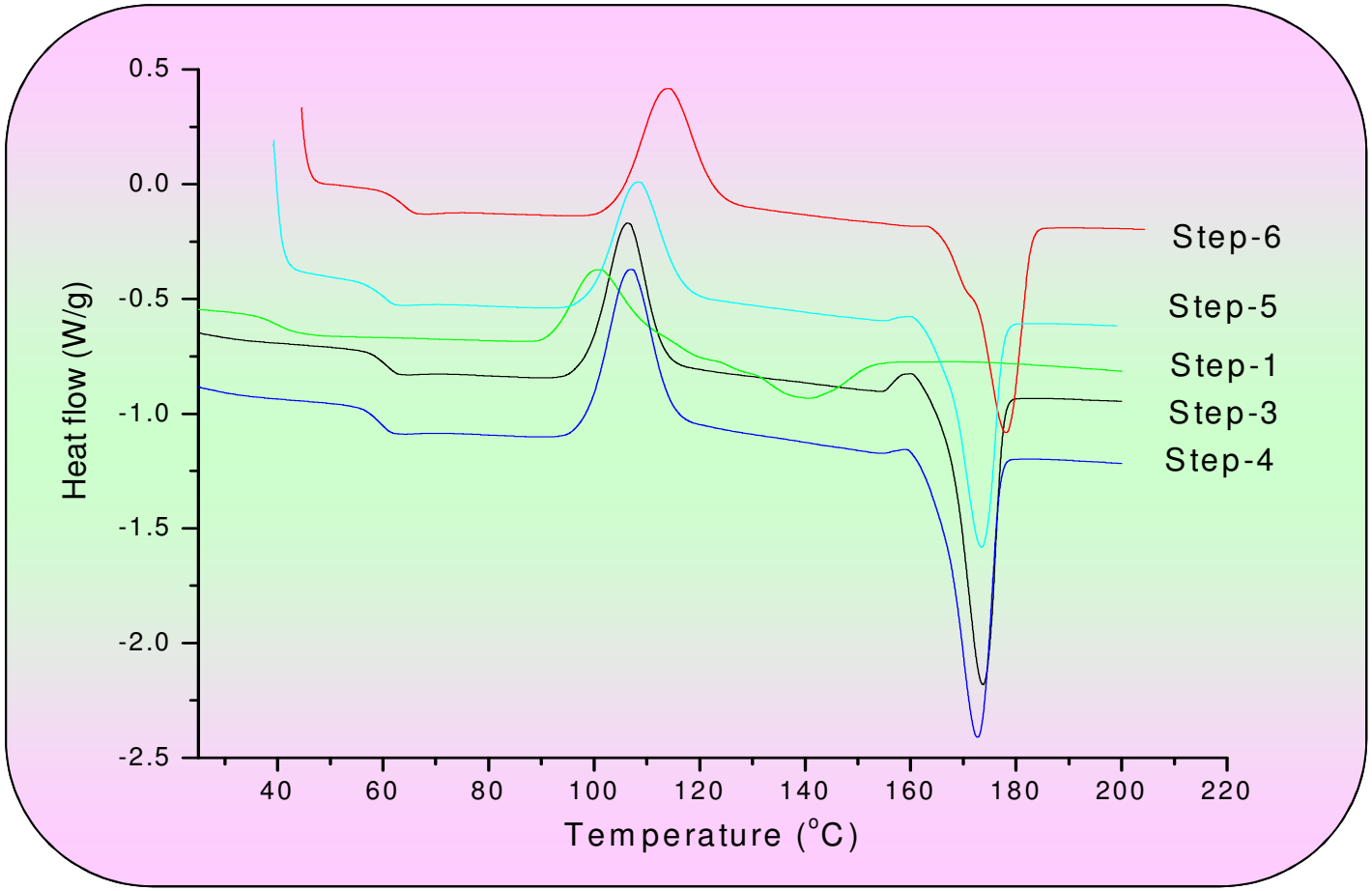
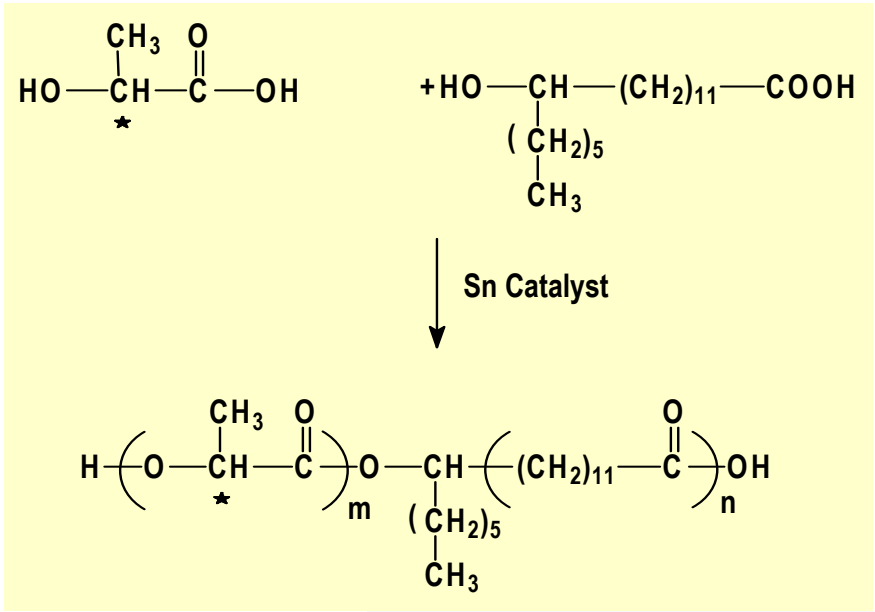
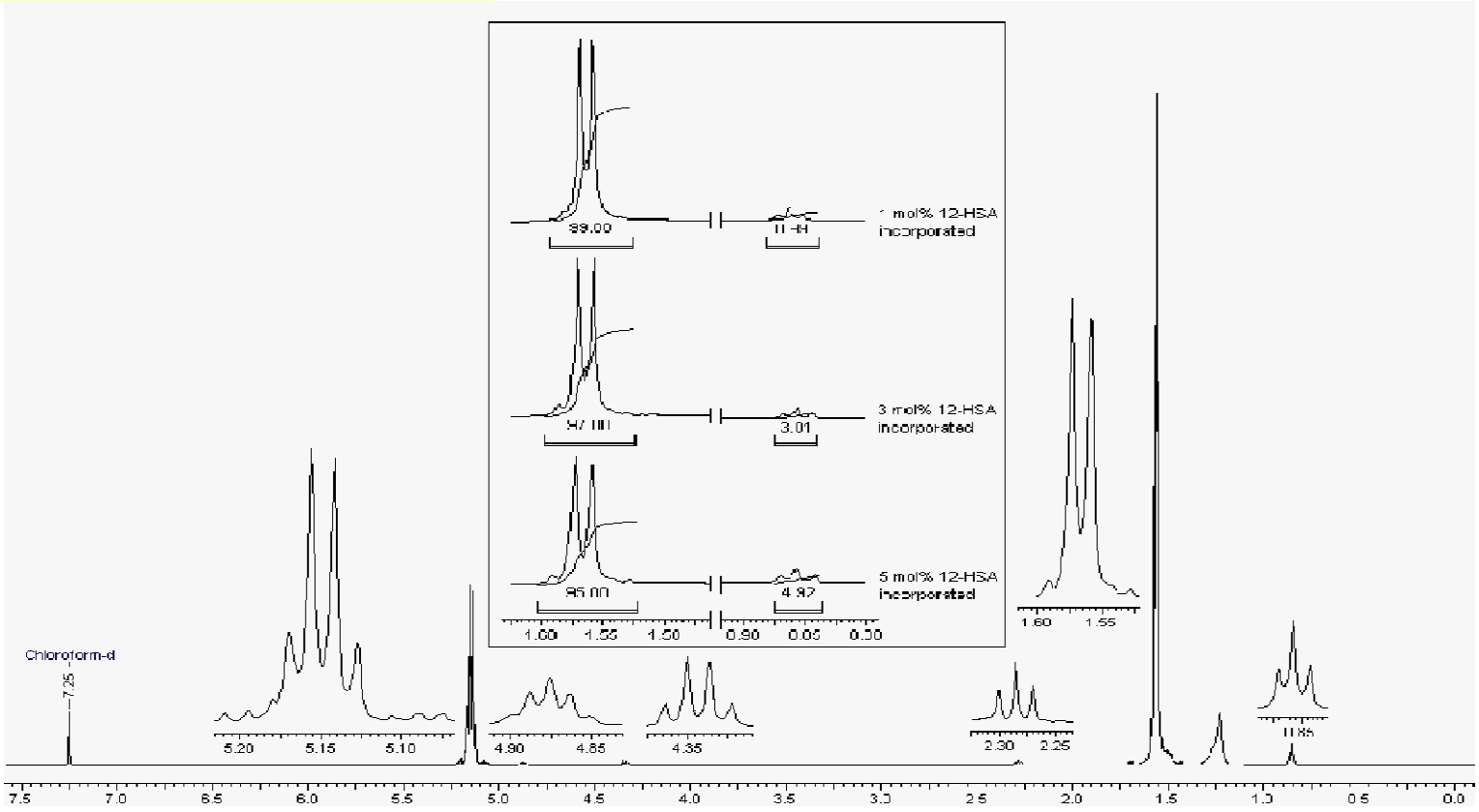


Fig. 9

12-HYDROXY STEARIC ACID AS COMONOMER



COPOLYMERS OF L (+) - LACTIC ACID WITH 12-HYDROXY STEARIC ACID

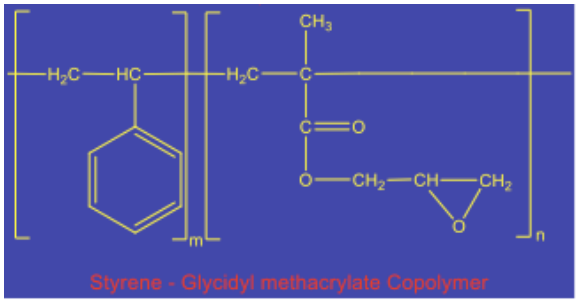


PROPERTIES OF L(+) LA – 12- HSA COPOLYMERS

mol% PLA	mol% 12-HSA		T_g (°C)	T_m (°C)	$\bar{M}_n$ (VPO)
	Feed	Product			
99	1	0.99	38	147	8,800
97	3	3.01	28	143	7,600
95	5	4.92	22	133	8,100
100	NIL		48	142	4,320

BRANCHING/CROSSLINKING USING STYRENE –GMA COPOLYMER

SYNTHESIS OF STYRENE-GMA COPOLYMER



Sty (%)	GMA (%)	IV[a] (dL/g)	Mn[b] (g/mol)	Mw[b] (g/mol)	PDI	Copolymer Comp[c]		Epoxy eq[d] (g/mol)
						Sty (%)	GMA (%)	
30	70	0.14	6620	25820	3.90	40	60	203
40	60	0.12	5020	17550	3.50	35	65	226
20	80	0.13	5240	20290	3.80	35	65	259
50	50	0.17	4570	16900	3.69	20	80	186

[a]Determined by Ubbelhode viscometer in chloroform at 30°C.
[b]Determined by gel permeation chromatography using chloroform solvent.
[c]Determined by ^{1}H NMR spectroscopy.
[d]Determined by titrimetry.

MELT COMPOUNDING AND RHEOLOGICAL MEASUREMENTS

Temp. : 180°C, Residence Time : 3 min in nitrogen
Speed : 100 rpm

ARES RHEOMETER

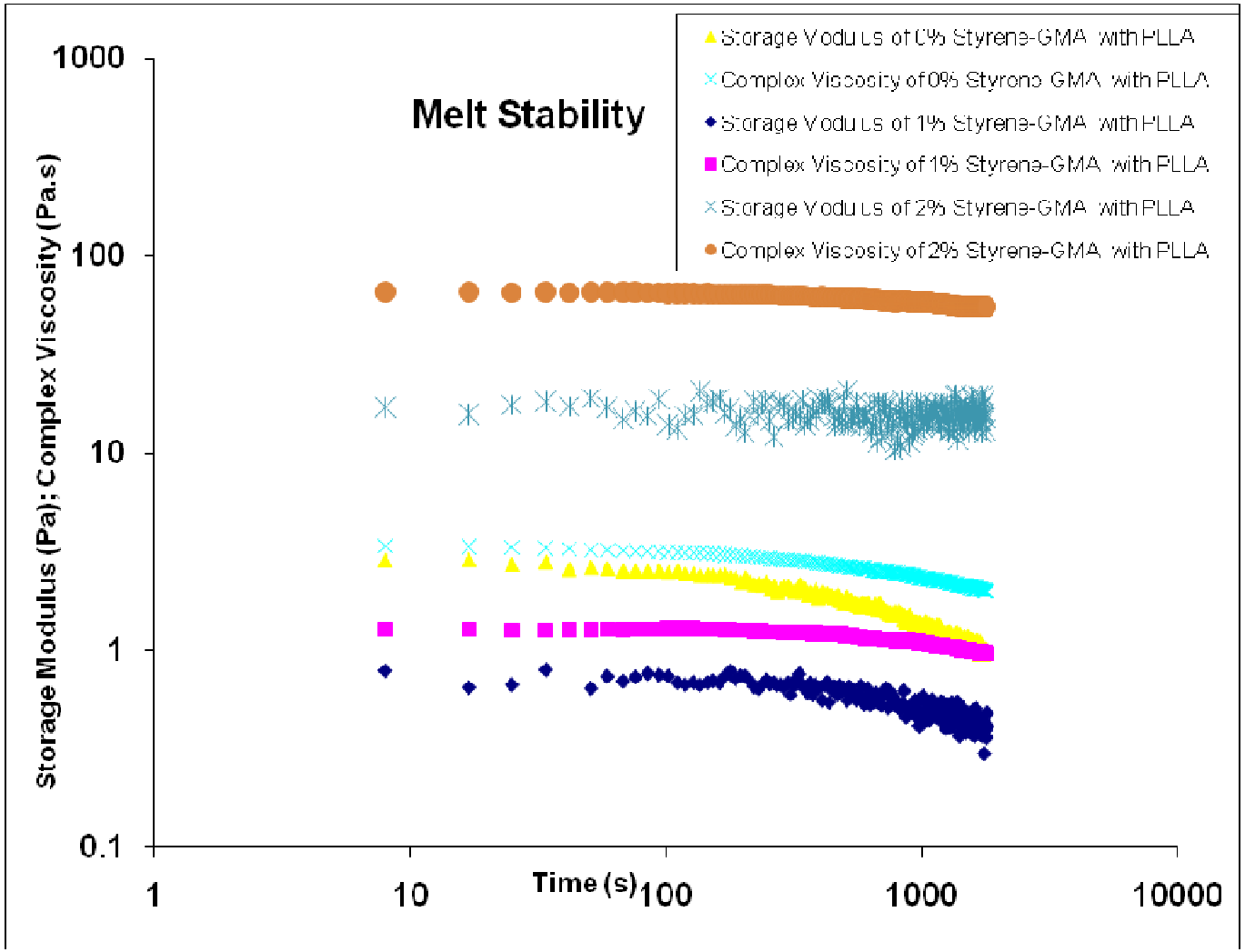
DSM MICROCOMPOUNDER

MELT COMPOUNDING OF STYRENE-GMA COPOLYMER WITH PLLA

Polymer Code	Sty:GMA (Comp.)	PLA (%)	St-GMA (%)	Mn[a] (g/mol)	Mw[a] (g/mol)	PDI
PLLA	-	100	-	46800	108000	2.50
PLLA1	50:50	99	1	41100	93100	2.26
PLLA2		98	2	39200	91400	2.33
PLLA3	40:60	99	1	53500	159000	2.96
PLLA4		98	2	56000	133000	2.36
PLLA5	30:70	99	1	44700	121000	2.71
PLLA6		98	2	54200	118000	2.18
PLLA7	20:80	99	1	43200	92900	2.33
PLLA8		98	2	49600	91900	1.85

[a]Determined by gel permeation chromatography using chloroform solvent.

STORAGE MODULUS AND COMPLEX VISCOSITY OF PLLA- GMA BLENDS



Addition of 2 % GMA enhances melt viscosity of PLLA

SUMMARY

- ***Tm improved using isosorbide as comonomer***

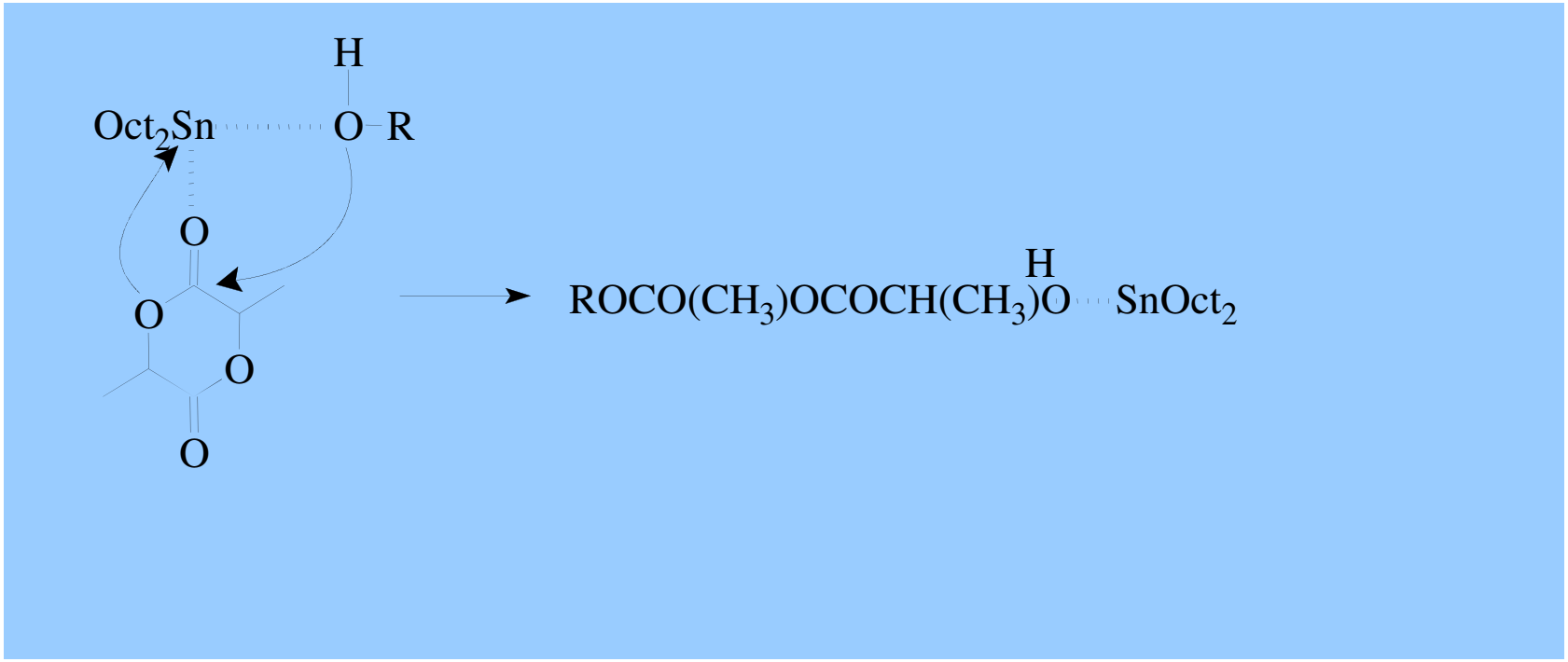
- ***Tg decreased using 12- hydroxystearic acid as comonomer***

- ***Branching and crosslinking with S-GMA copolymer improves melt viscosity of PLLA***

THANK YOU

SYNTHESIS OF PLLA OLIGOMERS CONTROLLED END GROUPS

- Controlled ROP of purified LL-dilactide performed 120 °C/ 12 h



R = H, WATER used as initiator to get carboxylic acid end groups

$$\bar{M}_n = ([M] / [I]) \times M_{Lactide} \times \text{conversion \%}$$
$$\text{and} \quad \bar{DP}_n = ([M] / [I]) \times \text{conversion \%}$$

MOLECULAR WEIGHT DETERMIATION OF PLLA SAMPLES

Number average molecular weights of the PLA oligomers synthesized by ROP of L-lactide with water as co-initiator and $Sn(Oct)_2$ as initiator.

PLA sample	[Lactide]/ $[Sn(Oct)_2]$	[Lactide]/ $[H_2O]$	Conv. (%)	$\overline{DP}_{n,\,Calc}$	$\overline{DP}_{n,\,NMR}$	$\overline{M}_{n,\,NMR}$	$\overline{M}_{n,\,VPO}$
3.1	200	32	86	55	60	4320	4400
3.2	400	45	87	79	77	5544	5692

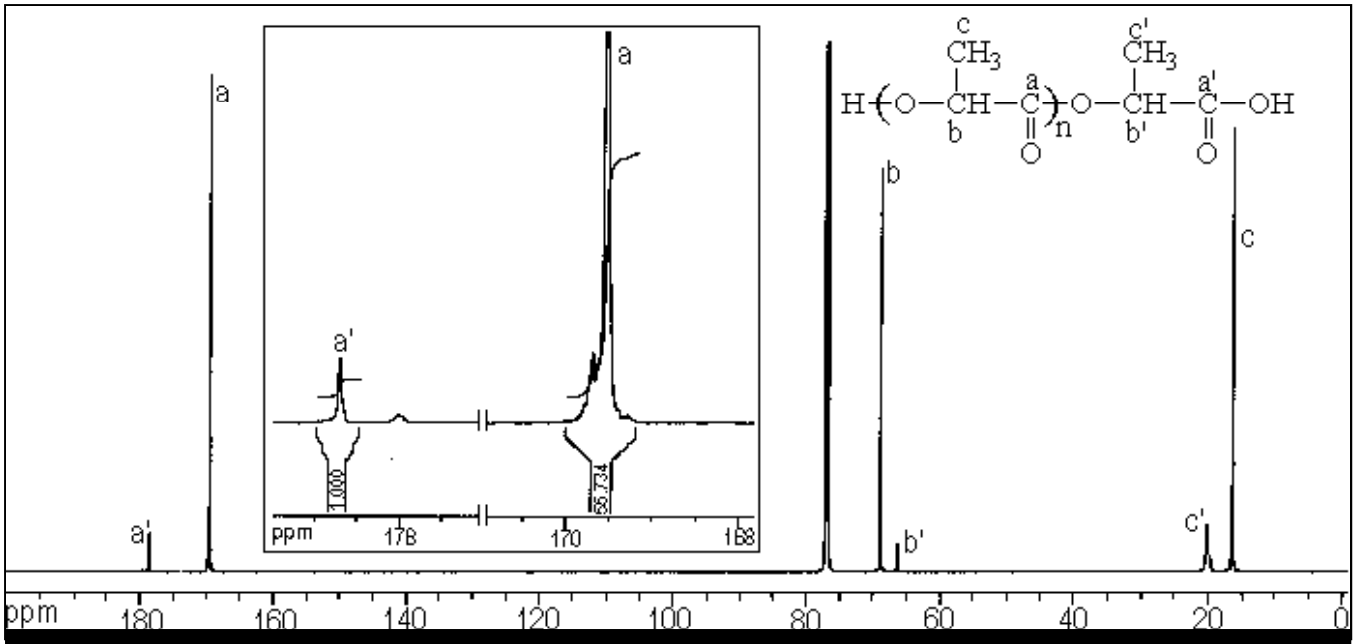


Fig. 3.1: 13C-NMR spectrum (500 MHz) of PLLA oligomer 3.1 synthesized by ROP : Inset showing ester carbonyl region (ester as well as carboxylic acid)

DSC OF PLA OLIGOMERS HAVING HYDROXYLA AND CARBOXY END GROUPS

PLA samples	T_g (°C)	T_m (°C)	$\Delta H_{melting}$ ($J.g^{-1}$)	% Crystallinity from powder XRD
3.1	48	141	53.4	85

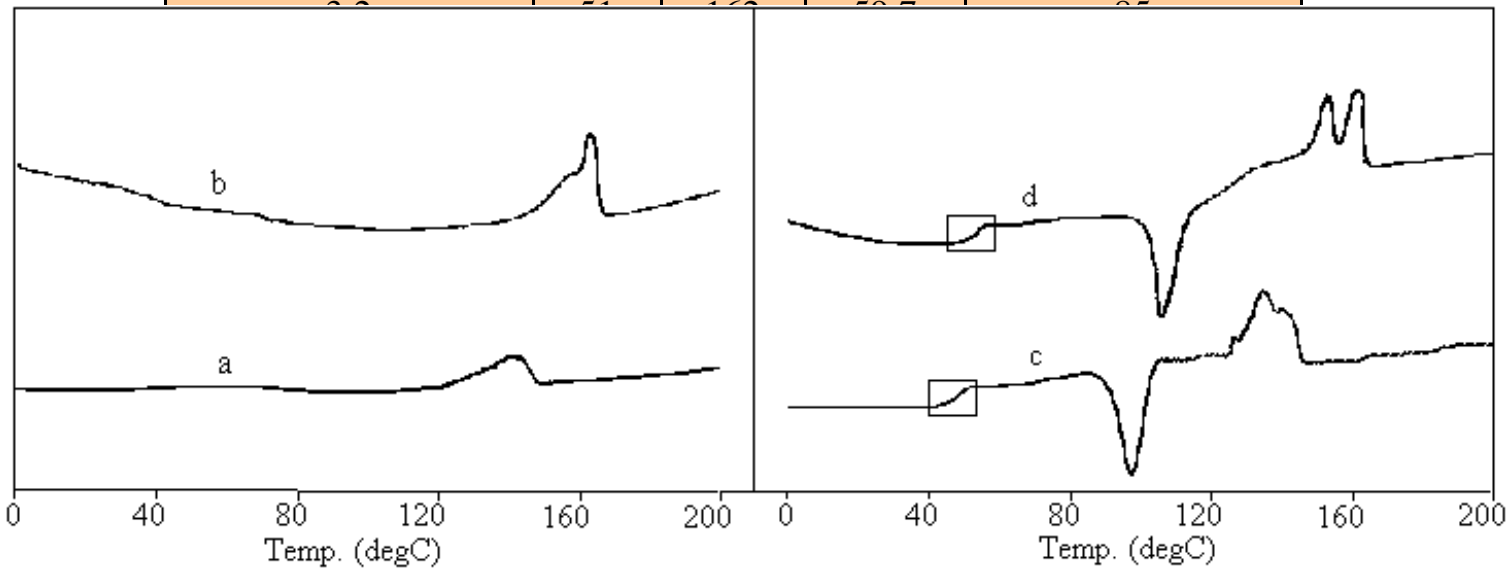


Fig. 3.2: Thermal characterization (DSC) first and second heating showing Tm and Tg, respectively of PLA oligomers: (a) 3.1, first heating; (b) 3.2, first heating; (c) 3.1, second heating and (d) 3.2, second heating