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Synthesis and thermal properties of novel poly(potassium 1-hydroxy acrylate-*co*-potassium acrylate) based copolymer

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ABSTRACT

Water soluble based copolymer poly(potassium 1-hydroxy acrylate-*co*-potassium acrylate) i.e. P(KHA-*co*-KA) and poly(1-oxa-2-oxobutane-1,4:3,3-tetrayl)/potassium 1-hydroxy acrylate-*co*-potassium acrylate) i.e. P(LAC/KHA-*co*-KA) were synthesized by radical polymerization of 2-isopropyl-5-methylene-1,3-dioxolan-4-one (MD) and acrylic acid (AA) monomers followed by alkaline ring opening hydrolysis of P(MD-*co*-AA). The P(KHA-*co*-KA) copolymer generates a new lactone segment by the intramolecular cyclodehydration of two neighbouring groups in the presence of acidic condition, resulting P(LAC/KHA-*co*-KA) copolymer. This change enhances the thermal properties of P(LAC/KHA-*co*-KA) copolymer as compared to P(KHA-*co*-KA) copolymer.

1. Introduction

Poly(α-hydroxyacrylic acid) is a known polyelectrolyte and can be used for interesting applications such as stabilizer, metals binding capability and excellent detergency performance for multicomponent-soiled cotton fabric [1,2]. The PKHA and PKA segment of P(KHA-*co*-KA) copolymer show impedance responding to changes in pH and ionic strength, leading to change in its properties in aqueous solution. The swelling behaviour of the copolymer segments depends on the pH which occurs at pH above 2 for poly (α-hydroxy acrylic acid) and above 3 for polyacrylic acid respectively [3]. The copolymer of PKHA with AA is not yet reported; although few studies of its copolymer have been reported. Miyagawa et al. synthesized the copolymer of 5-methylene-1,3-dioxolan-4-one with vinyl acetate, styrene and methylmethacrylate. The effect of monomer reactivity ratios and initiator or additives on the molecular weight of copolymer was investigated [2,4,5]. Tanaka et al. prepared the acrylate based copolymer for control molecular weight and tacticity by controlled radical polymerization of 5-methylene-1,3-dioxolan-4-one with styrene and methylmethacrylate [6,7]. Kumar et al. studied Poly(potassium 1-hydroxy acrylate-*co*-styrene) copolymer, synthesized from the radical copolymerization of 5-methylene-1,3-dioxolan-4-one and styrene monomer followed by the alkaline ring opening hydrolysis. The synthesized copolymer exhibited the thermal stability up to 183 °C [8].

In this study, we synthesized a novel P(KHA-*co*-KA) and P(LAC/KHA-*co*-KA) copolymer containing hydroxy acrylate, potassium acrylate and lactone segments in the polymeric chain. Further, we investigate the thermal properties, water absorption capacity (WAC) and weight-average molecular weight of the P(KHA-*co*-KA) and P(LAC/KHA-*co*-KA) copolymer.

2. Experimental

2.1. Materials

The MD monomer was synthesized by previously synthetic procedures (Supporting Information, SI). Acrylic acid (AA) monomer was purchased from Himedia. Potassium hydroxide (KOH) was procured from Merck. Azoisobutyronitrile (AIBN) taken from Spectrochem. The characterization technique detail was described in (SI).

2.2. Synthesis of P(MD-co-AA) copolymer

To a 100 ml two neck round bottom flask equipped with a magnetic stirrer, MD (7.0 mmol), AA (7.0 mmol) and AIBN (3 wt%) were charged. The reaction mixture was stirred at 60 °C for 24 h in N_2 atmosphere. The resulting reaction mixture was dissolved in acetone and precipitated with diethyl ether and the copolymer was dried at 40 °C in vacuum oven. The obtained yield 82%.

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^{1}H NMR (500 MHz, D_2O) δ 4.1–4.38 ppm (–O–CH^{d}–O–), 2.17–2.48 (–CH_2–CH^{c}–), 2.53–2.83 (CH_3–CH^{e}–CH_3), 1.73–2.04 (–CH_2^{a}–), 1.3–1.7 (–CH_2^{b}–CH–), 0.98–1.12 (CH_3^{f}–CH–), 0.71–0.95 (CH_3^{g}–CH–). FT-IR (KBr, cm^{-1}): 3418, 2977, 2933, 1801, 1728, 1466, 1393, 1300, 1255 and 1198.

2.3. Synthesis of P(KHA-co-KA) copolymer

To a 100 ml round bottom flask equipped with a magnetic stirrer, P(MD-*co*-AA) copolymer (1.2 g), potassium hydroxide (1.5 g) and tetrahydrofuran (THF) 25 ml were added. The resulting

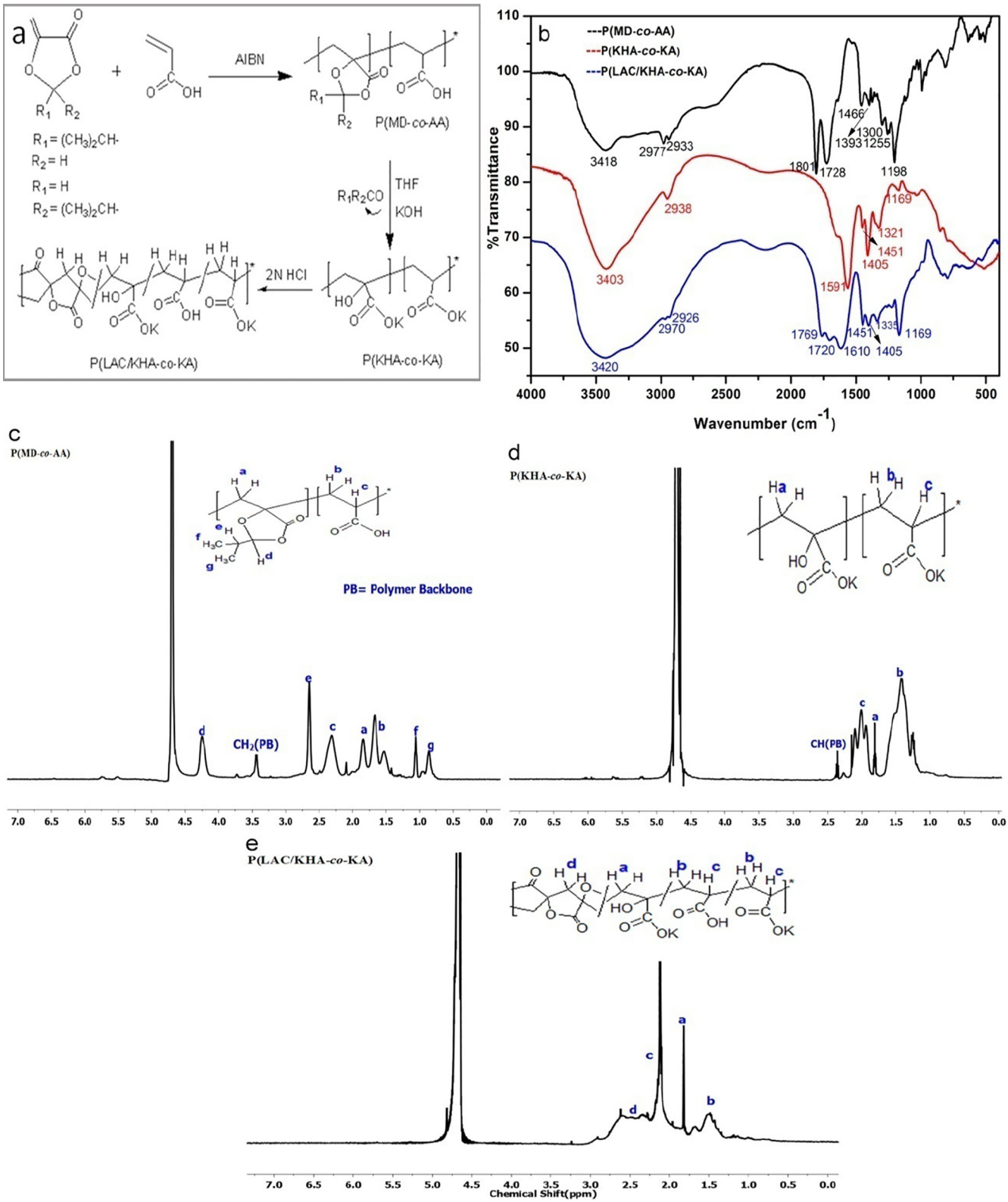

Fig. 1. (a) Reaction scheme of P(MD-*co*-AA), P(KHA-*co*-KA) and P(LAC/KHA-*co*-KA) copolymer; (b) FT-IR spectra P(MD-*co*-AA), P(KHA-*co*-KA) and P(LAC/KHA-*co*-KA) copolymer; (c) ^{1}H NMR spectrum of P(MD-*co*-AA); (d) P(KHA-*co*-KA); (e) P(LAC/KHA-*co*-KA) copolymer.