Synthesis and characterization of novel value added biodegradable poly(aleuritic acid) from renewable resources (shellac) and invertible amphiphilic behaviors in various solvents

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Abstract: A novel biodegradable polymer poly(aleuritic acid) (PAA) (Mw ~ 120,000) was prepared from aleuritic acid, which was obtained from renewable resources (Lac) by using tin catalyst. Aleuritic acid (AL) was protected at 9, 10 position by dimethoxy propane. The protected AL (Pro.AL) was further polymerized to obtain linear protected polyaleuritic acid (PAL) by dehydropolycondensation. Effects of various kinetic and thermodynamic parameters were studied. After polymerization, the deprotection of PAL was carried out. The synthesized PAL and PAA were characterized by using various techniques such as FT-IR, LC-MS, SEC, NMR (1H and 13C), 13C CP/MAS (Cross Polarization / Magic Angle Spinning) of solid PAA, DSC, SEM and TEM etc. The micelle and inverted micelle –structure in polar and nonpolar solvents are highlighted.

Introduction

Aliphatic polyesters constitute an important class of polymers because of their biodegradability [1], and biocompatibility, [2a, b], which 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 Lac 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 in a insoluble product [10]. 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, aldehydes, lactones and esters which ultimately become infusible and insoluble three dimensional network structures.

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

![Chemical structure](image)

**Fig. 1.** Structures of monomer and polymer.

We demonstrate for the first time that the linear homopolymer of aleuritic acid (PAA) is obtained from aleuritic acid. 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 strategy behind this is that two hydroxyl functionalities in each monomeric unit should facilitate the phase segregation of the amphiphilic moieties within the polymer assembly. Monomer grade aleuritic acid has been converted to protect 9,10-hydroxy groups of aleuritic acid in presence of p-Toluene sulphonic acid. The protected aleuritic acid was polymerized by polycondensation in presence of tetraphenyltin (TPT) catalyst. The deprotection of the same groups with a suitable deprotecting agent under mild condition is highlighted. The reaction scheme is shown in Figure 1. We also highlight the micelle and inverted –micelle structure in polar and nonpolar solvents.

**Result and discussion**

Poly(aleuritic acid) was obtained from protected poly(aleuritic acid) by simple deprotection. The protected PAL was prepared from methyl ester of ProAL in presence of tetraphenyltin (TPT) and xylene as a solvent. FT-IR spectrum showed the peaks at 1377.55 cm\(^{-1}\) and 1368.7 cm\(^{-1}\) which are attributed the presence of –(O-C(CH\(_3\))\(_2\)-O-) group. \(^1\)H NMR spectrum showed the peak at 3.60 ppm (bs, 2H, –CHO–CH(O)) which confirms the protection of hydroxyl groups on 9 and 10 carbons. In the literature, similar measurements have been carried out and the protection of hydroxyl groups on No.9 and No.10 carbons has been shown [14]. At the outset, study was made of the effects of polymerization on reaction time (5 to 20 h) as shown in Table 1. The number average molecular weight (\(\bar{M}_n\)) and weight average molecular weight (\(\bar{M}_w\)) increased with reaction time to a certain extent (15 h) and thereafter declined. The obtained homopolymer in all the cases were linear and soluble in various solvent such dioxane and dimethylformamide etc. It was observed that at low molecular weight range i.e. up to 15,500, the distribution is completely lower than the high molecular weight i.e. up to 120, 000 Da. The highest molecular weight was obtained as 120,000 Da at 15 h (PAL-3).

**Tab 1.** Effect of reaction time on polymerization.

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Time (hr.)</th>
<th>Yield (%)</th>
<th>Temp. (°C)</th>
<th>(\bar{M}_n)</th>
<th>(\bar{M}_w)</th>
<th>PD</th>
<th>(T_m_1) (°C)</th>
<th>(T_m_2) (°C)</th>
<th>(\Delta H_1) (J/g)</th>
<th>(\Delta H_2) (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAL-1</td>
<td>5</td>
<td>99.2</td>
<td>145</td>
<td>2,800</td>
<td>6,400</td>
<td>2.2</td>
<td>-47.0</td>
<td>-13.6</td>
<td>3.2</td>
<td>0.85</td>
</tr>
<tr>
<td>PAL-2</td>
<td>10</td>
<td>99.0</td>
<td>145</td>
<td>34,100</td>
<td>82,000</td>
<td>2.4</td>
<td>-41.2</td>
<td>-14.2</td>
<td>2.9</td>
<td>0.52</td>
</tr>
<tr>
<td>PAL-3</td>
<td>15</td>
<td>98.0</td>
<td>145</td>
<td>46,100</td>
<td>120,000</td>
<td>2.6</td>
<td>-39.0</td>
<td>-17.0</td>
<td>2.2</td>
<td>0.34</td>
</tr>
<tr>
<td>PAL-4</td>
<td>20</td>
<td>98.0</td>
<td>145</td>
<td>5500</td>
<td>15,500</td>
<td>2.8</td>
<td>-42.1</td>
<td>-13.2</td>
<td>-2.9</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Xylene as a solvent

DSC data of PAL-3 showed two melting points (\(T_m\)) at -39.0 and -17.0 °C. These two different melting temperatures may be due to different crystalline structure in the polymer molecule. It has also been reported in the literature that splitting of water from Shellac during polymerization is a reversible process, when polymerized Shellac heated under pressure in an autoclave in the presence of water. It is converted in to an alcohol soluble resin with other properties similar to the original Shellac. The \(^13\)C
spectra of 4 or PAL are shown in (Figure 2a) and dept in (Figure 2b). The $^{13}$C spectra of 4 show a resonance peak at 173.81 ppm that corresponds to carbonyl carbon. The peak at 107.76 ppm is due to the quaternary carbon atom of the protecting group. The peak at 80.97 ppm is attributed due to 9 and 10 methine groups linked covalently to the oxygen atom of protecting groups. The peak shown at 64.27 ppm appeared due to primary alcohol group (-CH$_2$OH), which is attached to the end groups of the polymer. The peaks at 34.30 ppm, 32.93 ppm, 29.11 ppm, 26.03 ppm and 24.93 ppm are due to the methylene groups present in the polymer backbone. The peak at 27.31 ppm is attributed due to methyl group of the protecting group. The peak at 51.43 (-COOCH$_3$) is appeared due to CH$_3$ group attached to ester linkage. The $M_n$ calculated from $^{13}$C NMR (quantitative) spectra is 15600 Da. All the assignments confirm the structure of 4. The end groups of the homopolymers were -COOCH$_3$ and -CH$_2$OH.

![Fig. 2a](image1.png)
![Fig. 2b](image2.png)

**Fig. 2.** (a) $^{13}$C NMR (500 MHz) of protected poly(aleuritic acid)(4) (b) DEPT of (4).
The protected poly(aleuritic acid) (PAL) was dissolved in methanol and catalytic amount of p-toluene sulphonic acid was added into it. The reaction mixture was stirred for 6 h under argon atmosphere. The resultant solid poly(aleuritic acid) was filtered, washed several times with methanol and dried under vacuum at 40 °C. The yield was 99%.

The structure of PAA-5 is shown in Figure 3. $^{13}$C CP/MAS NMR shows the resonance, which corresponds to various groups such as 27.30-34.07 ppm (-CH$_2$ group), 65.11 ppm (-COOCH$_2$) and 75.47 ppm (-CHOH—CHOH-) and 174.75 ppm (-COO-) respectively. The peak at 75.47 ppm showed an up field shoulder peak (74.9 ppm) which is attributed to the aggregation behavior of hydroxyl groups due to hydrogen bonding. Similar aggregation behavior of hydroxyl groups in a polymer chain due to hydrogen bonding has also been observed [15].

![Fig. 3. $^{13}$C CP/MAS (Cross Polarization/ Magic Angle Spinning) N.M.R. (500 MHz) of poly(aleuritic Acid) (5).](image)

The soluble resin has been proved to be linear. Table 2 shows the effect of catalyst concentration on polymerization reaction. The catalyst concentration was varied from 0.1- 0.4-wt %. The molecular weight and molecular weight distribution increased up to 0.3 wt % as the catalyst concentration increased and thereafter decreased irrespective of yield. The result shows the reaction proceeds linearly up to 0.3 wt % catalyst. The higher concentration of catalyst accelerates the depolymerization reaction and decelerates the polymerization reaction.

**Tab. 2.** Effect of catalyst concentrations on polymerization reaction.

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Cat. Conc. (wt.%)</th>
<th>Yield (%)</th>
<th>Temp. (°C)</th>
<th>Mn</th>
<th>Mw</th>
<th>PD</th>
<th>$T_{m1}$ (°C)</th>
<th>$T_{m2}$ (°C)</th>
<th>$\Delta H_1$ (J/g)</th>
<th>$\Delta H_2$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAL-5</td>
<td>0.1</td>
<td>99.2</td>
<td>145</td>
<td>2,500</td>
<td>5,000</td>
<td>2.0</td>
<td>-38.2</td>
<td>-18.1</td>
<td>2.4</td>
<td>0.36</td>
</tr>
<tr>
<td>PAL-6</td>
<td>0.2</td>
<td>99.0</td>
<td>145</td>
<td>3,100</td>
<td>6,900</td>
<td>2.2</td>
<td>-38.4</td>
<td>-17.9</td>
<td>2.3</td>
<td>0.29</td>
</tr>
<tr>
<td>PAL-3</td>
<td>0.3</td>
<td>98.0</td>
<td>145</td>
<td>46,100</td>
<td>120,000</td>
<td>2.6</td>
<td>-39.0</td>
<td>-17.0</td>
<td>2.2</td>
<td>0.34</td>
</tr>
<tr>
<td>PAL-7</td>
<td>0.4</td>
<td>98.0</td>
<td>145</td>
<td>8200</td>
<td>24,000</td>
<td>2.9</td>
<td>-39.4</td>
<td>-16.9</td>
<td>2.1</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Xylene as a solvent
Table 3 illustrates the effect of reaction temperature on polymerization reaction. The polymerization reactions were carried out in various sets of nonpolar solvents starting from xylene (145 °C), mesitylene (165 °C) and decaline (190 °C). Similarly the reaction was carried out in polar solvents i.e. anisole (154 °C) and diphenylether (190 °C). The yield of the polymer was comparable either in nonpolar solvent or polar solvents. It is important to note that the molecular weight increased with increase in reaction temperature i.e. reflex temperature of the solvent.

DSC data shows two melting temperatures, which increase with increase in reaction temperature. The reaction was carried out at 190 °C (decaline reflux temperature) and showed cross-linking. The structure of the crosslinked polymer by $^{13}$C CP/MAS NMR is shown in Figure 4 and shows resonance at various positions.

**Tab. 3.** Effect of temperature on polymerization reactions.

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Solvent</th>
<th>Yield (%)</th>
<th>Temp. (°C)</th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_w$</th>
<th>PD</th>
<th>$T_{m1}$ (°C)</th>
<th>$T_{m2}$ (°C)</th>
<th>$\Delta H_1$ (J/g)</th>
<th>$\Delta H_2$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAL-8</td>
<td>Xylene</td>
<td>99.2</td>
<td>145</td>
<td>2,800</td>
<td>6,400</td>
<td>2.2</td>
<td>-47.0</td>
<td>13.6</td>
<td>3.2</td>
<td>0.85</td>
</tr>
<tr>
<td>PAL-9</td>
<td>Mesitylene</td>
<td>98.0</td>
<td>165</td>
<td>17,600</td>
<td>46,000</td>
<td>2.6</td>
<td>-38.2</td>
<td>17.8</td>
<td>1.6</td>
<td>0.3</td>
</tr>
<tr>
<td>PAL-10</td>
<td>Decaline</td>
<td>-</td>
<td>190</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PAL-11</td>
<td>Anisole</td>
<td>99.0</td>
<td>154</td>
<td>821</td>
<td>2,100</td>
<td>2.6</td>
<td>-40.6</td>
<td>14.7</td>
<td>1.2</td>
<td>0.5</td>
</tr>
<tr>
<td>PAL-12</td>
<td>Diphenyl ether</td>
<td>-</td>
<td>190</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Reaction time: 5 h

**Fig. 4.** $^{13}$C CP/MAS of cross-linked polymer (PAL-11).

A number of reactions occurred in crosslinking reaction i.e. etherification as well as small esterification. The products formed were fusible ethers, lactones and small amount of ester group, insoluble product of three-dimensional structures which were confirmed by solid-state $^{13}$C CP/MAS NMR spectroscopy. The peaks correspond to 81.59 ppm due to intermolecular reaction result (-CH-OCH-). The peak for two carbon involved in the intramolecular ether groups appeared at 67.08 ppm. Both the carbons in CH-O-CH structure have the same environment. The peak at 65.93 ppm
is due to (-CH-O-CH-) group. The peak region from 26.5 to 37.2 ppm corresponds to methylene region. All the three hydroxyl and one-carboxylic groups of aleuritic acid capable of entering into reactions both in the form of inter and intra-molecular condensation.

The polymer obtained in anisole showed $\bar{M}_n = 821$, $\bar{M}_w = 2100$ and dispersity 2.6 respectively. The two observed $T_m$s are $-40.6$ and $-14.7$ °C. Similar reaction was carried out in diphenylether at 190 °C and low molecular weight polymer was observed.

Table 4 shows the comparison results of PAL-3 and PAA. The number average molecular weight ($\bar{M}_n$), weight average molecular weight ($\bar{M}_w$) and distribution of PAL-3 are shown in Table 4. The melting temperatures $T_{m1} = -39.0$ and $T_{m2} = -17.0$ °C were observed in PAL-3. $T_g$ of PAL-3 was not observed until $-90$ °C. $T_g$ may be lower than $-90$ °C, which is beyond our instrument limitation. PAL-3 was deprotected with mild experimental condition. DSC data showed a single melting temperature at 75.07 °C, which may be attributed due to aggregation of pendent hydroxyl groups and similar crystallite structure.

Tab. 4. Comparison of PAA and PAL.

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Mn</th>
<th>Mw</th>
<th>PD</th>
<th>$T_g$ (°C)</th>
<th>$\Delta C_p$ (J/g*°C)</th>
<th>$T_{m1}$ (°C)</th>
<th>$T_{m2}$ (°C)</th>
<th>$\Delta H_1$ (J/gm)</th>
<th>$\Delta H_1$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAL-3</td>
<td>46,100</td>
<td>120,000</td>
<td>2.6</td>
<td>&gt;-100</td>
<td>nd</td>
<td>-39.0</td>
<td>-17.0</td>
<td>2.2</td>
<td>61.72</td>
</tr>
<tr>
<td>PAA</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>-15.50</td>
<td>0.075</td>
<td>75.07</td>
<td>-</td>
<td>nd</td>
<td>-</td>
</tr>
</tbody>
</table>

The $M_w = 120,000$, $M_n = 46,100$, PDI = 2.6 and average DP were determined by size exclusion chromatography (SEC) against polystyrene standards. Hydrolysis of protected poly(aleuritic acid) 4 afforded free hydroxyl groups at 9,10 position of each monomeric unit of the polymer 5. The homopolymers are linear and soluble in various solvents such as N,N-dimethyl formamide (DMF) and dioxane etc.

The consequences of 9,10 hydroxyl groups and aliphatic methylene groups in the main chain of the polymer, the key hydrophilic and hydrophobic functionalities in PAA polymer, within the same monomer of homopolymer should be interesting from an intermolecular phase separation perspective [16]. The hydrophilic hydroxyl unit and methylene moiety will be placed on the opposite sides of the polymer backbone in solvents of different polarity. The hydrophobic and the hydrophilic functionalities are stitched together within the same monomer in polymers. Therefore, it may be expected that the spatial distribution of the interior groups of the assembly closely follow the distribution of the functionalities in the corona.

Close examination of the normal structure is shown in (Figure 5). The core part of the new structure is folded methylene groups, which are dark, and hydroxyl pendant groups are in the periphery. Multiple morphologies of PAA in various solvents such as polar solvents and nonpolar solvents and structure property relationship through morphologies were obtained by using TEM.

The polymeric solution in polar solvents was optically clear. Typical TEM photographs for the poly(aleuritic Acid) are displayed in (Figure 5) and explained the structure of the assemblies. The images obtained from PAA polymer in dioxane and DMF are shown in Figure 5(A and B) respectively. The observed solubility characteristics may be attributed to the formation of micelle like structure in dioxane,
N,N-dimethyl formamide (DMF), in which the hydrophilic hydroxylic groups are exposed to the bulk solvent and the hydrophobic methylene groups are tucked in the interior of an assembly (Figure 5 A,B).

![TEM images of the micelle-like and inverted micelle-like structures formed by PAA polymer (A) image of normal micelle-like particle from dioxane. (B) Image of micelle-like particle from DMF. (C) Image of inverted micelle-like particle formed by a toluene solution of PAA. (D1-D4) Image of PAA in 1:1 dioxane: water forms brush like structures](image)

Fig. 5. TEM images of the micelle-like and inverted micelle-like structures formed by PAA polymer (A) image of normal micelle-like particle from dioxane. (B) Image of micelle-like particle from DMF. (C) Image of inverted micelle-like particle formed by a toluene solution of PAA. (D1-D4) Image of PAA in 1:1 dioxane: water forms brush like structures

Similarly, an inverted micelle-like structure would be expected in a nonpolar solvent, in which the functional group placements are reversed (Figure 5C). The structural hypothesis also suggests that the hydrophilic hydroxyl groups and hydrophobic methylene moiety will be placed on the opposite sides of the polymer backbone in the solvents of different polarity. The image obtained from polymer exhibit darker core compared to the corona. The darker contrast provided by methylene chains of backbone of PAA are shown in TEM images (Figure 5 A, B). For the interaction of the electron beam with material of the polymer, carbon forms a decisive amongst majority of the elements. Further the density of backbone carbon is slightly greater than that of hydroxyl group and hence we except PAA having higher density to appear dark in the TEM image. The TEM picture of pure PAA reflects this explanation. The image obtained in Figure 5C from toluene solution of polymers is consistent with the expected features. The images obtained from mixed solvents (1:1 dioxane and water) are shown in Figure 5 (D1-D4) respectively. Figure 5(D1-D4) show brushes like structures. The amphiphilic brushes with switchable micellar surface structures have been observed [17 a, b]. Eisenberg et al [7c]. have shown six
different stable aggregate morphologies such as spheres, rods, lamella, vesicles etc. However, nonspherical micelles in solution have been observed only rarely and mostly indirectly.

**Conclusions**

In summary, a new class of amphiphilic linear homopolymers containing both hydrophilic (hydroxyl pendant groups) and lipophilic functionalities (backbone) in each repeat unit has been synthesized where all the hydroxyl pendant groups aggregate and form new structures. Amphiphilic functions reported here are likely to form the basis for new nanoscale aggregates in solution, which could have implications in a broad range of applications.

**Experimental part**

*Materials and Methods*

Aleuritic acid, tetraphenyltin (Aldrich, USA), para toluene sulfonic acid (PTSA) (Aldrich, USA), xylene (S.D Fine Chemicals, India), anisole (Aldrich, USA), sodium sulphate and Chloroform (S.D Fine Chemicals, India), mesitylene (Aldrich, USA), decaline (Aldrich, USA), and diphenyl ether (Fluka, Germany).

Passivation of Glass Surface: Inner surface of glass reactors were passivated by treating with TMSCl (30% w/v acetone solution), washed with methanol, dried at 150 °C in an oven and cooled immediately before polymerization reaction.

*Synthesis of poly(aleuritic acid)s with both hydroxyl and carboxylic acid end groups*

-Methyl Ester of Aleuritic acid

Crude aleuritic acid (1) was converted to methyl ester (2) 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 ester (II) was recrystallized using ethyl acetate, the crystal was dried under vacuum and the yield was calculated as 90 %. MP: 71-72 °C, FT-IR (KBr) ν cm\(^{-1}\) : 1740.17 cm\(^{-1}\) (COOCH\(_3\)). \(^1\)H NMR (500 MHz): δ 3.66 (s, 3H, COOC\(_3\)H\(_3\)), 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\(_2\)-)

*Synthesis of Monomer*

Pure methyl ester of aleuritic acid (methyl 9,10,16 trihydroxy hexadecanoate) (9 g, 0.028 M) 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 with Na\(_2\)SO\(_4\) and finally stripped off. Finally it was vacuum dried to give (8.2 g, yield 82%). The structure of protected methyl ester of aleuritic acid (3) (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-
\[^{1}\text{H NMR (500 MHz)} : \delta 3.66 (s, 3H, \text{-COOCH}_3), 3.64 (t, j = 5.64, 2H, \text{CH}_2\text{OH}), 3.56 (bs, 2H, \text{-CH(O)-CH(O)-}), 2.17 (t, j = 7.44, 2H, \text{-CH}_2\text{COOCH}_3), 1.38, (s, 6H, \text{-C-(CH}_3)_2-), 1.50-1.31 (s, 22H, \text{-CH}_2-).\]

Homopolymerization of Monomer

The monomer (3) was taken in three-neck flask and equipped with Dean Stark apparatus; the requisite amount of tetraphenyl tin (TPT) catalyst was used for the polymerization using various solvents. The characterization of these polymers (PAL 4) were carried by SEC, DSC, SEM and \[^{13}\text{C NMR}.\]

Deprotection of Homopolymer

The homopolymer (PAL-3 i.e. 4) was dissolved in chloroform in a single neck flask and equal amount of methanol, catalytic amount of p-toluene sulfonic acid PTSA was added into it. The reaction mixture was stirred at room temperature (25°C) under inert atmosphere (Argon) for 6 h. The resultant polymer was washed with methanol several times and GC confirmed the absence of dimethoxy propane. The structure of PAA (5) was confirmed by \[^{13}\text{C CP/MAS NMR}.\]

Analysis

-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, \(\overline{M}_n\) and \(\overline{M}_w\)) and polydispersity (\(\overline{M}_w / \overline{M}_n\)) were determined with respect to polystyrene standards by SEC on waters 150 C machine at 25°C eluting PAL solutions 1 mg/mL concentration in CHCl\(_3\), with toluene as internal standard, through a series of five \(\mu\)-Styrage 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 refractive index detector (Spectra series RI-150C) was used for detection of different molecular weight fraction. Molecular weights were calculated with respect to polystyrene calibration. Intrinsic viscosities were determined using three- arm Schott-Gerate Ubelohde viscometer.

-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°C at a heating rate of 10°C / min and at a cooling rate of 100°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 5 mm dia .NMR tubes at room temperature.\[^{1}\text{H NMR spectra were recorded on Bruker DRX 500 MHz with 4 \text{ % 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}\)

10
The sample concentration for $^{13}$C NMR measurements was 10% by weight. Proton decoupled $^{13}$C NMR spectra with NOE were recorded on Bruker DRX 500 MHz spectrometer working at 125.577 MHz for carbon-13. A digital resolution of 32 K data points/18,000 Hz spectral width was used with a pulse angle of about 30° along with a relaxation delay of 2s and $10^3$-$10^4$ transients were accumulated. CDCl$_3$ served as solvent and TMS as internal standard for all $^{13}$C NMR measurements. Relative peak areas were proportional to the number of carbon atoms. Peak areas were calculated by deconvolution method using XWIN-PLOT software.

$^{13}$C Cross polarization / magic angle spinning ($^{13}$C CP/MAS)

$^{13}$C CP/MAS NMR Spectra were measured with Bruker MSL-300 NMR Spectrometer (75.5 MHz) with CP/MAS accessory at room temperature (25 °C). The sample powder (ca. 200 mg) was placed in a cylindrical ceramic rotor and spun at 3 KHz. Contact time and repetition time were 2 ms and 5 s respectively. Spectral width and data points were 27KHz and 8 K, respectively. The $^1$H field strength was 2mT for both the CP and decoupling processes. The number of accumulations were 160-200, $^{13}$C Chemical shifts were calibrated indirectly with reference to the higher field adamantane peak (29.5 ppm relative to tetramethly silane ((CH$_3$)$_4$Si). The Hartmann-Hann condition was matched using adamantane in each case. The experimental errors for the chemical shifts were within ± 0.1 ppm for broad peaks as described.

Transmission electron microscopy (TEM)

Sample Preparation: Samples for TEM imaging were dissolved in different polar and non-polar solvent and were sonicated. The sample were dropped and collected on 300 mesh carbon coated copper grids. The copper grids were kept overnight on filter paper for drying. TEM imaging was done 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.

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References