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Polymer 46 (2005) 4005–4012

polymer

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Kinetic study on free radical polymerization of alkyl acylamidoacrylates by pulsed laser polymerization using nitrogen laser

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Received 1 November 2004; received in revised form 18 March 2005; accepted 23 March 2005
Available online 21 April 2005

Abstract

Radical polymerization of captodatively substituted alkyl acylamidoacrylates was studied by pulsed laser polymerization using a N_2 laser. Propagation rate coefficient of the acrylates was varied with solvents used in spite of a radical mechanism, but little varied with methyl, *n*-propyl, and isopropyl substituents on the acrylates. Arrhenius parameters for the propagation indicated that a solvent affected mostly on a frequency factor rather than a activation energy. In addition, it was suggested that these captodatively substituted propagating radicals were thermodynamically persistent but kinetically active in propagation, which resulted in rather smooth propagation in spite of bulky 1,1-disubstituted olefins. The mechanism of the polymerizations was discussed in detail on the basis of the kinetic studies and ESR spectroscopy.

Keywords: Radical polymerization; Pulsed laser polymerization; Captodative

1. Introduction

Radical polymerization has received considerable attention because of high reproducibility, application to wide variety of monomers, and simple reaction procedure with convenient apparatus [1]. In contrast to an ionic polymerization, however, steric effect becomes important, and sterically hindered olefins including bulky 1,1- or 1,2-disubstituted olefins represent poor polymerizability, and control of polymerization rate and stereostructure of polymer with additives including solvent is much more difficult in radical polymerization. However, captodatively (cd) [2] substituted olefins, so-called cd olefins, i.e. olefins substituted by both electron-withdrawing (captive) and -donating (dative) groups on the same atom, have often displayed special reactivity to give a polymer in high or moderate yield through a radical mechanism in spite of the sterically hindered 1,1-disubstitution and synergistic cd resonance stabilization of the resulting propagating radical [3]. In addition, the rate of polymerization of the cd olefins and molecular weight of the polymer have been influenced by the solvent used in spite of a radical polymerization [4], and the polymers obtained showed advanced solvent affinity, thermal behavior, optical and electronic properties, and metal adsorption due to their high polar, asymmetric, and bifunctional cd geminal substitution [5].

2-Acylamidoacrylic acid, i.e. *N*-acyldehydroalanine, belongs to the cd olefin [6], and has been reported to polymerize very easily by a radical initiator or spontaneous thermal polymerization [6] to give a polymer with super high molecular weight, e.g. number-average molecular weight $M_n = 7\text{–}15 \times 10^6$, in high yield [7] in spite of the resulting propagating radical to be persistent as demonstrated by the large resonance stabilization (Alfrey-Price Q value: 2.42) [8] and high synergistic stabilization enthalpy (-28.5 to $-45.2\ \mathrm{kJ\ mol^{-1}}$) [9] of analogous aminocarbonylmethyl radicals. In addition, polymerization of dehydroalanine (DHA) has also been interested in connection with a synthesis of new functional materials including thermoresponsive hydrogel, amphoteric coagulant, and biodegradable polymers [7,10]. Polymerization kinetics and mode including electronic and steric effects on the polymerization of the DHA, however, has not yet been clarified in detail.

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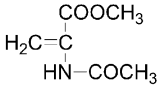
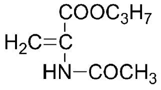
doi:10.1016/j.polymer.2005.03.049



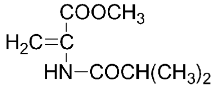
$\mathrm{H_2C{=}C(COOCH_3)(HN{-}COCH_3)}$

1



$\mathrm{H_2C{=}C(COOC_3H_7)(HN{-}COCH_3)}$

2



$\mathrm{H_2C{=}C(COOCH_3)(HN{-}COCH(CH_3)_2)}$

3

The present report deals with the kinetics of the radical polymerization of methyl 2-acetamidoacrylate (**1**), *n*-propyl 2-acetamidoacrylate (**2**), and methyl 2-isobutyramidoacrylate (**3**), and discusses on why such cd olefins can easily homopolymerize in spite of giving a thermodynamically persistent propagating radical. In such a kinetic study, propagation rate coefficient of **1**–**3** was examined by means of pulsed laser polymerization (PLP) [11] according to the following equation:

$$L_i = ik_\mathrm{p}[M]t_\mathrm{p}$$

where t_p stands for the time between two pulses, $[M]$ is a monomer concentration, $i=1, 2, 3,\ldots$, k_p is the propagation rate coefficient, and L_i denotes a chain length of the polymer formed in the time between two pulses, which can be determined by size exclusion chromatography (SEC). In the present study, N_2 gas laser was first used for PLP as a convenient light source since Nd:YAG [12,13] and excimer [14] lasers and UV flash-lamp [15] commonly used for PLP experiment were expensive and sometimes induced light ablation.

2. Experimental

2.1. Materials

Compound **1** was prepared by refluxing the mixture of methyl iodide and 2-acetamidoacrylic acid which was independently synthesized in the same manner as previous paper [6] in acetone containing anhydrous potassium carbonate for 9 h according to the procedure of Bueno and co-workers [16]. After removing a potassium carbonate by filtration and evaporating a solvent from the mixture under reduced pressure, resulting solid was recrystallized from *n*-hexane to give white needles in 50.0% yield, mp 50–52 °C (50–52 °C) [17]. ^{1}H NMR (DMSO-d_6, TMS, ppm): 2.03 (s, 3H, $COCH_3$), 3.77 (s, 3H, OCH_3), 5.72 (s, 1H, =CH), 6.18 (s, 1H, =CH), 9.29 (br s, 1H, NH). Anal. Calcd for $C_6H_9NO_3$: C, 50.35; H, 6.29; N, 9.79. Found: C, 50.14; H, 6.20; N, 9.62.

Compound **2** was synthesized according to the procedure similar to that of **1**, in which *n*-propyl iodide was used instead of methyl iodide, and purified by a column chromatography using a chloroform as a developing solvent. Compound **2** was obtained as a colorless oil in 7.2% yield. ^{1}H NMR ($CDCl_3$, TMS, ppm): 1.02 (t, $J=$ 7.2 Hz, 3H, CH_3), 1.75 (q, $J=7.2$ Hz, 2H, CH_2), 2.18 (s, 3H, $COCH_3$), 4.25 (t, $J=7.2$ Hz, 2H, CH_2), 5.89 (s, 1H, =CH), 6.69 (s, 1H, =CH). 8.02 (br s, 1H, NH). Anal. Calcd for $C_8H_{13}NO_3$: C, 56.13; H, 7.65; N, 8.18. Found: C, 56.25; H, 7.42; N, 7.98.

Preparation of **3** was also followed to the procedure of **1**, other than 2-isobutyramidoacrylic acid used instead of 2-acetamidoacrylic acid, where 2-isobutyramidoacrylic acid was synthesized by refluxing pyruvic acid 88.0 g (1 mol) and isobutylamide 43.5 g (0.5 mol) in benzene 400 ml for 10 h in a 500 ml three-necked flask equipped with a condenser and a Dean–Starks apparatus. The precipitated white solid in the flask was filtered, washed with benzene, and recrystallization of the solid from acetone gave 2-isobutyramidoacrylic acid as white needles 7.0 g in 9.0% yield, mp 160–162 °C. Then, an esterification of the acid was carried out with methyl iodide to give **3** as a colorless oil in 68.3% yield. ^{1}H NMR for 2-isobutyramidoacrylic acid (DMSO-d_6, TMS, ppm): 1.02 (d, $J=6.3$ Hz, 6H, CH_3), 2.73 (heptet, $J=6.3$ Hz, 1H, CH), 5.72 (s, 1H, =CH), 6.29 (s, 1H, =CH), 8.94 (br s, 1H, NH). Anal. Calcd for $C_7H_{11}NO_3$: C, 53.49; H, 7.05; N, 8.91. Found: C, 53.23; H, 6.93; N, 8.90. ^{1}H NMR for **3** (DMSO-d_6, TMS, ppm): 1.04 (d, $J=6.3$ Hz, 6H, CH_3), 2.74 (heptet, $J=6.3$ Hz, 1H, CH), 3.83 (s, 3H, OCH_3), 5.69 (s, 1H, =CH), 6.19 (s, 1H, =CH), 9.21 (br s, 1H, NH). Anal. Calcd for $C_8H_{13}NO_3$: C, 56.13; H, 7.65; N, 8.18. Found: C, 56.08; H, 7.37; N, 8.39.

Commercially available (Wako Chemicals) 2,2′-azobisisobutylonitrile (AIBN) and benzoin were used after recrystallization from ethanol and toluene respectively. Commercial grade 2,2′-azobis(2,4,4-trimethylpentane) (ATMP) was used without further purification. Methyl methacrylate (MMA) was purified by ordinary method, and distilled just before use.

2.2. Polymerization

PLP was performed in a UV-quartz cell (10 mm thickness) attached thermostat using a N_2 gas laser (Laser Science VSL-337ND-S: $\lambda=337$ nm, 0.6 mJ per pulse) with monitoring the light frequency on oscilloscope. N_2 gas was passed through the sample in the cell containing the required amounts of reagents including monomer, solvent, and benzoin as a photoinitiator to remove the oxygen before polymerization. Then, the cell was capped after filling out with N_2 gas.

Co-polymerization of **3** and preparation of standard polymer **1** were carried out in toluene and acetonitrile at 50 and 60 °C, respectively, in a sealed ampoule with shaking at given temperature. The ampoule that contained the required amounts of reagents including AIBN, solvent, and so forth was degassed several times by a freeze–thaw method and then sealed under reduced pressure and placed in a constant temperature bath. The resulting polymer was isolated by pouring the contents of the ampoule into a large amount of diethyl ether. Co-polymer composition was determined from the carbon content found by elemental analysis of the co-polymer which was purified by reprecipitation.