Tunable Hydrophilicity of Poly(ethyl lactate acrylate-*co*-acrylic acid)

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ABSTRACT: Four copolymers of poly(ethyl lactate acrylate-*co*-acrylic acid) were prepared by the solution polymerization technique by varying the comonomer content from 0.2 to 0.8 mole percent. The copolymers were characterized by FT-IR, ^{1}H-NMR and proton decoupled ^{13}C-NMR spectroscopic techniques. The reactivity ratio of ethyl lactate acrylate (ELA) and acrylic acid (AA) was calculated using the Fineman-Ross method and the values were found to be 0.101 and 0.186, respectively, indicating the formation of an alternating copolymer. From the wide-angle X-ray diffraction studies (WAXD), the average molecular interchain spacing (<R>) was calculated from the 2θ value of amorphous halo at about 20°. The <R> values varied from 5.20 to 5.64 Å and increased with an increase in the ELA content. The water absorption of copolymers followed Fickian absorption. Depending upon the copolymer composition, relative humidity and time, the water absorption of copolymers can be tuned to a wide range from 3 to 35% (w/w). The T_g of copolymers decreased from 106 to –27.4°C with an increase in the ELA content. The copolymers were thermally stable up to 150°C and thereafter exhibited three-step thermal degradation in nitrogen atmosphere. The thermal stability of polymers can be explained on the basis of <R> value.

KEYWORDS: Average molecular interchain spacing, copolymer, hydrophilicity, lactate, thermal stability

1 INTRODUCTION

Acrylic acid (AA) has been copolymerized with different comonomers such as alkyl (meth)acrylates [1], 2-hydroxyethyl methacrylate [2], acrylonitrile [3], acrylamide [4], N,N-dimethylacrylamide [5], N-isopropylacrylamide [6], vinyl alcohol [7], vinyl acetate [8], styrene [9], vinylimidazole [10], vinyl pyrrolidone [11], amidoamine [12], crotonic acid [13], alkyd resins [14], etc. The physical, chemical and thermal properties of these copolymers have been well documented in the literature. Each type of comonomers, like acidic, basic, neutral or their salts, tune the properties of the copolymers of poly(acrylic acid) (PAA), which make them suitable for a wide range of applications such as pressure-sensitive adhesives, sealants, insulators, lubricants, paints, coatings, textiles and paper manufacturing, super absorbents, cosmetics, damping elements, agricultural soil conditioners, seed coatings, water clarifiers, biomaterials, surfactants, ion conducting membranes, etc. [15].

By changing the comonomer of AA, the polarity can be tuned within almost the entire polarity spectrum from hydrophilic to hydrophobic. Water absorption of PAA is about 33% w/w [16]; upon copolymerization with hydrophobic comonomer, such as methyl methacrylate [17] and trifluoroethyl α-fluoroacrylate [18], water absorption decreased to 17.5 and 0.64% w/w, respectively. Further, different types of comonomers like acrylonitrile, N-isopropylacrylamide, N,N-dimethylaminoethyl methacrylate, etc., were used to tune the hydrophilicity of AA for different applications. Porous poly(acrylonitrile-*co*-acrylic acid) copolymers were found to meet different needs of biochemical probes or biomolecular scaffoldings. The water absorption capacity in these copolymers was found to affect the enzymatic reaction and efficiency of glucose biosensor [3]. In a copolymer of poly(N-isopropylacrylamide-*co*-acrylic acid) with a surface-modified aromatic polyamide, a potential reverse osmosis membrane was found to have better water permeability and fouling resistance

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and decreased salt permeability towards NaCl and Na_2SO_4 under neutral and alkali conditions [6]. The polymeric membrane derived from vinylimidazole and AA was found to have proton conductivities in the range of 10^{-2} S/cm up to 120°C under anhydrous conditions [10]. Poly(N,N-dimethylaminoethyl methacrylate-*co*-acrylic acid) composite membrane showed higher permeation rate for carbon dioxide when compared to methane [19]. The suitability of an acrylic acid resin as a leather finishing agent was investigated using poly(butyl acrylate-*co*-acrylic acid) as an emulsifier [1]. Copolymers of AA with sodium and potassium acrylate have enhanced rheological properties, thus finding application as circulation loss control materials in drilling mud [20]. Tertiary ammonium salt and AA copolymer coatings were found to show reliable antifouling properties on immersed surfaces [21]. Poly(2-ethylhexyl acrylate-*co*-acrylic acid) copolymer was used to provide the adhesive ability for membranes in transdermal drug delivery systems [22].

In our previous work, we synthesized a series of poly(alkyl lactate acrylate)s [23,24], among them, poly(ethyl lactate acrylate) exhibited the highest water absorption of about 10% (w/w) at 97% RH and 30 ± 1°C [23]. As a continuation of the previous work, we have copolymerized ELA with AA. The purpose of choosing AA as a comonomer is to further increase the hydrophilicity, as AA was found to have moisture absorption of about 35%·w/w at 97% RH and 30 ± 1°C. The effect of ELA comonomer on the properties of PAA was investigated in terms of <R>, water absorption, T_g and thermal stability. Due to the wide variation in water absorption, these copolymers can be chosen depending upon the requirement of a particular application.

2 EXPERIMENTAL

2.1 Materials

ELA was synthesized through azeotropic distillation as reported elsewhere [23]. AA, tetrahydrofuran (THF) and n-hexane were obtained from Merck (India) Ltd. THF was dried using sodium wires and distilled. It was then stored over 3 Å molecular sieves. 2,2'-azobisisobutyronitrile (AIBN, Spectrochem) was recrystallized twice from chloroform. All other chemicals were used as received.

2.2 Characterization

A Thermo Scientific Nicolet 6700 spectrometer was used to record the Fourier Transform Infrared (FT-IR)

spectra in the range of 4000 to 400 cm^{-1}. A Bruker AV-III 500 MHz NMR spectrometer was used for recording ^{1}H-nuclear magnetic resonance (^{1}H-NMR) and proton decoupled ^{13}C-NMR spectra. Inherent viscosity was measured using an Ubbelohde viscometer at 30 ± 0.1°C using THF containing 0.1 M $NaNO_3$ at 0.5 g/dL concentration of polymers. Wide angle X-ray diffraction (WAXD) measurements were carried out using a Shimadzu Lab XRD-6000 with CuK$_\alpha$ radiation (40 kV, 30 mA) having a wavelength of 1.54 Å. The moisture absorption at 30 ± 1°C was measured gravimetrically in different values of RH using a digital weighing balance. A Perkin Elmer Diamond Differential Scanning Calorimeter (DSC) was used to measure thermal transitions at a heating rate of 10°C/min using 4–6 mg of sample in an aluminum pan. Weight loss was examined using a Perkin Elmer Pyris1 TGA at a heating rate of 10°C/min under a nitrogen atmosphere with a sample weight of 4–6 mg.

2.3 Synthesis of Copolymers

Before polymerization, hydroquinone inhibitor was removed from ELA and AA by passing through aluminum oxide [25] and the monomers were distilled under vacuum. ELA (17.4 mmol, 2.99 g), AA (69.4 mmol, 5 g) and pre-dried THF (40 mL) were taken in a 100 mL 3-necked round bottomed flask. Solution polymerization was carried out under a dry nitrogen atmosphere at 60°C using AIBN (1% w/w) as a free radical initiator (Scheme 1). After 4 hours, the reaction mixture was added into a large volume of n-hexane to precipitate poly(ELA-*co*-AA). The above procedure is for the preparation of copolymer having a molar ratio of 0.2 ELA:0.8 AA (2E8A) in feed. Similarly, ELA and AA were copolymerized in different molar ratios of 0.4:0.6 (4E6A), 0.6:0.4 (6E4A) and 0.8:0.2 (8E2A) in feed. The polymers were dried for about 12 h at 60°C in a vacuum oven.

3 RESULTS AND DISCUSSION

Free radical solution polymerization was carried out to obtain copolymers of ELA with AA. Percentage conversion was found to be in the range of 10–15% for all the copolymers. The copolymers were found to be soluble in dimethylsulfoxide, N,N-dimethylformamide and THF (1%·w/v), and insoluble in hexane and toluene (1%·w/v), at room temperature.

3.1 FT-IR Spectroscopy

The typical FT-IR spectra of PAA, 2E8A, 8E2A and PELA are given in Figure 1. The FT-IR spectrum
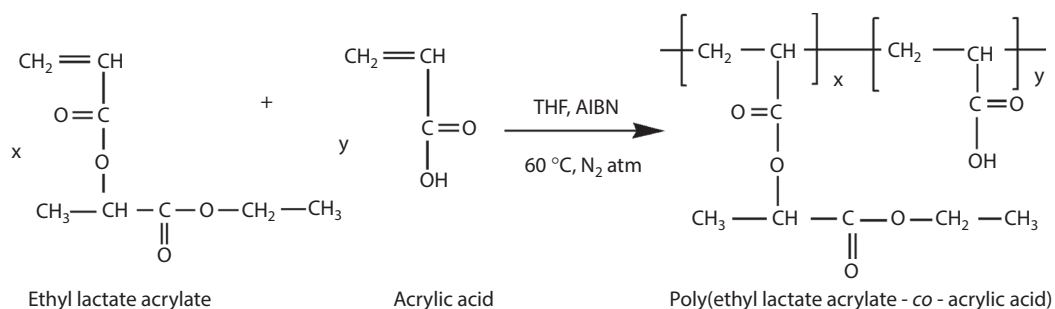
Scheme 1 Synthetic route for copolymerization of ELA with AA.
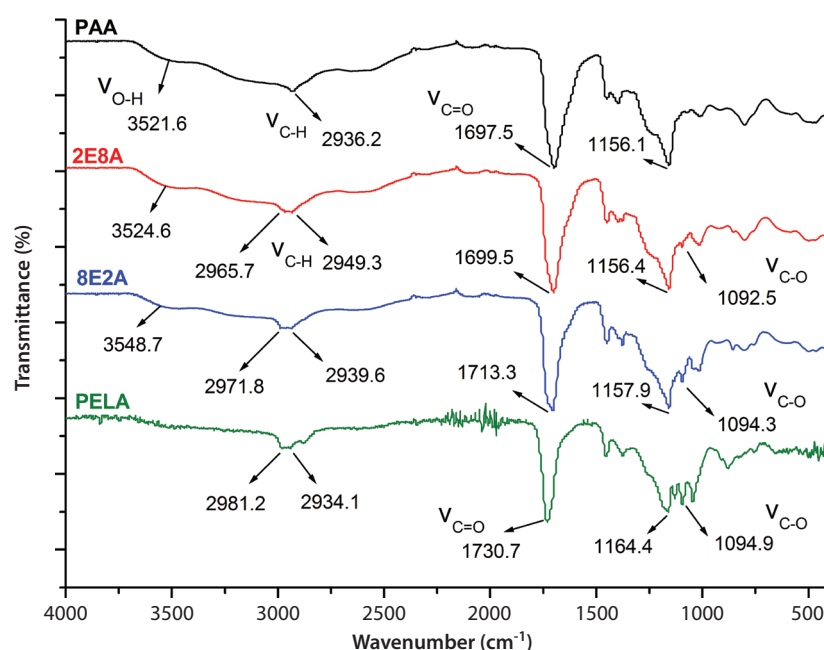
Figure 1 FT-IR spectra of (a) PAA, (b) 2E8A, (c) 8E2A and (d) PELA.

exhibited broad -OH, -CH$_2$ asymmetric, C=O and C-O stretching peaks around 3521.6, 2936.2, 1697.5 and 1156.1 cm^{-1} of PAA and -CH$_3$ asymmetric, -CH$_2$ asymmetric, C=O and C-O stretching peaks around 2981.2, 2934.1, 1730.7 and 1130.1 cm^{-1} of PELA, respectively. After the copolymerization of ELA with AA, the presence of the -OH stretching peak of AA at around 3520 cm^{-1} and -CH$_3$ asymmetric and C-O stretching peaks of ELA at around 2980 and 1090 cm^{-1}, respectively, confirmed their formations in all copolymers. The absence of an olefinic carbon peak ($v_{C=C}$) at around 1650 cm^{-1} confirmed that the copolymerization had taken place between ELA and AA.

The peak which appeared at a lower wave number of 1697.5 cm^{-1} with higher band width was due to the carbonyl group (C=O) of PAA, indicating that the C=O group had strong hydrogen bonding with a hydrogen donor group of -OH. While decreasing the AA content in copolymers, it increased the C=O stretching frequency from 1697.5 to 1730.7 cm^{-1}, and

the decrease in band width was due to the decrease in hydrogen bonding with the hydrogen donor group of -OH. A similar effect was reported for free and bonded -OH by Colthup *et al.* [26] and Lewell *et al.* [27]. Similarly, wavenumber values of -OH, -CH$_3$ asymmetric and C-O stretching peaks also shifted to higher values, which was due to the decreased AA content in copolymers.

3.2   ¹H-NMR Spectroscopy

The typical ¹H-NMR spectra of 2E8A and 8E2A are shown in Figure 2. In ¹H-NMR spectra of poly(ELA-*co*-AA), the appearance of the -O-C**H$_2$** peak and methine proton peak (-C**H**(CH$_3$)) of ELA at around 4.1 and 5 ppm, respectively, and the carboxylic proton peak (-COO**H**) of AA at around 12.2 ppm, confirmed the formation of copolymers (Table 1). Further, the methine proton (-C**H**(CH$_3$)) and methyl protons (-CH(C**H$_3$**)) of the lactate moiety of ELA exhibited a multiplet peak
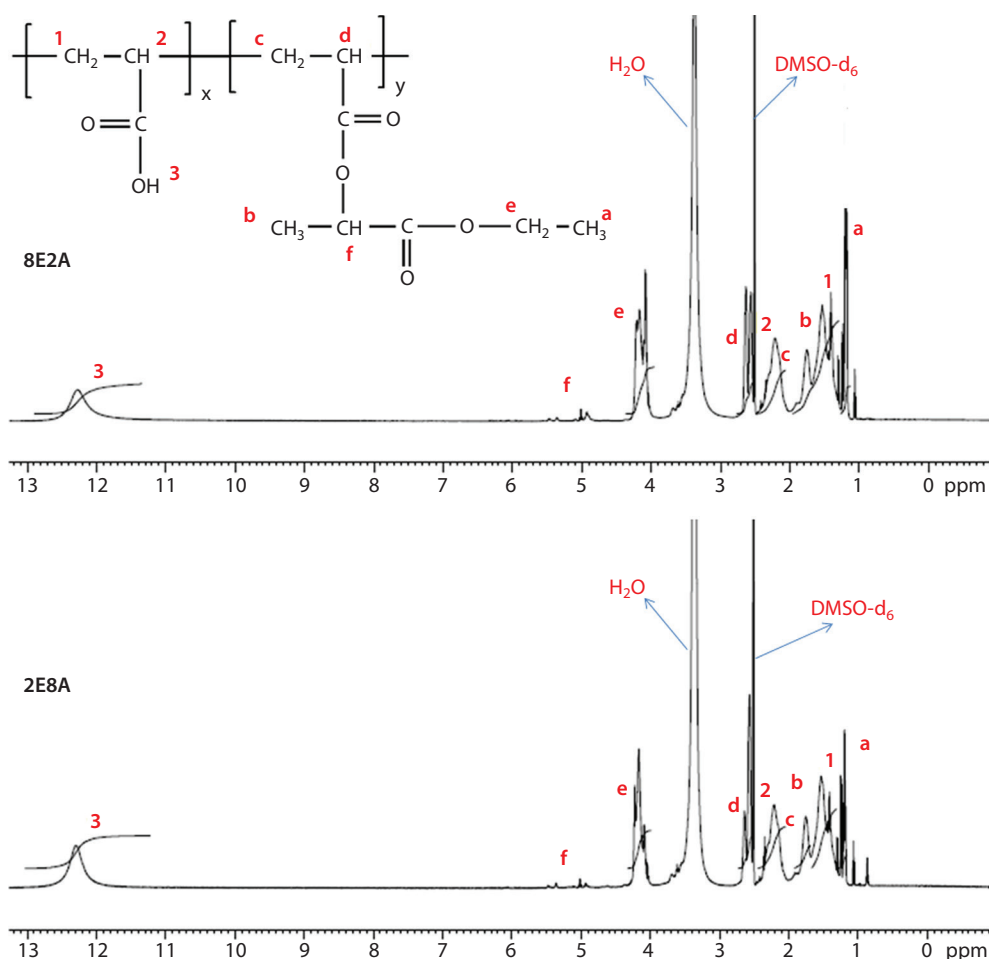
Figure 2 ^{1}H-NMR spectra of (**a**) 2E8A and (**b**) 8E2A.

Table 1 Composition analysis, η_{inh}, WAXD and T_g data of poly(ELA-*co*-AA).

Copolymer	Proton Intensity from NMR		Composition Analysis		η_{inh} (dL/g)	WAXD data		T_g (°C)
	O-CH$_2$	COOH	ELA	AA		2θ (°)	<R> (Å)	
PAA	-	-	0	1.0	0.41	21.34	5.20	106
2E8A	1.56	1.00	0.36	0.64	0.34	21.11	5.26	89.9
4E6A	1.00	0.77	0.39	0.61	0.29	21.09	5.27	62.1
6E4A	1.56	1.00	0.43	0.57	0.22	20.87	5.32	1.7
8E2A	1.00	0.43	0.53	0.47	0.19	20.69	5.37	-18.8
PELA	-	-	1.0	0	0.15	19.69	5.64	-27.4

instead of a quartet at around 4.9 ppm, and a doublet of a doublet instead of doublet at around 1.5 ppm was attributed to the presence of a chiral carbon in D and L optical isomers of lactic acid. This is in agreement with the observation reported by Schliecker *et al.* [28] and Sanchez and Collinson [29].

3.3 Composition Analysis and Reactivity Ratio of Monomers

The Fineman-Ross method was used to determine the reactivity ratio of ELA and AA. The proton intensities of the methoxy peak (-O-**CH**$_2$) of ELA and carboxylic

acid peak (-**C**OO**H**) of AA values obtained from ^{1}H-NMR were analyzed and compositions were calculated using the following equations:

$$\text{AA content in copolymer} = \frac{2x}{2x + y} \qquad (1)$$

$$\text{ELA content in copolymer} = \frac{y}{2x + y} \qquad (2)$$

where x and y are the proton intensities of -COO**H** group of AA and -O-C**H$_2$** group of ELA respectively obtained from ^{1}H-NMR analysis. The composition values are tabulated in Table 1. The increase in the ELA content in the feed has increased the ELA content in the copolymers. The obtained ELA and AA content values in the copolymer were plotted against $-m_2M_1^2/m_1M_2^2$ vs. $M_1(m_2-m_1)/M_2.m_1$ in Figure 3 using the Fineman-Ross method [30]. M_1 and M_2 are the feed ratios of monomers and m_1 and m_2 are the molar concentrations in copolymers. The obtained r_1 (AA) and r_2 (ELA) values are 0.186 and 0.101 respectively, which indicated that these copolymers are alternate.

3.4　^{13}C-NMR Spectroscopy

The typical ^{13}C-NMR spectra of 2E8A and 8E2A are given in Figure 4. In ^{13}C-NMR spectra of poly(ELA-*co*-AA), the appearance of the -**C**OOH peak at around 176.2 ppm of AA and carbonyl peaks of ELA at around 170.4 and 174.6 ppm of $(CH_3)CH-\underline{C(O)}$-O and $(CH_3)CH-O-\underline{C=O}$, respectively, confirmed the formation of copolymers. Apart from the carbonyl peaks of copolymers, the appearance of $\underline{CH_2}$-CH and $CH_2-\underline{CH}$ carbon

peaks at around 41 and 34 ppm respectively and the disappearance of olefinic carbon peaks (C=C) at around 128 and 130 ppm confirmed the formation of copolymers between ELA and AA (Figure 4).

3.5　Inherent Viscosity

The inherent viscosity (η_{inh}) values of copolymers are given in Table 1. η_{inh} values indicated that the polymers were of moderate molecular weight in the range of 0.15 to 0.41 dL/g. On increasing the ELA content, the molecular weight of copolymers decreased, which was due to the presence of lactate moiety. A similar effect was reported for poly(alkyl lactate acrylate)s [23,24] and poly(N-(2-hydroxypropyl) methacrylamide mono/di lactate) [31].

3.6　WAXD

The synthesized copolymers were amorphous, which was indicated by a broad amorphous halo peak at about 20°. The amorphous halo shifted from 21.34° to 19.69° with an increase in the ELA content in poly(ELA-*co*-AA). The average molecular interchain spacing (<R>) for amorphous materials was determined by the following equation [32]:

$$< R >= \frac{5}{8}\left(\frac{\lambda}{\sin\theta}\right) \qquad (3)$$

where λ is the wavelength of radiation and θ is the diffraction maximum angle. The values of 2θ and <R> are given in Table 1. The value of <R> varied in accordance with the ELA content. The long pendant group of
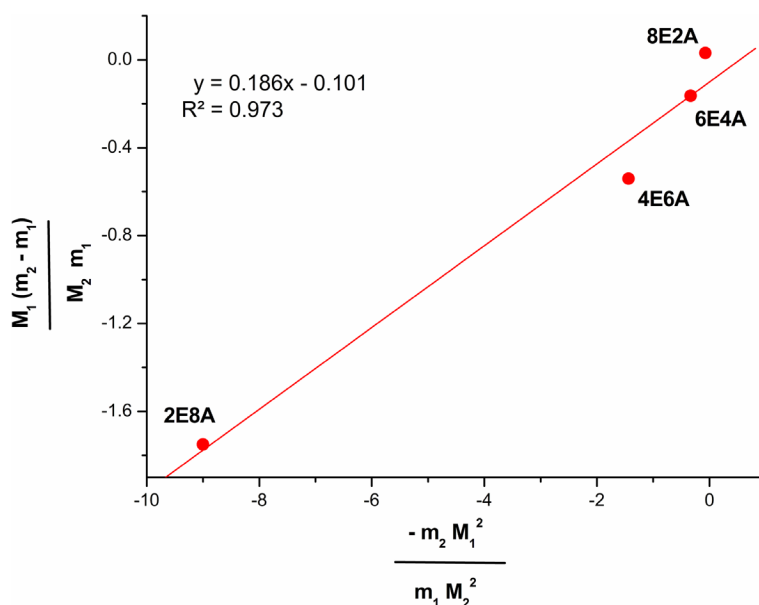

$$y = 0.186x - 0.101$$
$$R^2 = 0.973$$

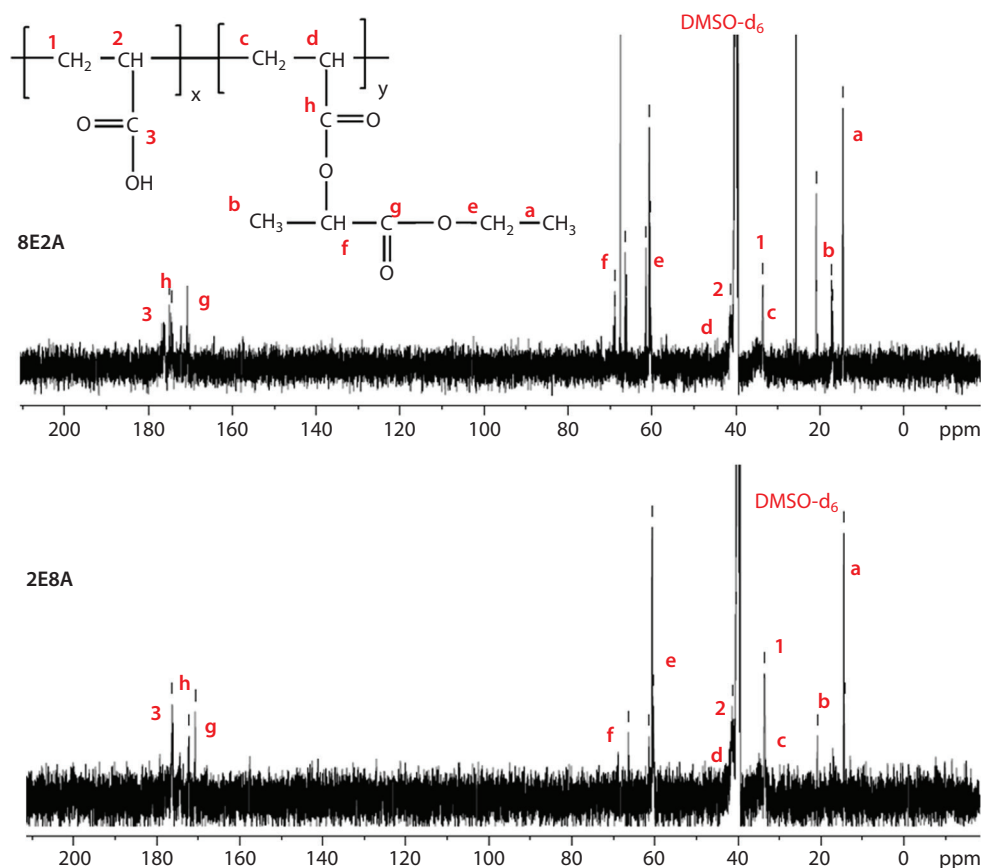**Figure 3** Fineman-Ross plot.

Figure 4 ^{13}C- NMR spectra of (a) 2E8A and (b) 8E2A.

ELA increased the <R> value, which indicated that the free volume had increased.

3.7 Water Absorption Capacity

The water absorption capacity of polymers mainly depends upon the hydrophilic groups present in the polymer network, van der Waals interaction and <R>. The different percentages of RH such as 69, 86 and 97% were maintained inside a glass chamber using saturated solutions of potassium iodide, potassium chloride and potassium chromate respectively. RH was continuously monitored by using a digital hygroscopic meter. The prepared polymers were initially dried to remove the absorbed water, if any. About 3 g of pre-dried copolymers in a petri dish were placed in closed glass chambers, which were preconditioned at the specific RH values at 30 ± 1°C, and the samples were weighed periodically. The moisture absorption percentage was calculated from the weight gain with respect to the dried sample weight.

In general, when both hydrogen bond acceptors such as carbonyl group of esters and donor groups such as hydroxyl group are present in the same molecule,

the water absorption value would be very high as in the case of PAA and poly(2-hydroxyethyl methacrylate). Their water absorption values were found to be 33 and 30% (w/w) at 90% RH by using TGA analyzer [16]. In copolymers, there are three types of hydrogen bond acceptors, namely: lactate and acrylate carbonyl groups of ELA, carbonyl group of AA and one donor group of AA, which has facilitated moisture uptake. The moisture absorption of copolymers as a function of time is plotted at 69, 86 and 97% RH and is shown in Figure 5(a), 5(b) and 5(c), respectively.

In all these cases, moisture absorption values decreased with an increase in the ELA content. Variation in the moisture absorption of copolymers from 3.2 to 22.1% (w/w) in 69% RH, 7.5 to 31.4% (w/w) in 86% RH and 9.1 to 35.2% (w/w) in 97% RH was due to the increase in AA content (Table 2).

Figure 5(d) represents the plot of the ELA content (in feed) vs. equilibrium moisture absorption (M_e) of poly(ELA-*co*-AA). From this plot, one can predict the M_e value at specified RH value for the other copolymer compositions. Depending upon the application requirements, the water absorption can be tuned with respect to copolymer compositions.
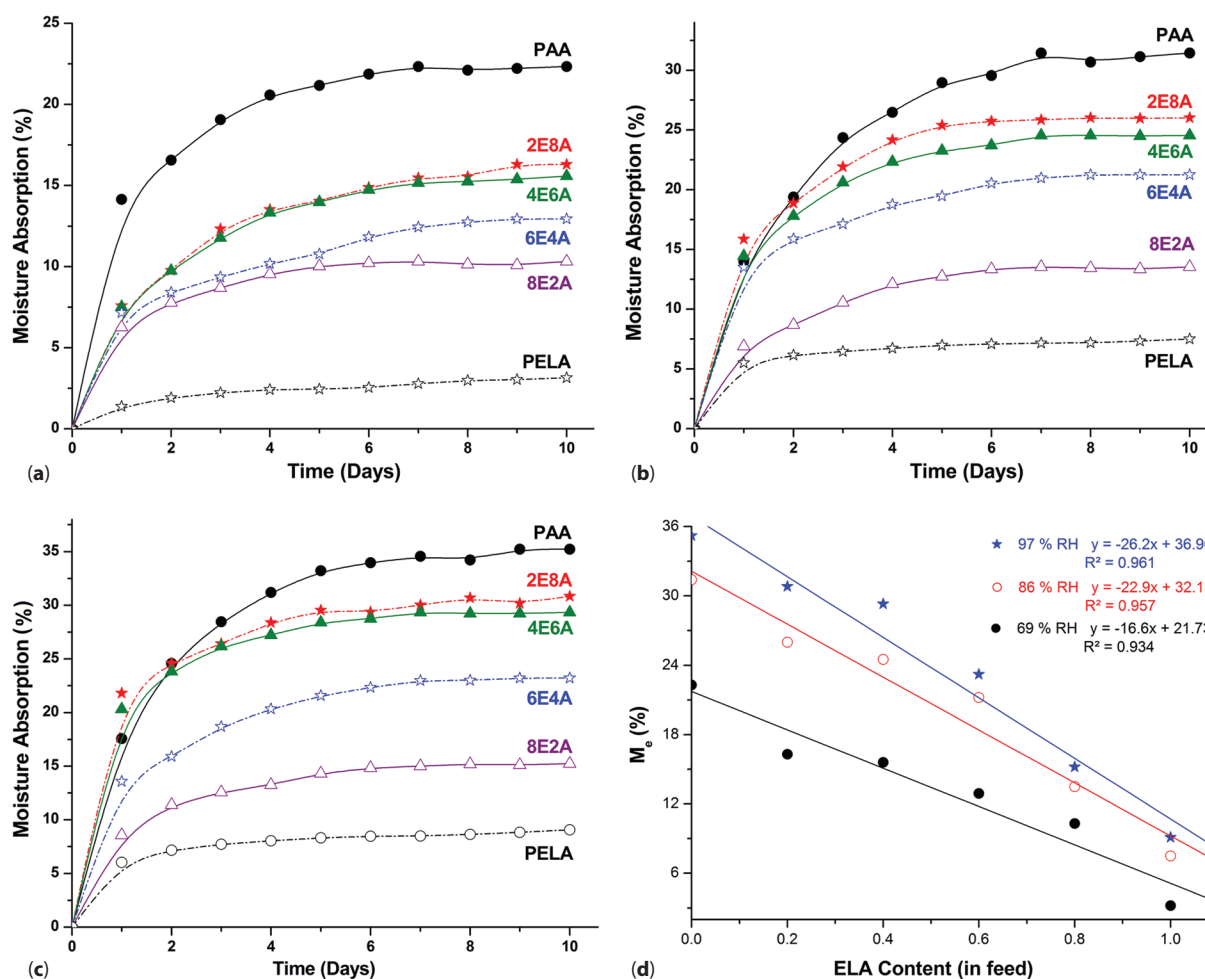
Figure 5 Plot of % moisture absorption vs. time of poly(ELA-*co*-AA) at (a) 69% RH, (b) 86% RH, (c) 97% RH, and (d) Plot of M_e vs. ELA content (in feed) of poly(ELA-*co*-AA).

Table 2 M_e, *n* and *k* parameters for the moisture absorption of poly(ELA-*co*-AA).
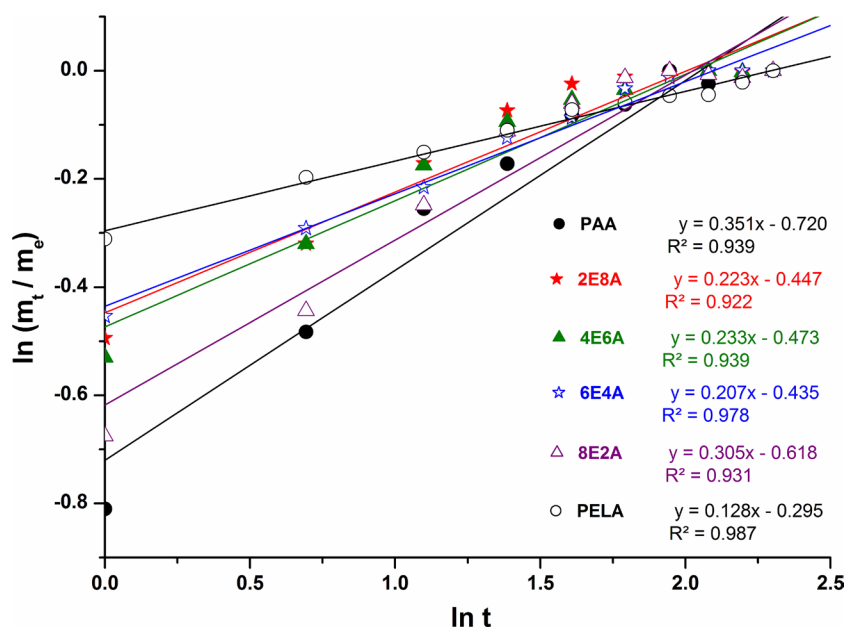
Copolymer	M_e (%)			*n*			k		
	69% RH	86% RH	97% RH	69% RH	86% RH	97% RH	69% RH	86% RH	97% RH
PAA	22.1	31.4	35.2	0.204	0.351	0.290	0.659	0.487	0.553
2E8A	16.3	26.0	30.8	0.335	0.223	0.151	0.489	0.640	0.723
4E6A	15.6	24.5	29.3	0.323	0.233	0.158	0.510	0.623	0.725
6E4A	12.9	21.2	23.2	0.277	0.207	0.247	0.543	0.647	0.599
8E2A	10.3	13.5	15.2	0.213	0.305	0.242	0.649	0.539	0.609
PELA	3.2	7.5	9.1	0.339	0.128	0.162	0.461	0.745	0.694

The water absorption data was analyzed using the following equation to know the type of absorption process:

$$\frac{M_t}{M_e} = kt^n \tag{4}$$

where M_t is the amount of moisture absorption at time *t* and M_e is the equilibrium moisture absorption, *k* is

the characteristic constant of polymer and *n* is a characteristic exponent of the mode of transport of the penetrating molecule [33]. It is noted that for Fickian absorption the value of *n* is less than 0.5, whereas the value of n between 0.5 and 1.0 indicates a non-Fickian absorption. A plot of ln (M_t/M_e) against ln *t* at 97% RH is given in Figure 6. The obtained values are tabulated

Figure 6 Plot of $\ln(M_t/M_e)$ vs. ln *t* for the moisture absorption of poly(ELA-*co*-AA) at 86% RH.

in Table 2. The *n* value of copolymers below 0.5 indicated that the copolymer followed Fickian absorption.

3.8 DSC

The obtained T_g values of copolymers by DSC analysis are given in Table 1. The T_g of copolymers decreased from 106 to –27.4°C with an increase in the ELA content, which was attributed to the increase in free volume. An increase in the <R> value of copolymers indicated an increase in free volume, which easily facilitated molecular segmental motion, leading to a decrease in T_g values. A similar observation was made by Greenwald and Luskin [34] for poly(sodium acrylate-*co*-AA), where T_g values dropped from 250 to 106°C, and by Jithunsa *et al.* [10] for poly(vinyl imidazole-*co*-AA), where T_g values dropped from 191 to 106°C. The decrease in the T_g value of these copolymers was due to the decrease in the rigid imidazole structure in copolymers.

3.9 TGA

The thermal stability of copolymers in nitrogen atmosphere was assessed by comparing 10, 25, 50 and 75% weight loss and the values are given in Table 3. All the copolymers were found to be thermally stable up to 150°C and showed three-step degradation, whereas PELA exhibited two-step degradation [23]. The degradation region at 150–280°C was assigned to the release of water, resulting in the formation of noncyclic anhydride in the AA repeat unit; while the degradation which started from 280 to 410°C is due

Table 3 TGA data of copolymers.

Copolymer	wt. loss (ºC)				T_{max1} (ºC)	T_{max2} (ºC)	T_{max3} (ºC)
	10 %	25 %	50%	75%			
PAA	211	236	301	404	229	376	563
2E8A	225	250	326	429	251	404	564
4E6A	226	253	327	423	255	379	571
6E4A	230	258	329	415	259	389	579
8E2A	235	265	317	401	286	349	584

to the degradation of pendant groups of AA and ELA. The final degradation at around 600°C belongs to the C–C bond cleavage of the polymer backbone [10]. The thermal stability of copolymers increased with an increase in the ELA content. The observed trend could be explained on the basis of <R> values, i.e., increase in the <R> value decreased the heat capacity and thermal conductivity. As a result, more thermal energy would be required for decomposition [35]. In this case, increased <R> values decreased the thermal conductivity, which in turn increased the thermal stability.

4 CONCLUSIONS

Four copolymers of poly(ELA-*co*-AA) were successfully prepared by varying the comonomer feed from 0.2 to 0.8 mole percent and characterization studies confirmed the formation of alternating copolymers. The water absorption of copolymers followed Fickian absorption and can be tuned to a wide range from 3 to 35% (w/w). The <R> values and thermal stability of copolymers increased with an increase in the ELA

content, but decreased the T_g value. A correlation existed between <R>, T_g and thermal stability.

ACKNOWLEDGMENT

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