Poly(alkyl lactate acrylate)s Having Tunable Hydrophilicity

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ABSTRACT: Four alkyl lactates and alkyl lactate acrylates having methyl, ethyl, propyl, and butyl as alkyl moiety were synthesized by azeotropic distillation. Their formation was confirmed by Fourier transform infrared (FTIR), mass, ^{1}H nuclear magnetic resonance (NMR) and proton decoupled ^{13}C NMR spectroscopic techniques. Solution polymerization was carried out for these alkyl lactate acrylates and the formed homopolymers were characterized by FTIR, ^{1}H NMR, proton decoupled ^{13}C NMR spectroscopic, and gel permeation chromatographic techniques. Shear thinning behavior was observed for all the polymers. Wide angle X-ray Diffraction studies showed that the polymers were amorphous in nature and also exhibited odd-even effect among alkyl lactate groups with respect to average molecular interchain spacing. Depending on the length of the alkyl lactate groups, relative humidity and time, the hydrophilicity of the polymers decreased with increase in the length of the alkyl lactate group among the odd and even series. Among the studied polymers, poly(ethyl lactate acrylate) may have the potential for hydrogel applications, due to its highly hydrophilic nature. T_g decreased with increase in length of alkyl lactate groups. Trend observed on the thermal stabilities of poly(alkyl lactate acrylate)s could be explained on the basis of average molecular interchain spacing. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40962.

INTRODUCTION

Poly(acrylic acid) (PAA) and its derivatives are widely used as adhesives,[1] emulsifiers,[2,3] super-absorbents,[4] hydrogels,[5] flocculants,[6] dispersive agents,[7] catalyst supports,[8] nano-reactors,[9] thickeners in toothpaste, cosmetics, hydraulic fluids, crude oil, and in liquid rocket fuels.[10] Formulated PAA is used to recover antibiotics and in secondary recovery of petroleum from crude oil.[11] Formulated polyacrylates impart green strength to molded articles such as ceramics or foundry core binders, thermoreversible self-healing materials, and high performance dental cements.[12] Strong laminates of aluminum foil with polypropylene and plastic interlayer in safety glasses are prepared using polyacrylates.[13] Cross-linked acrylic acid and methacrylic acid polymers provide a useful series of ion exchange resins where weak acids are desired instead of the strong sulfonic acid.[14] The desired properties for these applications mainly depend on the alkyl group present in the ester group of PAA. Such versatility makes it possible to develop a detailed understanding about the effects of ester substituent on polymer properties. With this knowledge, many new polymers with predefined characteristics have been synthesized.

PAA having different pendant groups such as methyl,[15–18] ethyl,[17,19,20] n-propyl,[17,20,21] isopropyl,[19] n-butyl,[17–21] n-pentyl,[17,20,21] n-hexyl,[17,20,21] cyclohexyl,[21] n-heptyl,[17] n-octyl,[17] n-nonyl,[17] decyl,[17] undecyl,[17] dodecyl,[17,22] n-octadecyl,[22,23] oleyl,[22] ethyl phenylglyoxylate groups,[24] fluorescent dyes,[25] phenylalanine,[26] 2-ethylhexyl,[27] 2-hydroxyethyl,[28] epoxy,[29,30] alkoxysilane groups,[29] and polyhedral oligomeric silsesquioxane[31] has been reported in the literature. Extensive studies on the physical, thermal, structural properties of poly(n-alkyl acrylate)s,[17,32] poly(n-alkyl methacrylate)s,[17,33,34] and poly(α-alkyl acrylate)s[35–37] have been well documented in this literature.

To the best of our knowledge, no report is yet available on poly(acrylic acid) containing alkyl lactates as a pendant group. In this study, a series of poly(alkyl lactate acrylate)s has been investigated in an attempt to analyze in detail, the effects of alkyl lactate substitution on moisture absorption capability, average molecular interchain spacing, glass transition temperature (T_g), and thermal stability. Our studies indicate that by changing alkyl substituent in poly(alkyl lactate acrylate)s, one can tune the hydrophilic nature of the polymer. The alkyl lactate acrylate with the highest hydrophilicity may find newer applications, such as hydrogel.
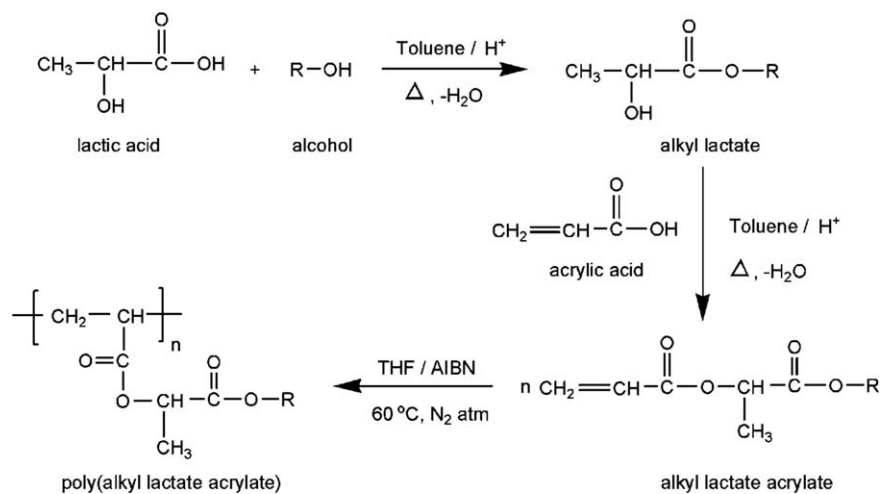
Scheme 1. Synthetic route for alkyl lactates, alkyl lactate acrylates, poly(alkyl lactate acrylate)s (where, R $=CH_3$—, CH_3CH_2—, $CH_3(CH_2)_2$— and $CH_3(CH_2)_3$—).

EXPERIMENTAL

Materials

D,L-Lactic acid, acrylic acid, ethanol, *n*-propanol, *n*-butanol, chloroform, *n*-hexane, toluene, tetrahydrofuran (THF), and anhydrous calcium chloride were procured from Merck (India). Methanol, concentrated sulfuric acid and aluminum oxide were obtained from Fisher Scientific (India). THF was dried using sodium wire, then distilled, and stored over 3 Å molecular sieves. 2,2′-azobisisobutyronitrile (AIBN, Spectrochem) was recrystallized from chloroform. All other chemicals were used as received.

Characterization

FTIR spectra were recorded using Thermo Scientific Nicolet 6700 FTIR spectrometer on diamond disc in the range of 4000–400 cm^{-1}. A Bruker AV-III 500 MHz NMR spectrometer was used for recording ^1H NMR and proton decoupled ^{13}C NMR spectra at room temperature using DMSO-d_6 as a solvent. Chemical shifts (δ) were reported in ppm and tetramethylsilane (TMS) was used as an internal standard. Electron impact (EI) and liquid chromatography (LC) mass spectra were recorded using a Micromass VG 7035 and Perkin Elmer Flexar SQ 300 MS, respectively. Ionization potential of 70 eV was used for EI mode. A high performance Single Quadrupole analyzer was used for LC. Molecular weights of the polymers were determined using GPC (PL-GPC 220, Agilent Technologies) with a 1260 Quat pump, differential refractive index (DRI) detector and PL gel column (10 μm mixed-B 300 × 75 mm). Polystyrene was used for calibration. THF at a flow rate of 1 mL/min was used as a mobile phase. Injection volume of 100 μL and a sample concentration of 2 mg/mL were used. Inherent viscosity was measured using Ubbelohde viscometer at 30 $\pm$ 0.1°C in THF at 0.5 g/dL concentration. Viscosity as a function of shear rate was determined using Thermo Scientific (HAAKE MARS) Rotational Rheometer at 30 $\pm$ 1°C. Wide-angle X-ray diffraction (WAXD) measurements of polymer were carried out using an X-ray diffractor unit (Shimadzu Lab XRD-6000) with CuK$_\alpha$ radiation (40 kV, 30 mA) at a wavelength of 1.54 Å. Moisture

absorption, as a function of time at specific relative humidity (RH) and 30 $\pm$ 1°C, was measured gravimetrically using digital weighing balance. Three replicates were conducted to obtain percentage moisture absorption and value varies in the range of ±0.2%. The average value was reported. Wettability of polymeric materials was measured by contact angle measurement using Holmarc Opto-Mechatronic (Model: HO-IAD-CAM-01). Differential scanning calorimetry (DSC; PerkinElmer Diamond DSC) was used to study T_g of the polymers. Heating rate of 10°C/min was used. Sample weight in the range of 4–6 mg was taken in aluminum pan for DSC measurements. Temperature and heat flow was calibrated using indium as a standard. Weight loss was examined using Perkin Elmer Pyris1 TGA at a heating rate of 10°C/min in nitrogen atmosphere. Sample weight was in the range of 4–6 mg for TGA measurements.

Synthesis

Synthesis of Alkyl Lactates. D,L-Lactic acid (45 g, 0.5 mol), methanol (32 g, 1.0 mol), and toluene (100 mL) were taken in a 250 mL three-necked round-bottomed flask fitted with a Dean-stark apparatus, thermometer, and condenser. The esterification reaction was carried out by gradual heating under a slow stream of dry nitrogen. When the reaction mixture reached a temperature of 60°C, few drops of concentrated sulfuric acid were added. Azeotropic distillation was carried out until there was no further collection of water. The reaction lasted for an hour and a half. The reaction is shown in Scheme 1. The unreacted methanol and toluene were removed by vacuum distillation and subsequently methyl lactate (ML) was distilled out. ML, a colorless liquid (94% yield, 1.5 h) was thus prepared and stored over 3 Å molecular sieves.

Other alkyl lactates namely ethyl lactate (EL), *n*-propyl lactate (*n*-PL), and *n*-butyl lactate (*n*-BL) were prepared using the same procedure as discussed above. The reaction time for EL, *n*-PL, and *n*-BL are 3.0 h (92% yield, 1.0 mol), 3.0 h (91% yield, 1.0 mol), and 4.5 h (95% yield, 1.5 mol). All the alkyl lactates thus prepared were colorless liquids.

Characterization data of alkyl lactates are assigned as follows:

1. ML:

   i. **FTIR** (cm^{-1}): v_{OH} = 3365.5; v_{C-H} = 2988.6 and 2942.1; $v_{C=O}$ = 1729.1; δ_{C-H} = 1453.0; v_{C-O} = 1126.7 (ester).
   ii. **^{1}H NMR**: 1.19 (*3H*, CH(OH)—C$\underline{H}_3$); 3.58 (*3H*, O—C$\underline{H}_3$); 4.14 (*1H*, —C$\underline{H}$(OH)—CH$_3$); 5.27 (*1H*, —O$\underline{H}$).
   iii. **^{13}C NMR**: 17.1 (CH(OH)—$\underline{C}$H$_3$); 51.9 (O—$\underline{C}$H$_3$); 66.0 (—$\underline{C}$H(OH)—CH$_3$); 170.8 (C=O).
   iv. **EI-MS** (m/z): 104 (M+).
   v. **LC-MS** (m/z): 105 (M+1).

2. EL:

   i. **FTIR** (cm^{-1}): v_{OH} = 3413.6; v_{C-H} = 2984.2 and 2940.1; $v_{C=O}$ = 1725.6; δ_{C-H} = 1451.5; v_{C-O} = 1125.1 (ester).
   ii. **^{1}H NMR**: 1.24 (*3H*, —O—CH$_2$—C$\underline{H}_3$); 1.24 (*3H*, CH(OH)—C$\underline{H}_3$); 4.06 (*2H*, —O—C$\underline{H}_2$—CH$_3$); 4.16 (*1H*, —C$\underline{H}$(OH)—CH$_3$); 5.29 (*1H*, —O$\underline{H}$).
   iii. **^{13}C NMR**: 14.3 (—O—CH$_2$—$\underline{C}$H$_3$); 17.0 (CH(OH)—$\underline{C}$H$_3$); 61.3 (—O—$\underline{C}$H$_2$—CH$_3$); 65.9 (—$\underline{C}$H(OH)—CH$_3$); 170.7 (C=O).
   iv. **EI-MS** (m/z): 119 (M+1), 118 (M+).
   v. **LC-MS** (m/z): 119 (M+1).

3. *n*-PL:

   i. **FTIR** (cm^{-1}): v_{OH} = 3441.1; v_{C-H} = 2971.3 and 2948.6; $v_{C=O}$ = 1732.0; δ_{C-H} = 1456.8; v_{C-O} = 1123.4 (ester).
   ii. **^{1}H NMR**: 0.89 (*3H*, —O—(CH$_2$)$_2$—C$\underline{H}_3$); 1.26 (*3H*, CH(OH)—C$\underline{H}_3$); 1.61 (*2H*, —O—CH$_2$—C$\underline{H}_2$—CH$_3$); 4.03 (*2H*, —O—C$\underline{H}_2$—CH$_2$—CH$_3$); 4.15 (*1H*, —C$\underline{H}$(OH)—CH$_3$); 5.31 (*1H*, —O$\underline{H}$).
   iii. **^{13}C NMR**: 10.6 (—O—(CH$_2$)$_2$—$\underline{C}$H$_3$); 17.1 (CH(OH)—$\underline{C}$H$_3$); 22.0 (—O—CH$_2$—$\underline{C}$H$_2$—CH$_3$); 66.0 (—$\underline{C}$H(OH)—CH$_3$); 68.7 (—O—$\underline{C}$H$_2$—CH$_2$—CH$_3$); 170.7 (C=O).
   iv. **EI-MS** (m/z): 133 (M+1), 132 (M+).
   v. **LC-MS** (m/z): 133 (M+1).

4. *n*-BL:

   i. **FTIR** (cm^{-1}): v_{OH} = 3469.1; v_{C-H} = 2959.7 and 2936.1; $v_{C=O}$ = 1730.9; δ_{C-H} = 1456.6; v_{C-O} = 1125.8 (ester).
   ii. **^{1}H NMR**: 0.96 (*3H*, —O—(CH$_2$)$_3$—C$\underline{H}_3$); 1.25 (*3H*, CH(OH)—C$\underline{H}_3$); 1.33 (*2H*, —O—(CH$_2$)$_2$—C$\underline{H}_2$—CH$_3$); 1.57 (*2H*, —O—CH$_2$—C$\underline{H}_2$—CH$_2$—CH$_3$); 4.06 (*2H*, —O—C$\underline{H}_2$—(CH$_2$)$_2$—CH$_3$); 4.12 (*1H*, —C$\underline{H}$(OH)—CH$_3$); 5.27 (*1H*, —O$\underline{H}$).
   iii. **^{13}C NMR**: 13.9 (—O—(CH$_2$)$_3$—$\underline{C}$H$_3$); 17.0 (CH(OH)—$\underline{C}$H$_3$); 19.0 (—O—(CH$_2$)$_2$—$\underline{C}$H$_2$—CH$_3$); 30.7 (—O—CH$_2$—$\underline{C}$H$_2$—CH$_2$—CH$_3$); 64.1 (—O—$\underline{C}$H$_2$—(CH$_2$)$_2$—CH$_3$); 66.2 (—$\underline{C}$H(OH)—CH$_3$); 170.9 (C=O).
   iv. **EI-MS** (m/z): 147 (M+1).
   v. **LC-MS** (m/z): 147 (M+1), 146 (M+).

Synthesis of Alkyl Lactate Acrylate. Alkyl lactate (0.25 mol), acrylic acid (0.25 mol), and toluene were taken in a 250 mL three-necked round-bottomed flask. The azeotropic distillation was carried out similar to the synthesis of alkyl lactates as discussed above. Toluene was separated by vacuum distillation and

subsequently alkyl lactate acrylate was distilled out. Synthesis of alkyl lactate acrylates is shown in Scheme 1. Alkyl lactate acrylates, namely methyl lactate acrylate (MLA), ethyl lactate acrylate (ELA), *n*-propyl lactate acrylate (*n*-PLA), and *n*-butyl lactate acrylate (*n*-BLA) are colorless liquids. The reaction time for MLA, ELA, *n*-PLA, and *n*-BLA are 9 h (91% yield), 11 h (93% yield), 16 h (81% yield), and 24 h (72% yield). Hydroquinone inhibitor was added and stored over 3 Å molecular sieves.

Characterization data of alkyl lactate acrylates are assigned as follows:

1. MLA:

   i. **FTIR** (cm^{-1}): v_{C-H} = 2992.3 and 2941.7; $v_{C=O}$ = 1725.8; $v_{C=C}$ = 1634.9; δ_{C-H} = 1452.4; v_{C-O} = 1127.8 (ester).
   ii. **^{1}H NMR**: 1.39 (*3H*, CH—C$\underline{H}_3$); 3.76 (*3H*, O—C$\underline{H}_3$); 4.98 (*1H*, —C$\underline{H}$—CH$_3$); 5.88 and 6.29 (*2H*, —CH=C$\underline{H}_2$); 6.08 (*1H*, —C$\underline{H}$=CH$_2$).
   iii. **^{13}C NMR**: 17.0 (CH—$\underline{C}$H$_3$); 51.9 (O—$\underline{C}$H$_3$); 70.2 (—$\underline{C}$H—CH$_3$); 128.3 (—$\underline{C}$H=CH$_2$); 130.2 (—CH=$\underline{C}$H$_2$); 165.8 (CH$_2$=CH—$\underline{C}$=O); 170.6 (CH$_3$—O—$\underline{C}$=O).
   iv. **EI-MS** (m/z): 158 (M+).

2. ELA:

   i. **FTIR** (cm^{-1}): v_{C-H} = 2983.5 and 2937.2; $v_{C=O}$ = 1727.8; $v_{C=C}$ = 1634.9; δ_{C-H} = 1454.2; v_{C-O} = 1128.2 (ester).
   ii. **^{1}H NMR**: 1.28 (*3H*, —O—CH$_2$—C$\underline{H}_3$); 1.41 (*3H*, CH—C$\underline{H}_3$); 4.12 (*2H*, —O—C$\underline{H}_2$—CH$_3$); 4.97 (*1H*, —C$\underline{H}$—CH$_3$); 5.87 and 6.34 (*2H*, —CH=C$\underline{H}_2$); 6.10 (*1H*, —C$\underline{H}$=CH$_2$).
   iii. **^{13}C NMR**: 14.4 (—O—CH$_2$—$\underline{C}$H$_3$); 17.1 (CH—$\underline{C}$H$_3$); 61.3 (—O—$\underline{C}$H$_2$—CH$_3$); 70.1 (—$\underline{C}$H—CH$_3$); 128.0 (—$\underline{C}$H=CH$_2$); 130.1 (—CH=$\underline{C}$H$_2$); 165.3 (CH$_2$=CH—$\underline{C}$=O); 170.7 (CH$_3$—CH$_2$—O—$\underline{C}$=O).
   iv. **EI-MS** (m/z): 172 (M+).

3. *n*-PLA:

   i. **FTIR** (cm^{-1}): v_{C-H} = 2971.4 and 2932.7; $v_{C=O}$ = 1728.3; $v_{C=C}$ = 1636.8; δ_{C-H} = 1453.6; v_{C-O} = 1129.7 (ester).
   ii. **^{1}H NMR**: 0.90 (*3H*, —O—(CH$_2$)$_2$—C$\underline{H}_3$); 1.41 (*3H*, CH—C$\underline{H}_3$); 1.63 (*2H*, —O—CH$_2$—C$\underline{H}_2$—CH$_3$); 4.06 (*2H*, —O—C$\underline{H}_2$—CH$_2$—CH$_3$); 4.98 (*1H*, —C$\underline{H}$—CH$_3$); 5.84 and 6.39 (*2H*, —CH=C$\underline{H}_2$); 6.09 (*1H*, —C$\underline{H}$=CH$_2$).
   iii. **^{13}C NMR**: 10.6 (—O—(CH$_2$)$_2$—$\underline{C}$H$_3$); 16.9 (CH—$\underline{C}$H$_3$); 21.9 (—O—CH$_2$—$\underline{C}$H$_2$—CH$_3$); 68.6 (—O—$\underline{C}$H$_2$—CH$_2$—CH$_3$); 70.1 (—$\underline{C}$H—CH$_3$); 128.5 (—$\underline{C}$H=CH$_2$); 130.4 (—CH=$\underline{C}$H$_2$); 165.1 (CH$_2$=CH—$\underline{C}$=O); 170.6 (CH$_3$—(CH$_2$)$_2$—O—$\underline{C}$=O).
   iv. **EI-MS** (m/z): 187 (M+1), 186 (M+).

4. *n*-BLA:

   i. **FTIR** (cm^{-1}): v_{C-H} = 2961.2 and 2905.1; $v_{C=O}$ = 1728.4; $v_{C=C}$ = 1636.9; δ_{C-H} = 1456.9; v_{C-O} = 1130.4 (ester).
   ii. **^{1}H NMR**: 0.95 (*3H*, —O—(CH$_2$)$_3$—C$\underline{H}_3$); 1.36 (*2H*, —O—(CH$_2$)$_2$—C$\underline{H}_2$—CH$_3$); 1.41 (*3H*, CH—C$\underline{H}_3$); 1.58 (*2H*, —O—CH$_2$—C$\underline{H}_2$—CH$_2$—CH$_3$); 4.08 (*2H*, —O—

$\underline{CH_2}$—$(CH_2)_2$—CH_3); 4.97 (*1H*, —$\underline{CH}$—CH_3); 5.85 and 6.34 (*2H*, —CH=$\underline{CH_2}$); 6.07 (*1H*, —$\underline{CH}$=CH_2).

iii. **^{13}C NMR**: 13.9 (—O—$(CH_2)_3$-$\underline{CH_3}$); 17.2 (CH—$\underline{CH_3}$); 19.0 (—O—$(CH_2)_2$—$\underline{CH_2}$—CH_3); 30.9 (—O—CH_2—$\underline{CH_2}$—CH_2—CH_3); 64.5 (—O—$\underline{CH_2}$—$(CH_2)_2$—CH_3); 70.3 (—$\underline{CH}$—CH_3); 128.5 (—$\underline{CH}$=CH_2); 130.2 (—CH=$\underline{CH_2}$); 165.9 (CH_2=CH—$\underline{C}$=O); 170.7 (CH_3—$(CH_2)_3$—O—$\underline{C}$=O).

iv. **EI-MS** (m/z): 201 (M+1).

Polymerization. Hydroquinone inhibitor was removed from the liquid monomers MLA, ELA, *n*-PLA, and *n*-BLA by passing over aluminum oxide.[38] Alkyl lactate acrylate (5 g) and THF (25 mL) were charged into a 100 mL three-necked round-bottomed flask. Free-radical solution polymerization was carried out using AIBN (0.05 g) as a free radical initiator. The reaction was conducted in dry nitrogen atmosphere at 60°C. The reaction is shown in Scheme 1. After a certain period of time, the reaction mixture was slowly added into a large volume of *n*-hexane to precipitate the poly(alkyl lactate acrylate)s. The polymers were dried for about 24 h at 60°C.

Characterization data of poly(alkyl lactate acrylate)s are assigned as follows:

1. Poly(methyl lactate acrylate) (PMLA):

   i. **FTIR** (cm^{-1}): v_{C-H}= 2996.5 and 2944.7; $v_{C=O}$ = 1714.5; δ_{C-H} = 1453.4; v_{C-O} = 1128.2 (ester).

   ii. **^1H NMR**: 1.54 (*3H*, CH—$\underline{CH_3}$); 1.75 (*2H*, —$\underline{CH_2}$—CH—C=O); 2.23 (*1H*, —CH_2—$\underline{CH}$—C=O); 4.03 (*3H*, O—$\underline{CH_3}$); 4.99 (*1H*, —$\underline{CH}$—CH_3).

   iii. **^{13}C NMR**: 17.1 (CH—$\underline{CH_3}$); 35.1 (—$\underline{CH_2}$—CH—C=O); 47.6 (—CH_2—$\underline{CH}$—C=O); 52.2 (O—$\underline{CH_3}$); 70.3 (—$\underline{CH}$—CH_3); 170.2 (CH_3—O—$\underline{C}$=O); 174.4 (—CH_2—CH—$\underline{C}$=O).

2. Poly(ethyl lactate acrylate) (PELA):

   i. **FTIR** (cm^{-1}): v_{C-H} = 2981.2 and 2934.1; $v_{C=O}$ = 1730.7; δ_{C-H} = 1454.3; v_{C-O} = 1130.1 (ester).

   ii. **^1H NMR**: 1.17 (*3H*, —O—CH_2—$\underline{CH_3}$); 1.56 (*3H*, CH—$\underline{CH_3}$); 1.72 (*2H*, —$\underline{CH_2}$—CH—C=O); 2.26 (*1H*, —CH_2—$\underline{CH}$-C=O); 4.07 (*2H*, —O—$\underline{CH_2}$—CH_3); 4.98 (*1H*, —$\underline{CH}$—CH_3).

   iii. **^{13}C NMR**: 14.4 (—O—CH_2—$\underline{CH_3}$); 17.0 (CH—$\underline{CH_3}$); 35.3 (—$\underline{CH_2}$—CH—C=O); 47.4 (—CH_2—$\underline{CH}$—C=O); 60.9 (—O—$\underline{CH_2}$—CH_3); 70.4 (—$\underline{CH}$—CH_3); 170.1 (CH_3—CH_2—O—$\underline{C}$=O); 174.5 (—CH_2—CH-$\underline{C}$=O).

3. Poly(*n*-propyl lactate acrylate) (P(*n*-PLA)):

   i. **FTIR** (cm^{-1}): v_{C-H} = 2971.9 and 2939.4; $v_{C=O}$ = 1727.1; δ_{C-H} = 1453.9; v_{C-O} = 1127.8 (ester).

   ii. **^1H NMR**: 0.92 (*3H*, —O—$(CH_2)_2$—$\underline{CH_3}$); 1.54 (*3H*, CH—$\underline{CH_3}$); 1.63 (*2H*, —O—CH_2—$\underline{CH_2}$—CH_3); 1.71 (*2H*, —$\underline{CH_2}$—CH—C=O); 2.26 (*1H*, —CH_2—$\underline{CH}$—C=O); 4.07 (*2H*, —O—$\underline{CH_2}$—CH_2—CH_3); 4.98 (*1H*, —$\underline{CH}$—CH_3).

   iii. **^{13}C NMR**: 10.4 (—O—$(CH_2)_2$—$\underline{CH_3}$); 17.3 (CH—$\underline{CH_3}$); 22.0 (—O—CH_2—$\underline{CH_2}$—CH_3); 35.0 (—$\underline{CH_2}$—CH—
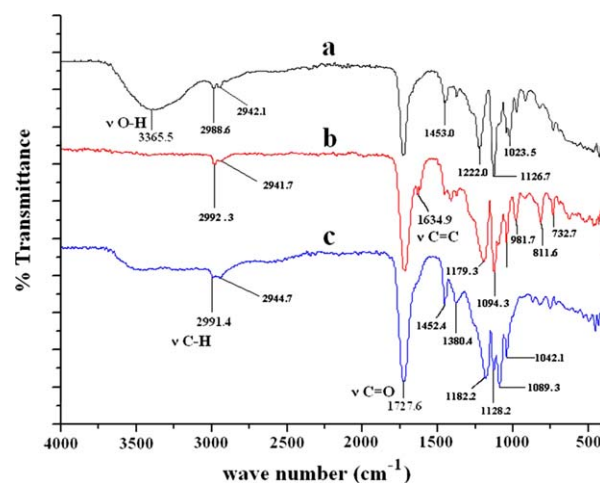

Figure 1. FTIR spectra of (a) ML, (b) MLA, and (c) PMLA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

C=O); 47.5 (—CH_2—$\underline{CH}$—C=O); 68.7 (—O—$\underline{CH_2}$—CH_2—CH_3); 70.3 (—$\underline{CH}$—CH_3); 170.3 (CH_3—$(CH_2)_2$—O—$\underline{C}$=O); 174.4 (—CH_2—CH—$\underline{C}$=O).

4. Poly(*n*-butyl lactate acrylate) (P(*n*-BLA)):

   i. **FTIR** (cm^{-1}): v_{C-H} = 2960.2 and 2935.9; $v_{C=O}$ = 1731.5; δ_{C-H} = 1458.2; v_{C-O} = 1125.5 (ester).

   ii. **^1H NMR**: 0.94 (*3H*, —O—$(CH_2)_3$—$\underline{CH_3}$); 1.35 (*2H*, —O—$(CH_2)_2$—$\underline{CH_2}$—CH_3); 1.53 (*3H*, CH—$\underline{CH_3}$); 1.58 (*2H*, —O—CH_2—$\underline{CH_2}$—CH_2—CH_3); 1.73 (*2H*, —$\underline{CH_2}$—CH—C=O); 2.25 (*1H*, —CH_2—$\underline{CH}$—C=O); 4.08 (*2H*, —O—$\underline{CH_2}$—$(CH_2)_2$—CH_3); 4.99 (*1H*, —$\underline{CH}$—CH_3).

   iii. **^{13}C NMR**: 13.8 (—O—$(CH_2)_3$—$\underline{CH_3}$); 17.0 (CH—$\underline{CH_3}$); 19.1 (—O—$(CH_2)_2$—$\underline{CH_2}$—CH_3); 30.9 (—O—CH_2—$\underline{CH_2}$—CH_2—CH_3); 35.2 (—$\underline{CH_2}$—CH—C=O); 47.3 (—CH_2—$\underline{CH}$—C=O); 64.5 (—O—$\underline{CH_2}$—$(CH_2)_2$—CH_3); 70.5 (—$\underline{CH}$—CH_3); 170.3 (CH_3—$(CH_2)_3$—O—$\underline{C}$=O); 174.4 (—CH_2—CH—$\underline{C}$=O).

RESULTS AND DISCUSSION

Acid catalyzed reaction of lactic acid with various alcohols have been well documented.[39] A series of alkyl lactates using lactic acid and various alcohols ranging from methanol to butanol and their corresponding acrylates were synthesized by azeotropic distillation. The molar ratio of the reactants and the respective reaction time were discussed in experimental section. The molar ratio of the reactant was chosen depending upon the solubility of alcohol in water. Methanol, ethanol, and *n*-propanol are soluble in water at room temperature, whereas *n*-butanol is insoluble in water. That is why, higher molar ratio was used in the case of methanol, ethanol, and *n*-propanol, when compared to *n*-butanol.

It has been reported that in the case of esterification reaction, methanol is more reactive than other primary alcohols.[40] Methanol takes lesser time for esterification with lactic acid compared to ethanol, *n*-propanol, and *n*-butanol which can be attributed to the high reactivity of methanol than other
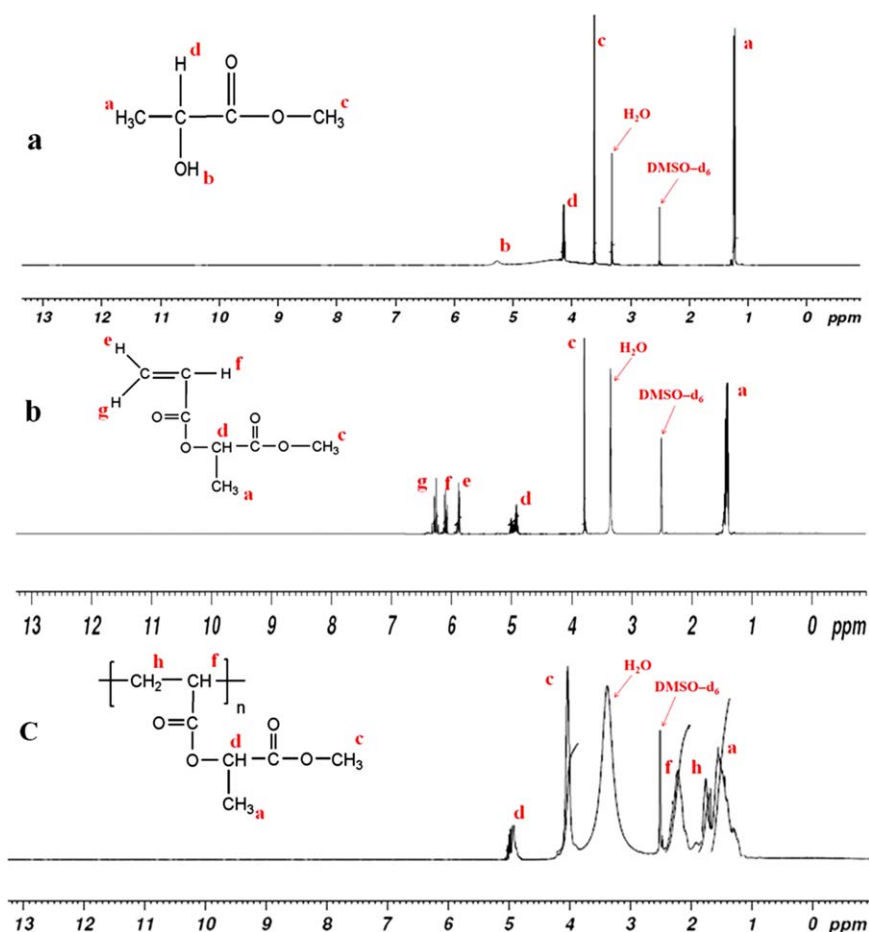
Figure 2. ^{1}H NMR spectra of (a) ML, (b) MLA, and (c) PMLA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

alcohols. Reaction time for the formation of alkyl lactate acrylate monomers increased with an increase in the side-chain length of alkyl lactates. Also, reaction time increased from 9 to 24 h as alkyl chain length of alkyl lactate increased from methyl to butyl group.

Poly (acrylic acid) containing side-chain alkyl lactates have been synthesized by free radical solution polymerization. The synthetic routes of alkyl lactates, alkyl lactate acrylates, and poly (alkyl lactate acrylate)s are shown in Scheme 1. All the polymers were found to be soluble in common solvents such as THF, chloroform, dichloromethane, dimethylsulfoxide and insoluble in toluene, hexane at room temperature.

FTIR Spectroscopy

FTIR spectra of alkyl lactates, alkyl lactate acrylates, and poly(-alkyl lactate acrylate)s are given in the experimental section. FTIR spectrum of ML [Figure 1(a)] indicated the presence of hydroxyl group, which appeared as a broad band at 3365.5 cm^{-1}. The absence of hydroxyl stretching peak and the presence of C=C stretching peak in MLA [Figure 1(b)] confirmed the reaction of acrylic acid with ML. The absence of $v_{C=C}$ at 1635 cm^{-1} in the FTIR spectrum of PMLA [Figure 1(c)] confirmed the occurrence of polymerization. The broad absorption peak around 3500 cm^{-1} in the FTIR spectrum

[Figure 1(c)] can be attributed to the traces of moisture absorption by hydrophilic PMLA.

^{1}H NMR Spectroscopy

^{1}H NMR data of alkyl lactate, alkyl lactate acrylates, and poly(-alkyl lactate acrylate)s are given in the experimental section. Figure 2 represents the ^{1}H NMR spectra of ML, MLA, and PMLA. Presence of hydroxyl proton ($\delta = 5.27$ ppm) and the absence of carboxylic proton of lactic acid indicated the formation of ML [Figure 2(a)]. ^{1}H NMR spectrum of MLA [Figure 2(b)] illustrates the presence of olefinic protons C$\underline{H}_2$=C$\underline{H}$ ($\delta = 5.81$, 6.12, and 6.46ppm) and the absence of hydroxyl and carboxylic protons confirmed the ester formation. Double doublets were observed for methyl protons at 1.19 ppm for ML and at 1.39 ppm for MLA. Multiplet was observed for methine protons at 4.14 and 4.98 ppm for ML and MLA, respectively. The presence of double doublets instead of doublet for methyl protons and multiplet instead of quartet for methine protons is attributed to the presence of D and L optical isomer of lactic acid moiety. Similar observation has been reported by Schliecker et al.[41] and Sanchez and Collinson.[42] Schliecker et al. have used D,L-Lactic acid for the preparation of oligomers.[41] Sanchez and Collinson have prepared ML from PLA and PET wastes.[42] In the optically pure MLA, Charlton has observed the presence of
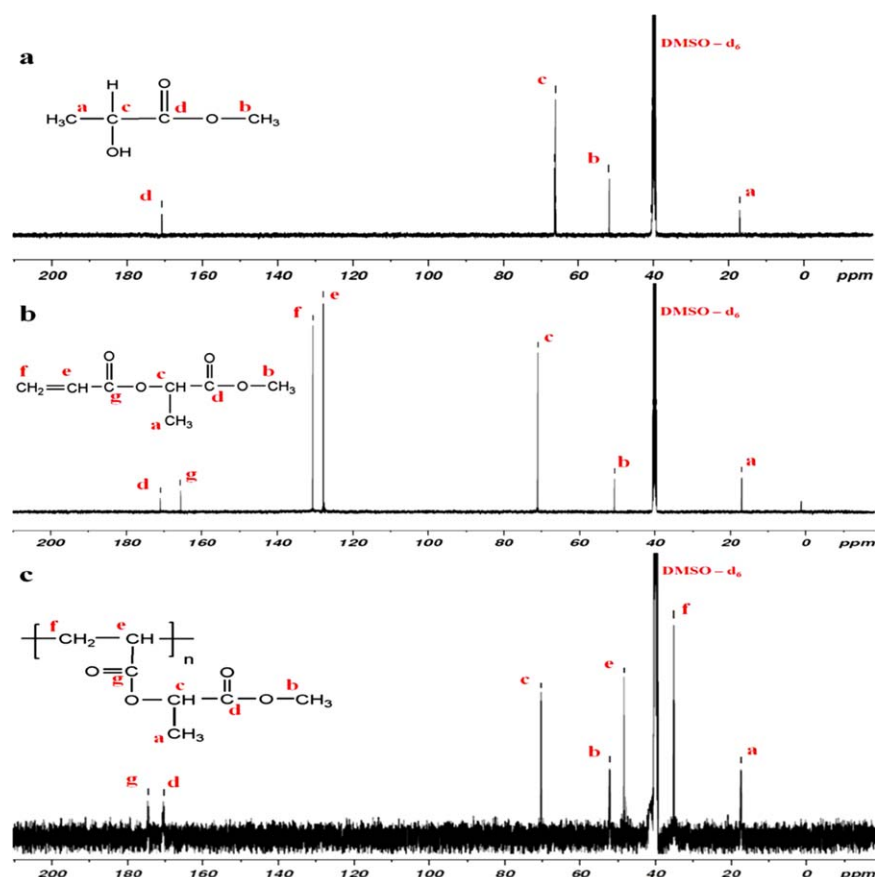
Figure 3. ^{13}C NMR spectra of (a) ML, (b) MLA, and (c) PMLA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

doublets and quartets in methyl and methine protons, respectively.[43] The absence of olefinic protons in the ^{1}H NMR spectrum of PMLA [Figure 2(c)] indicated the polymerization of MLA.

^{13}C NMR Spectroscopy

Proton decoupled ^{13}C NMR data of alkyl lactate, alkyl lactate acrylates, and poly(alkyl lactate acrylate)s are given in the experimental section. Figure 3 represents the ^{13}C NMR spectra of ML, MLA, and PMLA. The presence of hydroxyl carbon ($\delta = 65.3$ ppm) and ester carbonyl carbon ($\delta = 170.9$ ppm) confirmed the ML formation [Figure 3(a)]. The appearance of alkene carbon peaks at $\delta = 128.3$ and 130.2 ppm [Figure 3(b)] confirmed the formation of MLA. The disappearance of alkene peaks, observed for PMLA [Figure 3(c)], confirmed polymerization had taken place.

Mass Spectrometry

The appearance of M+1 peak in electron impact (EI) mode for alkyl lactates and alkyl lactate acrylates confirmed their formation. Further, the formation of alkyl lactates was confirmed by the appearance of M+1 peak in liquid chromatography (LC) mode. Typical mass spectra of *n*-BL and *n*-BLA are shown in Figure 4(a,b), respectively. M+1 peaks of *n*-BL and *n*-BLA were observed at 147 and 201, respectively. In the case of *n*-BL, the peak at m/z 56 accounted for the formation of CH_3—$C(H)$—$C\equiv O^+$, which was formed after the cleavage of

hydroxyl and alkoxy group. The fragmentation peak appeared at m/z 31, 45, 59 and 73 for ML, EL, *n*-PL, and *n*-BL, respectively, confirmed the formation of alkoxy group (R—O$^+$) namely CH_3—O^+, CH_3—CH_2—O^+, CH_3—CH_2—CH_2—O^+, and CH_3—CH_2—CH_2—CH_2—O^+. The appearance of fragmentation peak at m/z 55 in all the alkyl lactate acrylate monomers with 100 % intensity was due to the acrylate ion, that is, $CH_2=CH$—$^+C\equiv O$.[43]

Gel Permeation Chromatography

The weight average molecular weight (M_w) and polydispersity index (PDI) values are shown in Table I. All GPC curves indicated unimodal molecular weight distribution. The molecular weights of the polymers were found to be low, due to the influence of alkyl lactate side-chain. Similar effect was reported for poly (N-(2-hydroxypropyl) methacrylamide mono/di lactate).[44]

Inherent Viscosity

The inherent viscosity of polymers was determined by Ubbelohde viscometer at $30 \pm 0.1°C$ in THF and the values are given in Table I. They are in the range of 0.15 to 0.29 dL/g at 0.5 g/dL concentration.

Shear Viscosity

The shear viscosity of polymers was measured by rotational rheometer in the shear rate from 0.1 to 200 per sec at $30 \pm 1°C$. The shear thinning behavior was observed for all polymers. The

increase in the shear rate was attributed to the stretching and disentanglement of the polymer chain. At low shear rates, the polymer chain entanglements impede shear flow leading to a higher viscosity. When the shear rate is gradually increased, the polymer chain begins to orient and slip through each other in the direction of flow and disentangle from one another leading to the lowering of viscosity. Similarly, other polymers PELA, P(n-PLA) and P(n-BLA) exhibited the same manner of shear thinning.

WAXD

Figure 6 represents the XRD pattern of poly(alkyl lactate acrylate)s. The synthesized polymers were amorphous, which was indicated by a broad amorphous halo peak at about 20°. For amorphous materials, the average molecular interchain spacing ($<R>$) was determined by the following equation,[45]

$$\langle R \rangle = \frac{5}{8}\left(\frac{\lambda}{\sin \theta}\right) \tag{1}$$

where $<R>$ is the average molecular interchain spacing, λ is the wavelength of radiation (Cu K$_{\alpha}$, $\lambda = 1.5418$ Å), and θ is diffraction maximum angle. The values of $<R>$ are given in Table II. The values of $<R>$ varied in accordance with the length of the pendant alkyl lactate group. Comparing odd number of carbon containing alkyl groups in the poly(alkyl lactate acrylate)s, namely PMLA and P(n-PLA), the value of $<R>$ increased with the increase in the length of the alkyl lactate group. A similar trend was observed in even number of carbon containing alkyl groups, that is, in the case of PELA and P(n-BLA). An increase in the value of $<R>$ is indicative of the fact that free volume increased while increasing the length of odd or even number of carbon containing the alkyl groups. The unique pattern of average molecular interchain spacing was due to the arrangement of atoms in the side-chain. The arrangement of atoms in the chain depends on the degree of freedom for each carbon–carbon bond in terms of torsion angle between the atoms or groups. Similar odd-even trend is observed in tensile properties and moisture absorption in polymers such as polyamides[46] and vinyl polymers.[47]

Hydrophilicity

The moisture absorption by a polymer causes plasticization, lowering of glass transition temperature, and a reduction in mechanical strength. This is an important polymer characteristic for several applications such as personal care products, cement, agriculture, membranes, sensors, and in drug delivery. The moisture absorption of materials from air can be measured
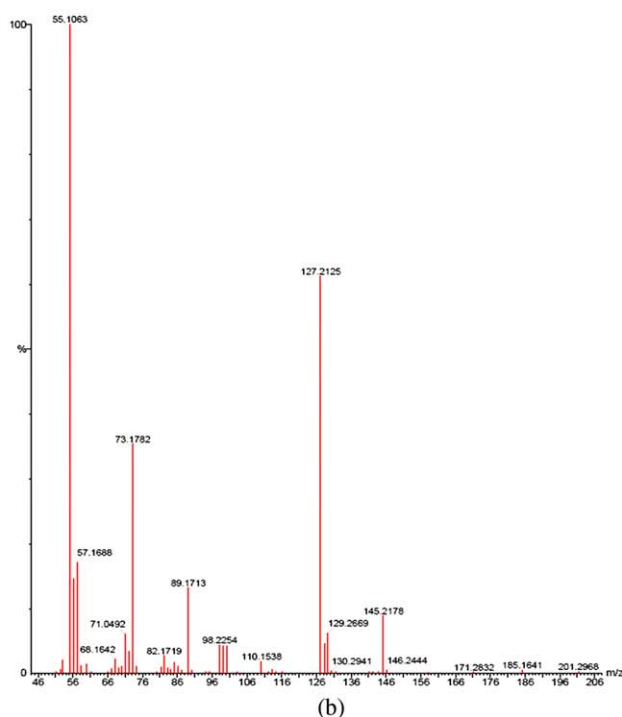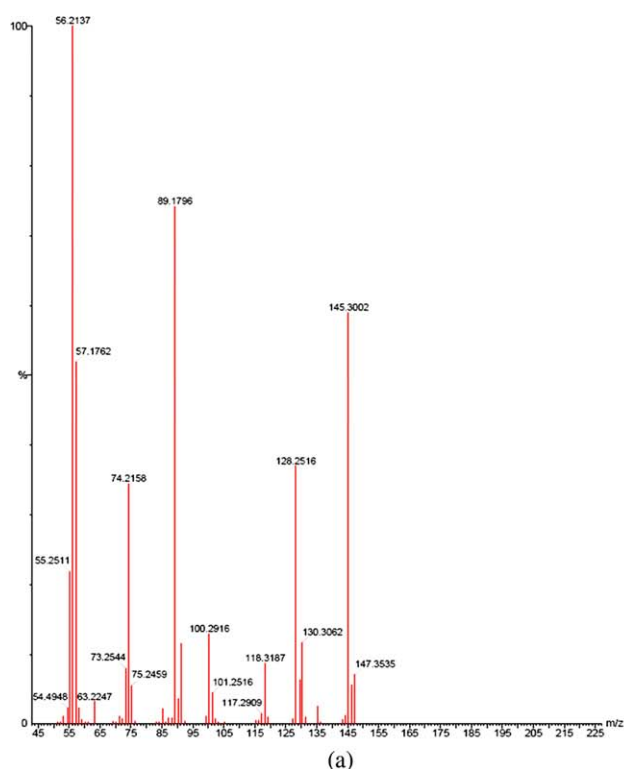
Figure 4. (a) Electron impact-mass spectra of n-BL and (b) electron impact-mass spectra of n-BLA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

typical plot between shear rate versus shear viscosity of PMLA was given in Figure 5, shows that it exhibited shear thinning behavior. Initially, the viscosity decreased drastically up to 50 rpm; and then gradually from 50 to 150 rpm, after which it remained almost constant. The decrease in viscosity with the

Table I. Molecular Weight, Inherent Viscosity (η_{inh}), and T_g Data of Poly(alkyl lactate acrylate)s

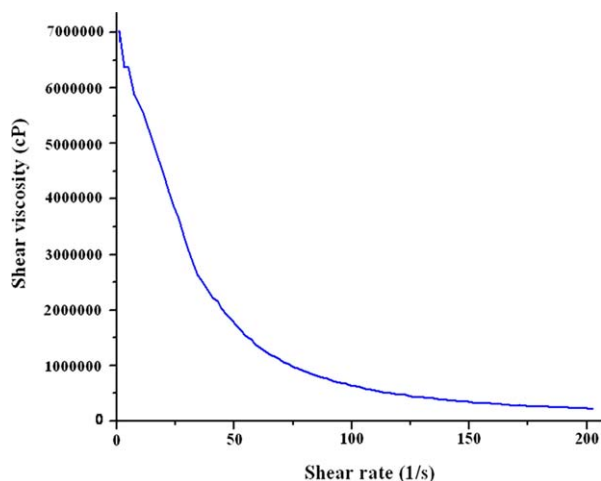| Polymer	Molecular weight		η_{inh} (dL/g)	T_g (°C)
	$\bar{M}_w$	PDI		
PMLA	13,493	1.82	0.167	−18.6
PELA	9123	1.70	0.154	−27.4
P(n-PLA)	13,755	1.81	0.149	−37.2
P(n-BLA)	18,249	2.13	0.298	−66.3

Figure 5. Shear thinning behavior of PMLA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. XRD pattern of poly(alkyl lactate acrylate)s: (a) PMLA, (b) PELA, (c) P(n-PLA), and (d) P(n-BLA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

using various equipments namely permeation analyzer,[48] dynamic vapor sorption instrument,[49] infrared near-field scanning optical microscope,[50] stress analyzer,[51] quartz crystal microbalance,[52] and electro-micro balance.[53] In this study, samples were kept in a glass chamber that was preconditioned at specific RH and the samples were weighed periodically. Different percentages of RH such as 69, 86, and 97% was maintained inside a glass chamber using saturated solutions of potassium iodide, potassium chloride, and potassium chromate, respectively. About 3 g of predried polymers taken in petridish which was housed in closed glass chambers and RH was continuously monitored by digital hygroscopic meter. Temperature was maintained at 30 ± 1°C. The moisture absorption percentage was calculated from the weight gain. The hydrophilicity mainly depends upon the following factors, namely: the hydrophilic groups present in the polymer moiety such as –OH, —NH₂, —CONH—, —CONH₂, —COOH, and —SO₃H, Vander Waals' interaction in terms of hydrogen bonding, average molecular interchain spacing $<R>$ and hydrophobicity of alkyl chain length. Poly(alkyl lactate acrylate)s were found to be highly hydrophilic in nature. In general, carbonyl of esters, which are known as primary hydrogen bond acceptors, are more prone to moisture uptake. In poly(alkyl lactate acrylate)s, there are two carbonyl groups of esters, namely: carbonyl of lactate and acrylate groups, which has facilitated moisture uptake. The moisture absorption as a function of time was plotted at 69, 86, and 97% RH. From the RH data, one can conclude that the length of
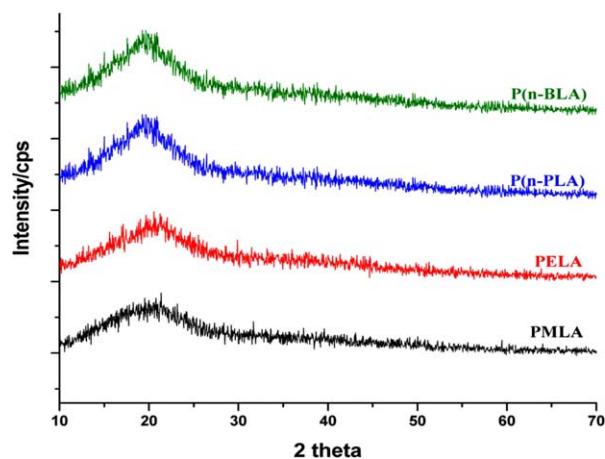
alkyl lactate group played a major role in changing the hydrophilic nature of polymers and so one can tune the hydrophilicity by changing the alkyl lactate group. The moisture absorption data of poly(alkyl lactate acrylate)s having odd number of carbon atoms containing primary alkyl group such as PMLA and P(n-PLA) is given in Figure 7 and for the primary alkyl groups containing even number of carbon atoms as in the case of PELA and P(n-BLA) is given in Figure 8. In all these cases, moisture absorption increased with the increase in time and RH. Poly(methyl methacrylate) (PMMA) having moisture absorption capacity of 0.06 % (w/w) at 30°C in 90% RH, showing more hydrophobicity.[54] Similar to PMMA, poly(methyl acrylate) is also reported to be a hydrophobic polymer and absorbs very less moisture from air[55] whereas PMLA has a moisture absorption of about 2.5, 4.0, and 5.0 at 69, 86, and 97% RH, respectively. The higher value is due to the presence of two carbonyl groups of ester in PMLA whereas in PMA, only one carbonyl group of ester is present. If both the hydrogen bond acceptor and the donor groups for water are present in the same molecule, then the moisture absorption value would be very high as in the case of poly(acrylic acid) (PAA). In PAA, carbonyl group and carboxylic acid group are hydrogen bond acceptor and donor, respectively, and reported moisture absorption value is 33% at 90% RH.[54] Poly(n-butyl acrylate) (PBA) is also a hydrophobic polymer whereas P(n-BLA) has water absorption of about 2.0, 6.4, and 7.2 at 69, 86, and 97% RH, respectively.

Table II. XRD and TGA Data of Poly(alkyl lactate acrylate)s

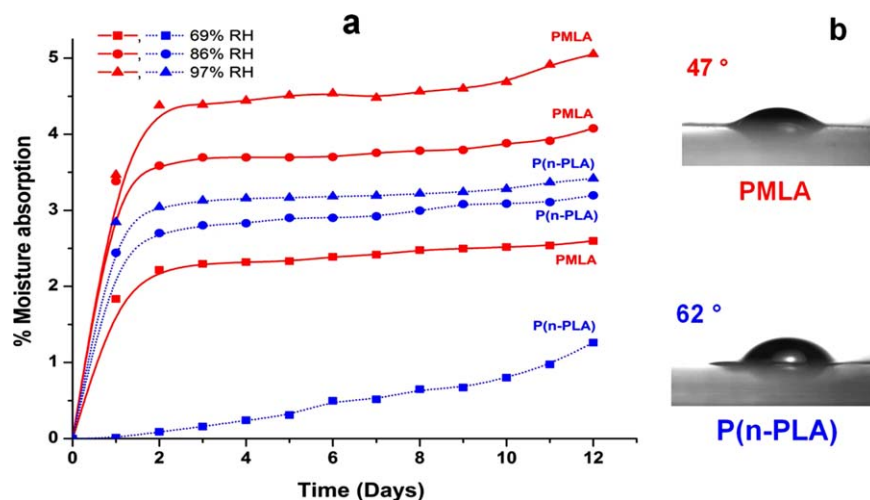| Polymers	XRD		TGA		
	2θ	$<R>$ (Å)	10% wt. loss (°C)	T_{max1} (°C)	T_{max2} (°C)
PMLA	19.98	5.555	209	218	391
PELA	19.69	5.636	193	236	396
P(n-PLA)	19.91	5.574	241	302	412
P(n-BLA)	19.64	5.650	223	276	438

Figure 7. (a) Plot of % moisture absorption versus time and (b) contact angle data of odd series. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The wettability of polymeric materials was characterized by contact angle measurements. Contact angle of PMLA, PELA, P(n-PLA), and P(n-BLA) are 47.2°, 25°, 62.2°, and 37.8°, respectively (Figures 7 and 8). Among the studied polymers, PELA was found to be most hydrophilic having lowest contact angle and highest moisture absorption capacity. P(n-PLA) was found to be least hydrophilic among the studied polymers and contact angle also confirmed hydrophobic nature as indicated by highest contact angle value.

Among the polymers studied, PELA has exhibited highest moisture absorption to about 10% (w/w). After suitably cross-linking, it may have the potential for hydrogel applications, due to its highly hydrophilic nature and good wettability as indicated by lowest contact angle. The moisture absorption decreased with an increase in the alkyl chain length among the odd and even series. This was due to an increase in the number of methylene groups, which has restricted the moisture absorption capability owing to its non-polar nature.

DSC

The glass transition temperature (T_g) of the polymers are shown in Table I. T_g values has dropped to -18.6, -27.4, -37.2, and -66.3°C for PMLA, PELA, P(n-PLA), and P(n-BLA), respectively, with an increase in the length of the alkyl group in poly(alkyl lactate acrylate)s. n-alkyl group in the pendant position increases the free volume with an increase in the length of the alkyl group, thereby resulting in a drop of T_g value. Similar T_g results have been reported for poly(alkyl acrylate)s of poly(methyl acrylate), poly(ethyl acrylate), and poly(n-butyl acrylate) having T_g of 13.4, -18.2, and -53.1°C, respectively.[56] When the T_g values of poly(alkyl acrylate)s with poly(alkyl lactate acrylate)s are compared, the latter has a lesser T_g value than the poly(alkyl acrylate)s. This was due to the presence of lactic acid group in the pendant position, which behaves like a plasticizer.

TGA

All the poly(alkyl lactate acrylate)s have a good thermal stability in nitrogen atmosphere up to 150°C and have shown two-step
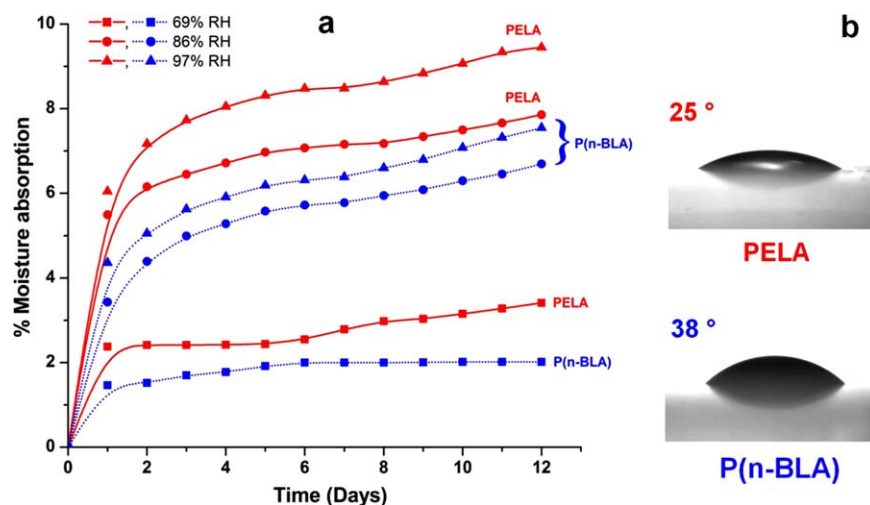

Figure 8. (a) Plot of % moisture absorption versus time and (b) contact angle data of even series. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
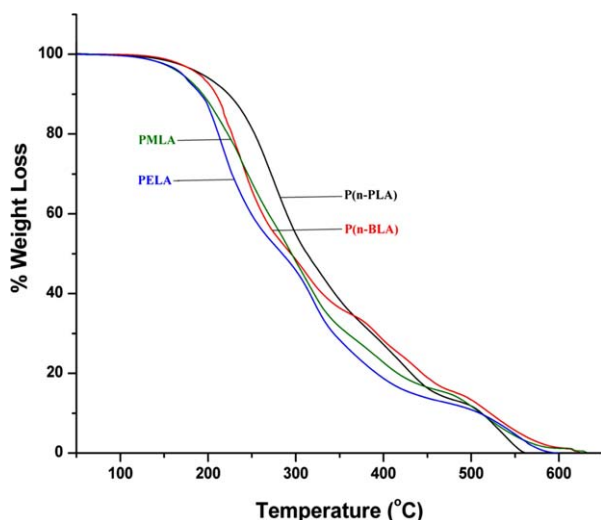
Figure 9. Thermogram of poly(alkyl lactate acrylate)s: (a) PMLA, (b) PELA, (c) P(n-PLA), and (d) P(n-BLA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

degradation in thermogram (Figure 9). The thermal stability of poly(alkyl lactate acrylate)s in nitrogen atmosphere were assessed by comparing 10% weight loss values and temperatures at which maximum rates of weight loss have occurred (T_{max1} and T_{max2}) and the values are given in Table II.

Comparing the poly(alkyl lactate acrylate)s having odd number of carbon containing alkyl groups, that is, PMLA and P(n-PLA), as the chain length increased, thermal stability increased as indicated by 10% weight loss, and T_{max1} and T_{max2} values. A similar trend was also observed in the case of poly(alkyl lactate acrylate)s containing even number of carbon containing alkyl groups, that is, PELA and P(n-BLA). The above observed trends could be explained on the basis of $<R>$ value. The increase in the $<R>$ value decreased the heat capacity and thermal conductivity. As a result, more thermal energy would be required for decomposition.[57] In this case, increased $<R>$ value decreased thermal conductivity, which in turn increased thermal stability.

CONCLUSIONS

We have successfully synthesized a series of poly(acrylic acid) with alkyl lactates as a pendant group. The characterization data confirmed the formation of precursors, monomers, and polymers. An odd-even effect was observed in the average molecular interchain spacing. A higher moisture absorption value exhibited by PELA, indicated that it may have the potential for hydrogel applications after cross-linking with a suitable cross-linker. An increase in the side-chain length of n-alkyl group of polymers resulted in a drastic drop in T_g. Two-step thermal degradation was observed for polymers in nitrogen atmosphere.

ACKNOWLEDGMENTS

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