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Research Article

COPLYMERIZATION OF ALEURITIC ACID WITH L-LACTIC ACID AND STUDY THE AGGREGATION BEHAVIOR IN DIFFERENT SOLVENTS

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ABSTRACT

In this present work, we highlight the copolymerization of L-lactic acid (L-LA with protected aleuritic acid in presence of Lewis acid catalyst using dehyropolycondensation method. The resulted copolymers are pliable, soft, waxy or even viscous liquid copolymers influenced by the aleuritic acid content. The purpose of this study is to investigate the physical properties. In addition, deprotected copolymers focus micelle-like aggregates in various organic solvents and mixed organic solvent at various proportions.

INTRODUCTION

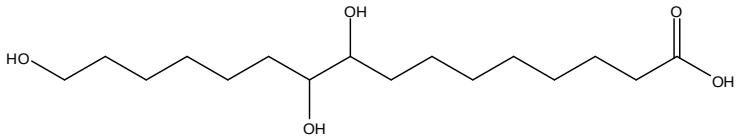
Aliphatic polyesters constitute an important class of polymers because of their biodegradability[1], and biocompability[2a, b], that enable their use in drug delivery systems, artificial tissues[3a,b], and commodity materials. Polyesters are commonly produced through either condensation or ring opening polymerization using various catalysts[4-6]. Self-organization of condensation polymer is rare in the literature. Particularly, self-organization of amphiphilic polymers has resulted in assemblies such as micelle, vesicles, fibers, helical, superstructures and macroscopic tubes. These materials have potential application in areas ranging from material science to biological science. Thermo or pH sensitive polymer micelles[7a, b], and vesicles[7c], have been reported in which the nature of the functionality at the corona changes in response to the stimulus. A little attention has been paid to realize an environment-dependent switch from a micelle-type assembly with a lipophilic corona[8]. Here, we report a new class of aliphatic polyester superstructures that exhibit such properties.

Shellac is the only known commercial resin of animal origin. It is an important natural resinous product secreted by an insect (Laccifer lacca), which lives on the sap of some host trees. India is the major shellac producing country in the world. Shellac (Lac) is known to comprise of several hydroxyl acid unit, aleuritic acid and its esters have great importance in industrial domain. It is a valuable starting material for preparation of transparent water-clear adhesive, plasticizers[9]. Aleuritic acid has been used as a raw material for the synthesis of macrocyclic musk like lactones such as ambrettolide, civetone and exaltone. There is only one literature report of poly aleuritic acid, where aleuritic acid has been polymerized thermally and resulted insoluble product[10]. We demonstrate for the first time that the linear homopolymer of aleuritic acid (PAA) is obtained from aleuritic acid (Fig 1). The change in the surface of the assembly is the amplified consequence of change in molecular level conformation with each polymer chain due to the presence of 9, 10-hydroxy group in each monomeric unit. These polymers with such properties could find use in the applications such as carriers for trafficking drugs and as components of smart adhesives. PAA is biocompatible and biodegradable polymer, which could find potential use in biological system.

Block copolymers are often used for a variety of supramolecular assemblies, in which the driving force involves the mutual immiscibility

of the block and/or the immiscibility of one of the blocks in the bulk solvent. In case of poly (styrene-co-acrylic acid) block copolymers exhibit several interesting amphiphilic assemblies[11-12]. We aimed to synthesize aliphatic polyester by polycondensation. The hydrophilic 9, 10-hydroxy functionality, the hydrophobic methylene moiety are stitched in the same polymer backbone. The methylene group's greater than five units in a polymeric chain show zigzag conformation in the polymer molecule[13].

The thermal polymerization of Aleuritic acid leads to insoluble product because both intra and intermolecular condensation are possible leading fast to the formation of fusible ethers, anhydrides, lactones and esters which ultimately become infusible and insoluble three dimensional network structures.



Aleuritic acid

Fig. 1: 9, 10, 16-trihydroxy, palmitic acid (aleuritic acid)

These functional polymers can be post modified to crosslink the polymer, or to attach bioactive molecules such as peptides or drugs and have shown potential application in drug delivery systems and scaffold materials. The functional polyesters have tunable mechanical properties with in vivo degradability[14]. Polyesters syntheses have been explored by both chemical synthesis and enzymatic approaches. Several hydroxyl functional polyesters[15-21], and poly (carbonate esters)[22], have been synthesized. Polymers with vicinal diols were prepared by chemical polymerization of L-lactide with protected sugars[23,24], followed by deprotection[25-27]. Use of monomers, initiators with unsaturated bond enabled the introduction of epoxide groups by post modification reaction with m-chloroperbenzoic acid (m-CPBA), while treatment of allylic side chains with NMO/OsO_4 resulted in dihydroxylation of side chains[28]. Chemical polymerization of unprotected hydroxyl functional caprolactones[29], and hydroxymethyl substituted 1, 4-dioxan-2-ones [30,31], resulted in hyper branched structures with comparable molecular weights and degree of branching.

The biodegradable polymers are intensively aliphatic polyester of both natural and synthetic origin. Polyesters can be synthesized by polycondensation of hydroxyl acids or by ring-opening polymerization of cyclic esters (lactones), grafting, chain extension, or transesterification[32]. A wide range of monomers has been used to produce biodegradable polyesters. Their polymerizations can be carried out either in the bulk or in solution. The most useful monomers used for polycondensation are lactic, glycolic, hydroxybutyric acid and hydroxycaproic acids. Polyesters of glycolic and lactic acids are the main group of interest due to their long history of safety.

Lactic acid can be condensed with other hydroxyl acids such as 6-hydroxycaproic acid, glycolic acid, and hydroxybutyric acid or in the presence of diols, diacids, and diamines. Direct condensation usually resulted in low molecular weight copolymers that can then be further linked to yield high-molecular-weight polymers. In the second step, linking molecules such as diisocyanates, bis (amino-ethers), phosgene, phosphate, and anhydrides takes place[33-35].

There is no report available so far, where the 9, 10 secondary vicinal diol is protected and the hydroxy and carboxylic acid groups are free to undergo dehydropolycondensation reaction to produce a linear high molecular weight homopolymer.

Fatty acids are suitable candidates for the preparation of biodegradable polymers[36,37], as they are natural body components and they are hydrophobic, and thus they may retain an encapsulated drug for longer time periods when used as drug carriers. Aleuritic acid (9, 10, 16-trihydroxy palmitic acid) is common C16 fatty acids with two secondary hydroxyl groups at 9, 10 positions and a primary hydroxyl group in the 16th position. It is produced from resin (Shellac).

The objective of this study is to incorporate aleuritic acid in lactic acid based polymers for the purpose of altering its physical properties. The trifunctionality of aleuritic acid (9, 10, 16-trihydroxy palmitic acid) does not allow forming the linear polymer. Previous study in our laboratory focused on the synthesis aleuritic acid (9, 10, 16-trihydroxy palmitic acid) homopolymer. The homopolymer synthesized

from aleuritic acid by protecting the 9, 10 hydroxyl groups with dimethoxy propane (DMP) to make –COOH and 16th position –OH group free for reaction to make linear polyester[38]. These copolymers have pendent hydroxyl groups for aggregation to form micro scale morphologies. Molecular self-assembly of organic molecules has generated a wide variety of objects with nanoscale or micrometer-scale morphologies including micelles[39,40], vesicles[41,42], ribbons[43], films[44], fibers[45, 46], and tubules[47-48].

The copolymerization of L-lactic acid (L-LA with protected aleuritic acid in presence of Lewis acid catalyst using dehyropolycondensation method. The resulted copolymers are pliable, soft, waxy or even viscous liquid copolymers influenced by the aleuritic acid content. The purpose of this study is to investigate the physical properties. In addition, deprotected copolymers focus micelle-like aggregates in various organic solvents and mixed organic solvent at various proportions.

MATERIALS AND METHOD

L-lactic acid was obtained from Purac as a 88% (w/w) aqueous solution with impurity , aleuritic acid, tetraphenyltin (Aldrich, USA), p-toluene sulfonic acid (PTSA) (Aldrich, USA), Xylene (S.D Fine Chemicals, India), anisole (Aldrich, USA), sodium sulphate, chloroform and methanol (S.D Fine Chemicals, India), mesitylene (Aldrich, USA), decaline (Aldrich, USA), and diphenyl ether (Fluka, Germany). All solvents were dried by using standard procedures for example toluene by distilling over metallic sodium. All liquids were transferred by syringe under dry argon atmosphere.

EXPERIMENTAL

Synthesis of methyl ester of aleuritic acid: Crude aleuritic acid was converted to methyl ester by using tetraphenyltin (TPT) as a catalyst in dry methanol solution at reflux temperature. The reaction mixture was refluxed for 9 h, during which reaction was monitored using TLC (solvent system; chloroform/ methanol 9/1). The ester was dried using rotavapour and further purified by column chromatography (chloroform/ methanol 9/1). The impurity profile was checked by gas chromatography (Fig 10 A and Fig10 B). The ester was recrystallized using ethyl acetate, the crystal was dried under vacuum and the yield was calculated as 90 %. MP : 71-72 ^{0}C , FT-IR (KBr) ν_{cm-1} : 1740-1720 cm^{-1} (COOCH$_3$). ^{1}H NMR (500 MHz): δ 3.66 (s, 3H, COOCH$_3$), 3.64 (t, j = 5.24, 2H, CH$_2$OH, 3.39 (bs, 2H –CH(OH)-CH(OH)), 2.30(t, j = 7.44,2H,-CH$_2$-COOCH$_3$), 1.61-1.31(s, 22H, -CH$_2$-).

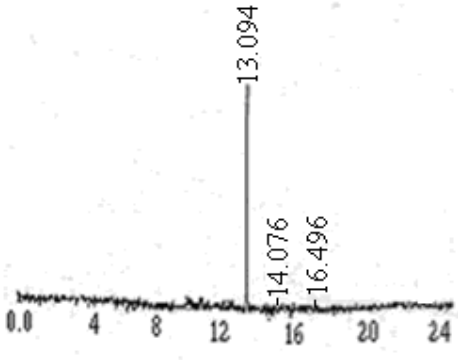


Fig. 10A: GC of methyl ester of aleuritic acid purification

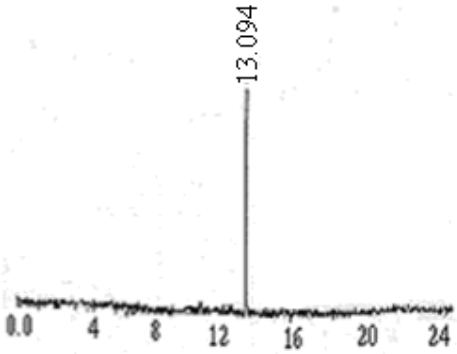


Fig. 10 B: GC of methyl ester of before aleuritic acid after purification

Synthesis of protected aleuritic acid: Pure methyl ester of aleuritic acid (9, 10, 16 tri hydroxy hexadecanoate) (9 gm, 0.028M) was taken in a two-neck flask and equimolar quantity of dimethoxy propane was added, p-toluene sulfonic acid (PTSA) and the toluene were used as catalyst and solvent respectively. The reaction mixture was refluxed under the blanket of inert atmosphere (argon) for 6 h. After the completion of the reaction, the toluene was removed using rotavapour. The reaction mixture was washed several times with deionized water and extracted with chloroform. The chloroform layer was dried over Na_2SO_4 and finally stripped off. Finally, it was vacuum dried to give 8.2 gm (yield- 82%). The structure of protected methyl ester of aleuritic acid (ProAL) (monomer) FT-IR (KBr) ν_{cm-1} : 1740.17cm^{-1}(-COOCH$_3$) , 1377.55 cm^{-1} and 1368.73 cm^{-1} (-O-C(CH$_3$)$_2$-O-). ^{1}H NMR (500 MHz) : δ 3.66 (s, 3H, -COOCH$_3$), 3.64 (t, j = 5.64, 2H, CH$_2$OH),

3.56 (bs,2H –CH-(O)-CH(O)-), 2.17 (t, j =7.44,2H, -CH_2-$COOCH_3$), 1.38,(s, 6H, -C-$(CH_3)_2$-) , 1.50-1.31 (s, 22H, -CH_2-). 1.31 (s, 22H, -CH_2-).

CHARACTERIZATIONS

FT-IR: IR spectra were recorded as KBr pellets, on Perkin-Elmer Infrared Spectrometer Model 16PC FT-IR, using sodium chloride optics. IR bands are expressed in frequency (cm^{-1}).

Size Exclusion Chromatography Molecular weight (SEC): Molecular weights (relative, $\bar{M}_n$ and $\bar{M}_w$) and polydispersity ($\bar{M}_w$/ $\bar{M}_n$) were determined with respect to polystyrene standards by size exclusion chromatography on a Thermo Finnigan Spectra Series AS300 machine at 25 ^{0}C by eluting PLA solutions of 10 mg/ mL concentration in $CHCl_3$, with toluene as internal standard, through a series of five μ-Styragel columns of pore sizes 10^5, 10^4, 10^3, 500, and 100 A^0 respectively, and length 30 cm each. $CHCl_3$ was used as the mobile phase (flow rate 1 mL/ min) and a refractive index detector (Spectra Series RI-150) was used for detection of different molecular weight fractions. Molecular weights were calculated with respect to polystyrene calibration.

Differential Scanning Calorimetry (DSC): Differential scanning calorimetry (DSC) measurements were performed on a thermal analyzer in nitrogen atmosphere. The measurements were run from –90 to 200 ^{0}C at a heating rate of 10 ^{0}C / min and at a cooling rate of 100 ^{0}C/min. The glass- transition temperature (T_g) and the crystallinity data were recorded from the second and first heating curves, respectively.

Nuclear Magnetic Resonance Spectroscopy (NMR): For NMR measurements, the polymer samples were dissolved in chloroform–d in 5mm diameter. NMR tubes at room temperature.^{1}H NMR spectra were recorded on Bruker DRX 500 MHz with 4 % w/v concentration of solution. The chemical shifts in parts per million (ppm) are reported up field with reference to internal standard chloroform-d at 7.25 ppm. Peak areas were calculated by deconvolution method using XWIN-PLOT software.

Transmission Electron Microscopy (TEM)

Sample preparation: The sample was dissolved in solvents and mixture of solvents to understand the aggregation behavior. The solutions were collected on 300 mesh carbon coated copper grids. The copper grids were kept overnight on filter paper for drying. TEM imaging was performed using a JEOL 1200EX electron microscope operating at an accelerating voltage of 80 kV. Images were captured using charged couple detector camera and viewed using Gatan Digital Micrograph software.

RESULT AND DISCUSSIONS

The synthesis of protected aleuritic acid was carried out and characterized. The synthesis of L-lactic acid- protected aleuritic acid copolymers was accomplished by dehydropolycondensation using Lewis acid (tetraphenyltin) as a catalyst and shown in Figure 5.8. 5 mL of L-lactic acid (88% aqueous solution) was taken a in three neck flask and xylene was added (1:1 v/v) proportion The reactant was refluxed for 6h using Dean Stark apparatus to remove water as an azeotrope and requisite amount of protected aleuritic acid was added into the reaction flask. The reaction mixture was further continued up to 15h. The reaction mixture was cooled and the extra xylene was removed by vacuum distillation. The copolymer of various compositions ranging from 90:10 to 50:50 ratios were prepared accordingly. Reaction scheme for copolymerization is shown in Fig 1 The resulting copolymer was dissolved in chloroform in a single neck flask and equal amount of methanol, catalytic amount of PTSA was added into it. The reaction mixture was stirred at room temperature (25 ^{0}C) under inert atmosphere (Argon) for 6 h. The deprotected copolymer was dissolved in chilled methanol and filtered using Whatman filter paper. The resulting copolymer was characterized by ^{1}H NMR, GPC, DSC and aggregation behavior in different solvent was observed by TEM.

SEC Analysis

The SEC thermograms of protected copolymer samples are all shown in Fig 2A.The copolymers and homopolymers were prepared by dehydropolycondensation method using tetraphenyltin as a catalyst and p-xylene as a solvent. Copolymers (COP-1 to COP-5) showed a single peak (Fig 2A) whereas COP-2 and COP-3 showed a shoulder peak on them. These results are attributed due to very low molecular weight oligomeric species in equilibrium with each other. The copolymer COP-1 showed $\bar{M}_n$, $\bar{M}_w$ and molecular weight distribution as 7,500, 13,200 and 2.2 respectively.

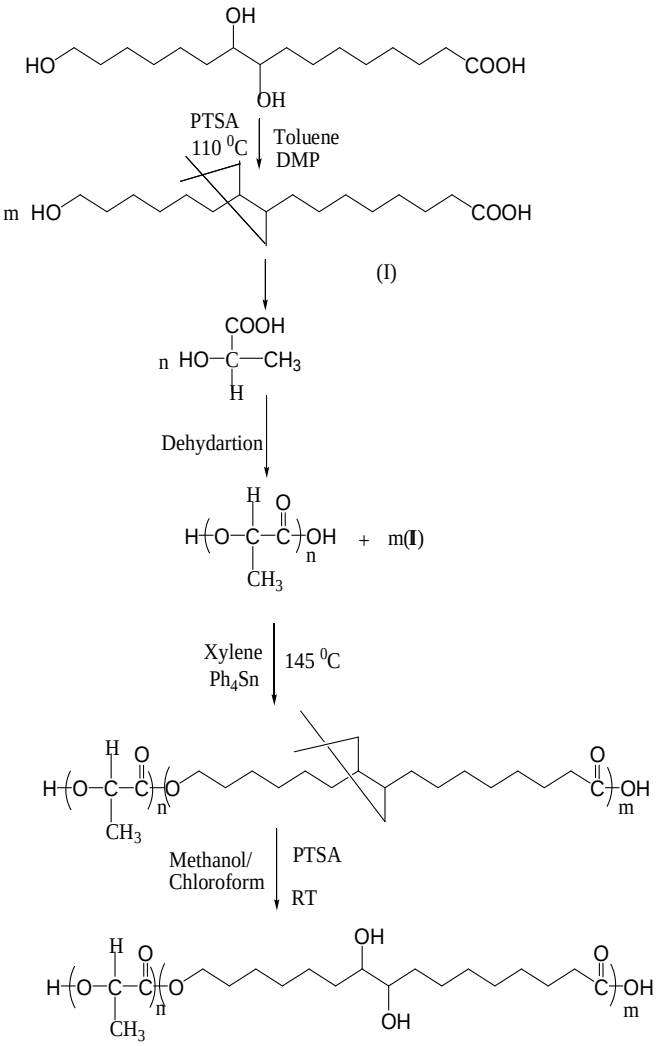
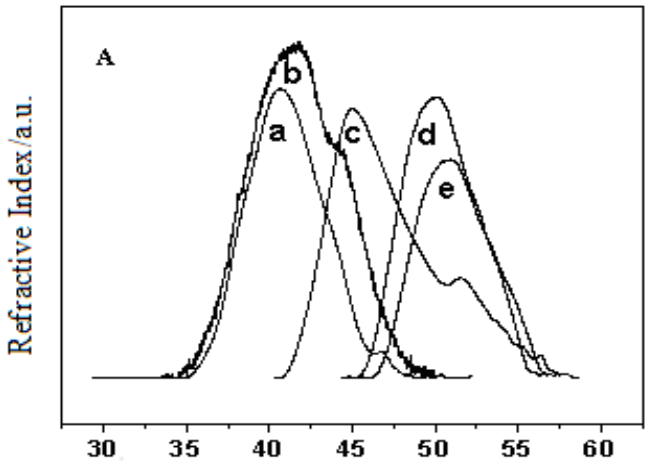
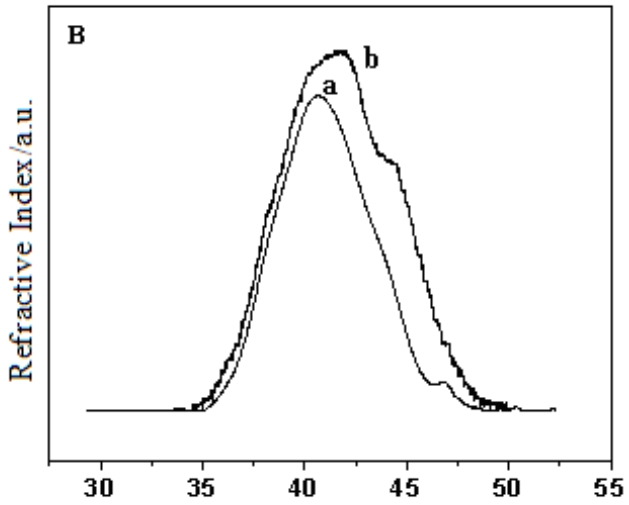


Fig. 1: Reaction scheme of copolymerization



Elution Volume (Vel, µL)

Fig. 2A: Size Exclusion Chromatography (SEC) of protected copolymers (a) COP-1, (b) COP-2, (c) COP-3, (d) COP-4 and (e) COP-5



Elution Volume (Vel, µL)

Fig. 2B: Size Exclusion Chromatography (SEC) of deprotected copolymers (a) DCP 1 and (b) DCP-2

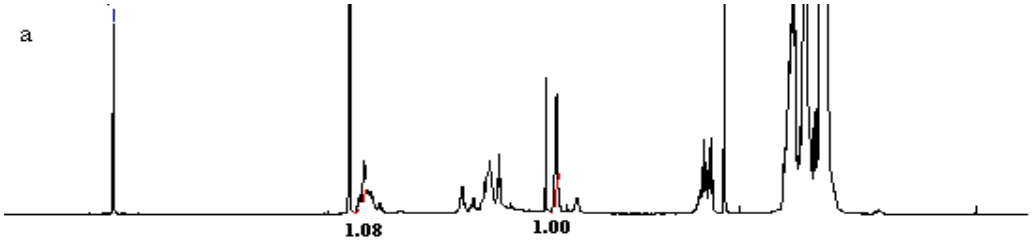
Table 1: Properties of L-lactic acid protected aleuritic acid copolymers

Copolymer samples	Feed ratio	Copolymer comp	$\bar{M}n$ (GPC)	$\bar{M}w$ (GPC)	PDI	Tm (0C)	ΔHf (J/g)	Tg (0C)	ΔCp (j/g*0C)
PLA	100:0	100:0	900	2,100	2.3	146.0	42.0	44.5	0.46
COP-1	90:10	85:15	7,500	13,200	1.7	161.4	4.1	10.62	0.50
COP-2	80:20	75:25	5,700	12,700	2.2	175.5	0.80	-11.5	0.33
COP-3	70:30	70:30	2,100	6,400	3.0	127.3	5.7	-22.0	0.37
COP-4	60:40	60:40	1,250	1,750	1.4	148.7	0.41	-30.2	0.44
COP-5	50:50	50:50	800	2,000	2.5	138.8	1.2	-31.5	0.41

Temperature of polymerization 195 ^{0}C and time for polymerization 8 hr

Table 2: Properties of L-lactic acid- protected and deprotected aleuritic acid copolymers

Copolymer sample.	Feed ratio	$\bar{M}n$ (GPC)	$\bar{M}w$ (GPC)	PDI	Tm (0C)	ΔHf (J/g)	Tg (0C)	ΔCp (j/g*0C)
COP-1	90:10	7,500	13,200	1.7	161.4	4.1	10.62	0.50
COP-2	80:20	5,700	12,700	2.2	175.5	0.80	-11.5	0.33
DCP-1	90:10	7,500	13,000	1.7	135.6	5.2	34.7	0.43
DCP-2	80:20	5,700	12,700	2.2	140.0	5.5	40.5	0.27



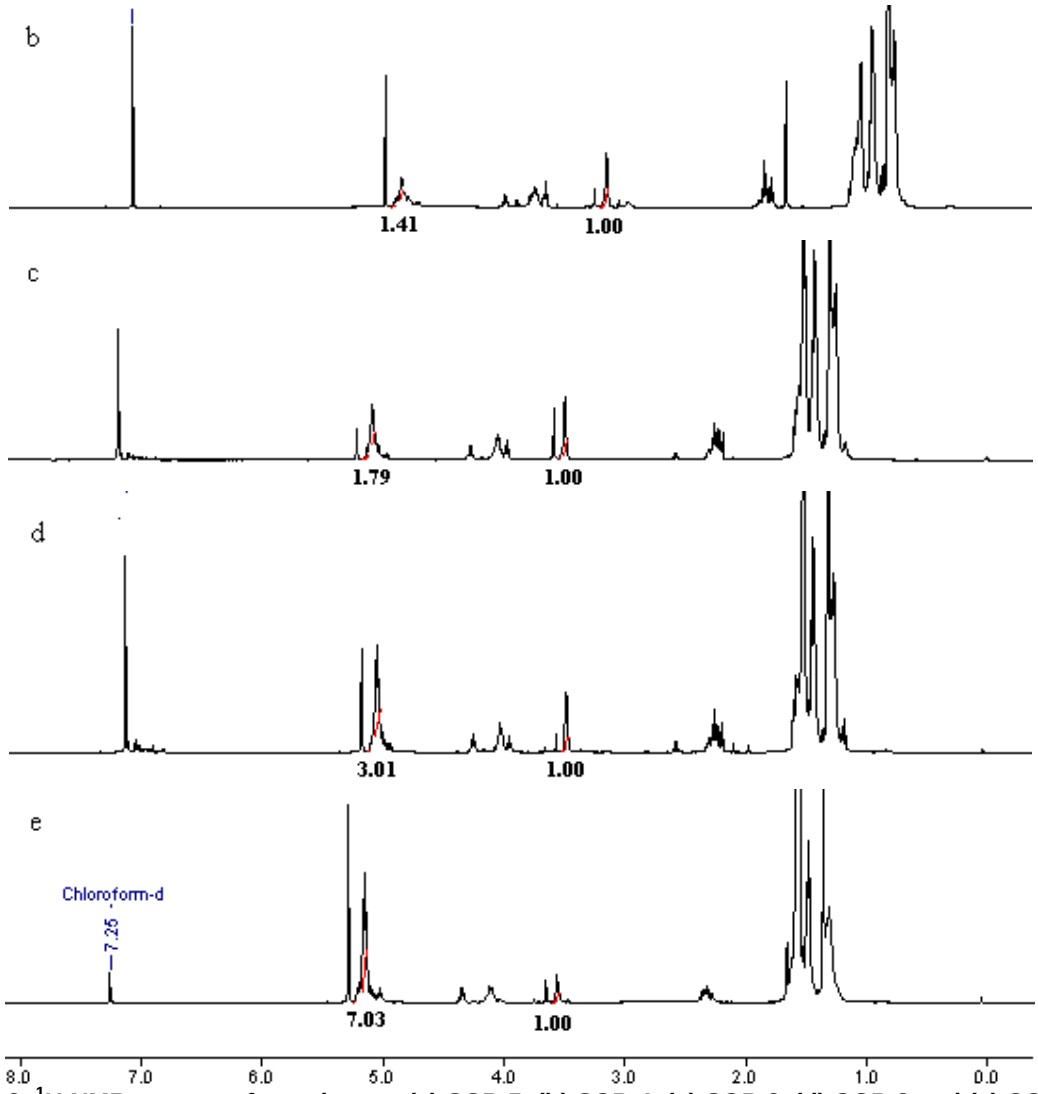


Fig. 3: ^{1}H NMR spectra of copolymers (a) COP-5, (b) COP-4, (c) COP-3, (d) COP-2 and (e) COP-1 COP-2 showed $\bar{M}_n$, $\bar{M}_w$ and molecular weight distribution as 5,700, 12,700 and 2.2 respectively with a small shoulder peak. Similar observation was obtained in case of COP-3. COP-4 which showed a single peak and the calculated $\bar{M}_n$, $\bar{M}_w$ and molecular weight distribution are 1250, 1750 and 1.4 respectively.

The copolymer COP-5 also showed a single peak and the calculated $\bar{M}_n$, $\bar{M}_w$ and molecular weight distribution are 800, 2000 and 2.5 respectively. The SEC elugrams of deprotected copolymer samples (DCP-1 and DCP-2) are all shown in Fig 2B.

Nuclear Magnetic Resonance

The copolymer compositions were determined from peak area in ^{1}H NMR spectra and shown in Fig 3. Comparison of the peak area in the region δ=3.56 ppm due to disustituated proton contributed by aleuritic acid (9,10 position) with the area of the proton at δ= 5.15 ppm due to methine group of the L-lactic acid enables the estimation of the copolymer composition. Samples obtained from mole ratios of protected aleuritic acid: L-lactic acid = 10: 90 to 50: 50 were soluble in $CDCl_3$. The results of COP-1 to COP-5 along with PLA and protected poly aleuritic acid are shown in Tab 1. The results of protected copolymers (CAP-1, CAP-2) and deprotected copolymers (DCP-1, DCP-2) are shown in Tab 2.

Thermal properties

Results of thermal characterization are shown in Tab 1 and thermograms are shown in Fig 4A**.** The glass transition temperature, T_g, of the copolymers varied from 31.46 to 10.62 ^{0}C. A gradual reduction in the Tg was observed with increase in comonomer incorporation as

shown in Tab 1 and Fig 4A thereby indicating increased mobility of the amorphous phase. The crystalline melting point, T_m of PLA phase was also found to be disturbed. The depression of the glass transition temperature was more prominent than T_m of PLA.

Although the absence of Tg characteristic of protected PAA could not be ascertained, yet the absence of a glass transition characteristic of pure homopolymer PLA was, however, sufficient proof of plasticization. Therefore, the lowering of glass transition temperature of PLA by a statistical copolymerization with molar proportions of protected PAA can indeed be called a case of "internal plasticization".

The copolymers (COP-1 and COP-2) were dissolved in chloroform, equal amount of methanol and catalytic amount of p- toluene sulphonic acid (PTSA) was added into it. The reaction mixture was stirred at room temperature (25 ^{0}C) under inert atmosphere (argon) for 6 h. The resultant copolymer was washed with methanol several times and G.C analysis result confirmed the absence of dimethoxy propane. The structures of DCP-1 and DCP-2 were confirmed by ^{1}H NMR. Results of thermal characterization of DCP-1 and DCP-2 are shown in Tab 2 and thermograms are shown in Fig 4B. The protected copolymer COP-1 (waxy mass) and deprotected copolymer DCP-1 (solid powdery mass) showed dramatic increase of T_g values from 10.62 (COP-1) to 34.7 ^{0}C (DCP-1) and also affected T_m value. The increase in T_g value may be attributed due to aggregation of hydroxyl groups present at 9 and 10 position of aleuritic acid unit in the copolymer chain. Similarly copolymer COP-2 (highly viscous mass) and after deprotection (DCP-2) also showed increase of T_g value from -11.5 to 40.5 ^{0}C and also affected T_m value.

Transmission Electron Microscopy (TEM)

The thermal characteristic result showed the aggregation behavior, which was further examined by TEM. Functionalized interfacial organic and polymer layers fabricated from molecular segments with different amphiphilicity can be designed to act as a smart or switchable surface. These surfaces are capable of responding to very suitable changes in the surrounding environment such as pH, surface pressure and temperature, light and solvent quality. In the present system, these deprotected copolymer DCP-1 and DCP-2 aggregate in various solvents and their structures are slightly different from each other. These structures are responsible for controlling physical properties in term of application such as drug delivery and biomimetic materials. The copolymer DCP-1 and DCP-2 used in this study is L-lactic acid and protected aleuritic acid, which was synthesized by dehydropolycondensation and followed deprotection. The polydispersity indices of the copolymers, estimated by gel permeation chromatography were 1.7 and 2.2 respectively.

The consequences of 9, 10 hydroxyl groups of aleuritic acid unit and methylene groups of aleuritic acid and L-lactic acid unit in the main chain of the copolymer, the key hydrophilic and hydrophobic functionalities in copolymer, within the different monomers of copolymers should be interesting from an intermolecular phase separation perspective.

The hydrophilic and the hydrophobic will be placed on the opposite sides of the copolymer backbone in solvents of different polarity. The hydrophobic and hydrophilic functionalities are stitched together within different monomers in copolymers. Fig 5.A and 5. A' showed the morphologies of the aggregates of DCP-1 and DCP-2 copolymers in N, N-dimethylformamide (DMF). DCP-1 gives micelles of low polydispersity whereas DCP-2 shows slightly elongated form. They consist of a hydrophobic units core covered with hydrophilic units forming the corona. Similar observation have been made by Lifeng Zhang et al[39]. Fig 6 B and 6 B' showed the morphologies of the aggregates from DCP-1 and DCP-2 copolymers in tetrahydrofuran (THF). DCP-1 formed micelles of low polydispersity whereas DCP-2 showed polydispersity. The hydrophobic units core are covered with hydrophilic units forming the corona. Fig 7 C and 7 C' showed the morphologies of the aggregates from DCP-1 and DCP-2 copolymers in dioxane. DCP-1 and DCP-2 give spherical micelles of low polydispersity.

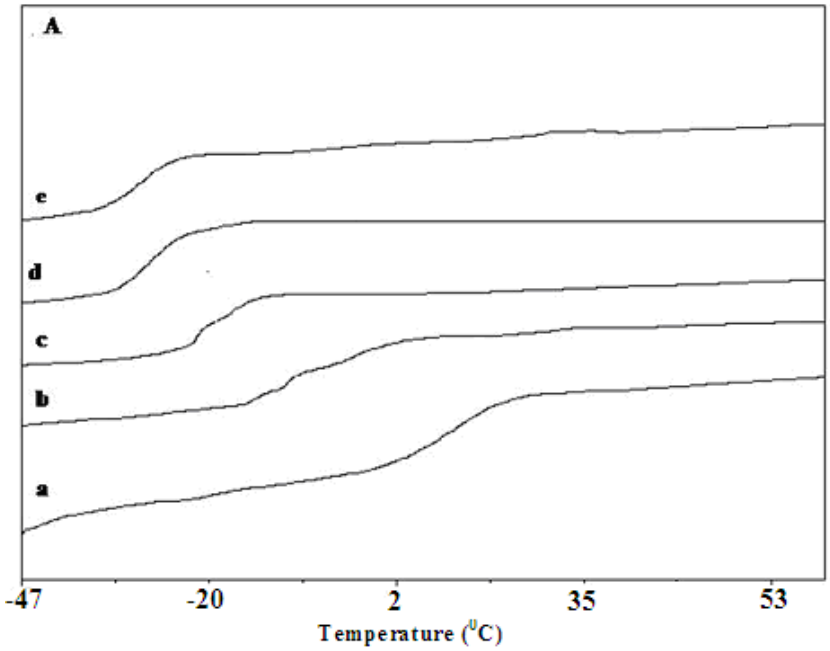


Fig. 4A: Differential Scanning Calorimetry (DSC) second heating thermograms (a) COP-1, (b) COP-2, (c) COP-3, (d) COP-4 and (e) COP-5

In fact, DCP-2 gives better size of spherical micelles with low polydispersity. These copolymers are not soluble in toluene, whereas PLA is soluble in chloroform. Therefore mixed solvents of toluene and chloroform at various proportions (50:50 and 60:40) were taken and morphologies of these two copolymers (DCP-1 and DCP-2) are shown by TEM. Fig 8 D and 8 D' shows the morphologies of the aggregates in mixed solvents (50:50 ratio of toluene: chloroform). DCP-1 and DCP-2 showed narrow distribution.

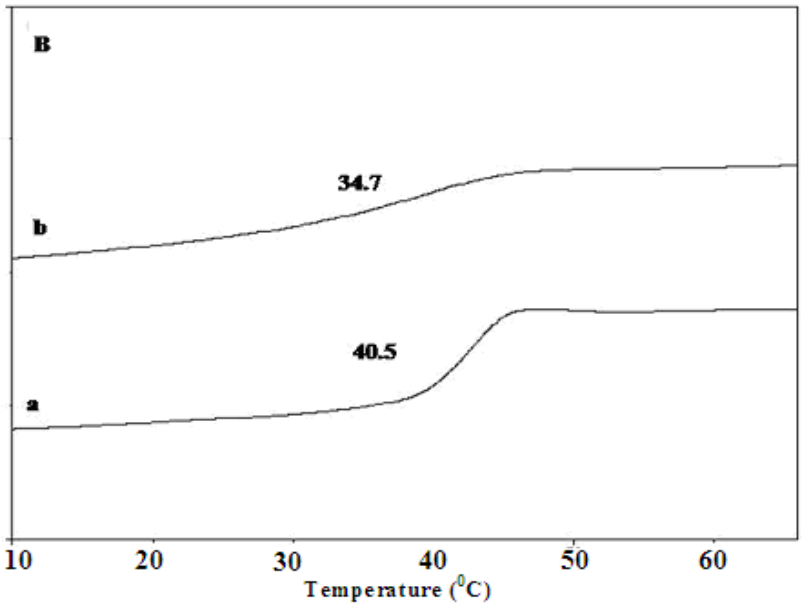


Fig. 4B: Differential Scanning Calorimetry (DSC) of second heating thermograms (a) DCP-1 and (b) DCP-2

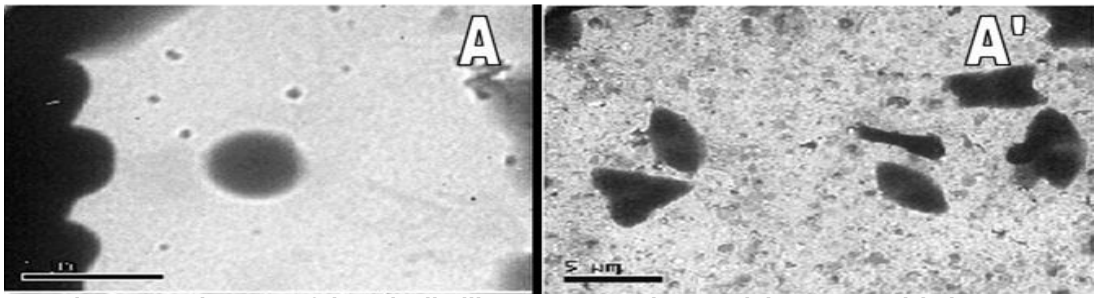


Fig. 5: TEM images of the micelle-like aggregates in DMF (A) DCP-1 and (A') DCP-2

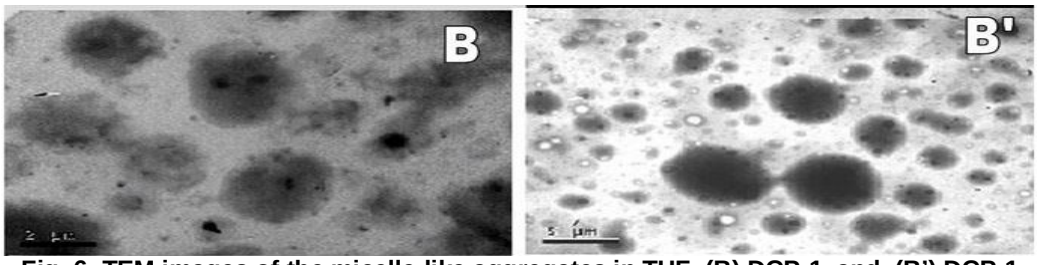


Fig. 6: TEM images of the micelle-like aggregates in THF (B) DCP-1 and (B') DCP-1

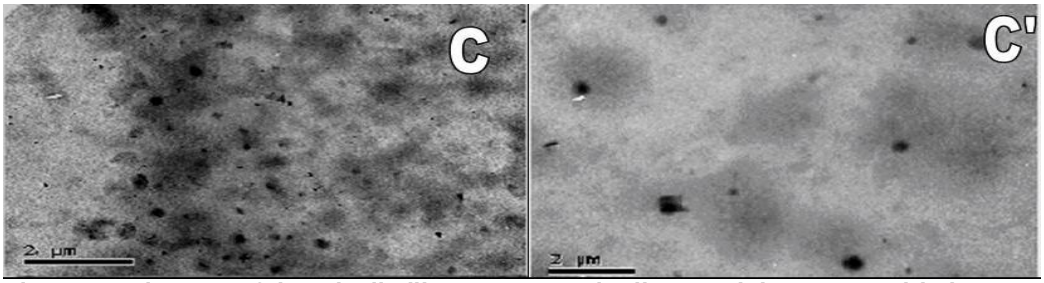


Fig. 7: TEM images of the micelle-like aggregates in dioxane (C) DCP-1 and (C') DCP-2

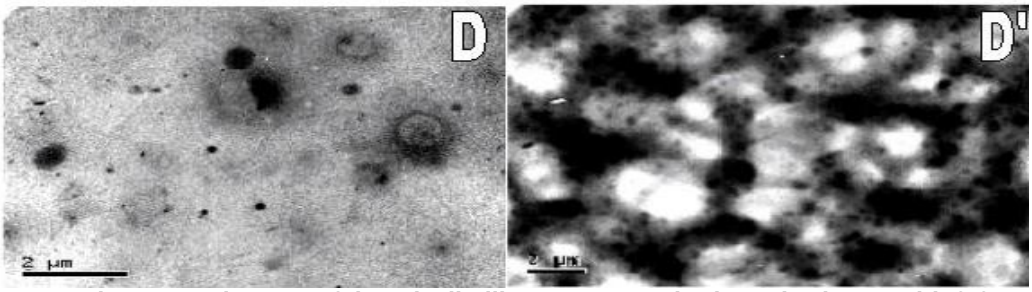


Fig. 8: TEM images of the micelle-like aggregates in (50:50) toluene :chlofoform (D) DCP-1 and (D') DCP-2

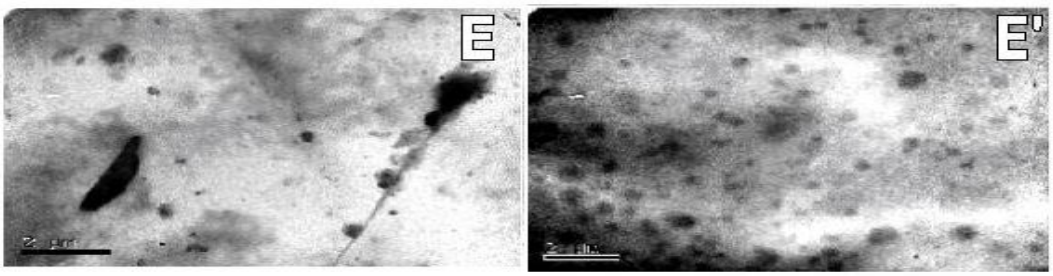


Fig. 9: TEM images of the micelle-like (E) DCP-1 and (E') DCP-2 in toluene-chloroform mixtures (60:40)

The hydrophilic groups (hydroxyl groups) are present in core and hydrophobic groups are covered as corona of the spherical micelle. Similar observations were observed in case of mixed solvents (60:40 ratio of toluene: chloroform) at room temperature. The Fig 9 E and 9 E' shows precised narrow distribution of micelles-like aggregates in mixed organic solvents. The hydrophilic moieties are directed towards the interior and hydrophobic groups are directed towards the exterior in the micelle-aggregates. Similar observation has also been reported [12].

CONCLUSIONS

A new class of copolymers showed internal plasticization effect when protected aleuritic acid was incorporated in the PLA backbone chain at different molar compositions. These copolymers behaved differently after deprotection of aleuritic acid at 9 and 10 positions. Amphiphilic copolymers containing both hydrophilic and hydrophobic functionalities in repeat units has been synthesized. These amphiphilic copolymers are soluble in organic and mixed organic solvents and assemble into micelle-like structures. Amphiphilic functions reported here is likely to form the basis for micro scales assembles in solution, which could also have implications in a broad range of applications.

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