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Property and quantum chemical investigation of poly(ethyl α-cyanoacrylate)

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Abstract

The poly(ethyl α-cyanoacrylate) (PEtCNA) was synthesized by anionic polymerization. With the composed PEtCNA, its IR spectrum, ^{1}HNMR spectrum and configuration are measured. Meanwhile, molecular geometry, electronic structure, IR spectrum and thermodynamic property of reactant and transition state on the reaction potential energy level of ethyl α-cyanoacrylate with hydroxyl have been completely optimized and calculated for the first time by the density functional theory DFT-B3LYP method and on the level of 6-31+G* group. The order of 10^{10} s^{-1} of initiating rate constant in gas phase was obtained for the reaction. These were reported the quantum chemical calculation results so as to deepen researches on the relationship between structure and properties.

Keywords: Anionic polymerization; Degradation; Density functional theory; Initiator; Poly(ethyl α-cyanoacrylate)

1. Introduction

Poly(ethyl α-cyanoacrylate) play an important role in biomedical applications [1,2] such as in controlled drug delivery, stopping internal bleeding, joining ruptured tissue, etc. due to their biocompatibility and biodegradability. Therefore, much attention has been paid to poly(ethyl α-cyanoacrylate) about synthesis, properties and degradation mechanism.

In anionic polymerization, ethyl α-cyanoacrylate is very active for their strong electronic drawing group. It can be polymerized by weak initiator such as water and alcoholate at room temperature [3,4]. Therefore, an attempt has been made to understand the nature of poly(ethyl α-cyanoacrylate).

Here we report the anionic polymerization of EtCNA is initiated by water or water with catalyzing by sodium hydroxide under the conditions of no additives and the quantum chemical calculation results so as to deepen researches on the relationship between structure and properties.

2. Experimental part

2.1. Main reagents

Ethyl α-cyanoacrylate (C.R., Beijing Chemical Plant, China) was purified by decompressed distilling before using. Sodium hydroxide (NaOH, A.R., Nanjing Chemical Plant, China) was used as received. Cyclohexane (A.R., Nanjing Chemical Plant, China) was disposed by 4A molecular sieve and decompressed distilling. Argon (99.99%) was disposed by drier. Double distilled water was used in our experiments.

2.2. Preparation of PEtCNA

2.2.1. Polymerization by water

Ethyl α-cyanoacrylate was polymerized with water as initiator. In a dry four-necked flask with sediment base in

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argon, the temperature was kept at 100 °C to eliminate air and water, 1 μL water was injected into it to make gasification and 2 mL ethyl α-cyanoacrylate steam disposed with decompressed distilling was led in. Then gas was stopped to pass through and the mouths were sealed, but it still reacted for 18–48 h on the surface of base. The sediment base was taken for collecting polymer.

2.2.2. Polymerization by water with sodium hydroxide

Ethyl α-cyanoacrylate was polymerized in a four-necked flask and added certain amount of sodium hydroxide as catalyst in argon. The four-necked flask as gas reactor was heated, which connected to a three-necked flask as receiving flask fitted with a stirrer. Cyclohexane as receiving solution was added into it. Then 2 mL disposed ethyl α-cyanoacrylate was added slowly into it in a dropping funnel when temperature reached 80 °C. It reacted acutely when touching sodium hydroxide solid, and produced white mist instantly, which was led into the receiving flask by argon. The reaction lasted for 1 h. Then gas was stopped to pass through, the mouths were sealed, it was left unstirred for 24 h at room temperature. The solvent was volatilized completely and the product was dried at 60 °C.

2.3. Characterization of PEtCNA

The PEtCNA was characterized by the American NICOLET company's 560 model FT-IR (KBr pressed pellets) and German Bruker 300 MHz superconductive nuclear magnetic resonance (^{1}HNMR spectrum of $CDCl_3$ solution). Its morphology was observed by American AMRAY 1840 model scanning electronic lenses (SEM). The number average (M_n) and weight average (M_w) molecular weight, and molecular weight distribution of the polymers were determined by eluting 1.0% solution of the polymer in tetrahydrofuran, through styragel packed columns by using polystyrene standard on a Shimadsu gel permeation chromatography analyzer of American 244-model SEC instrument produced by WATERS company.

2.4. Degradation percentage of PEtCNA

Five segments of dried PEtCNA were weighed and put into five separate conical beakers, then 20 mL buffer solution of pH = 3.10, 4.00, 6.86, 7.00, 9.11 were added in turn. The prepared ones were placed unstirred in bain-maries at 37 °C for 24 h, and then swilled out by distilled water time and again, oven dried to constant weight and weighed. The degradation percentage can be calculated with the following formula (1) [5].

$$\text{Degradation percentage} = \frac{W_0 - W_1}{W_0} \times 100\% \quad (1)$$

In the above formula, W_0 is the weight (g) before the degradation of PEtCNA, and W_1 is the weight (g) after the degradation of PEtCNA.

2.5. Method of quantum chemical calculation

The molecular geometry, electronic structure, IR spectrum and thermodynamic property of reactant and transition state (TS) on the reaction potential energy level of ethyl α-cyanoacrylate with hydroxyl have been completely optimized and calculated by the density functional theory DFT-B3LYP method, on the level of 6-31 + G* group [6,7] for the first time. The simulation of solvent effect is based on the Onsager self-consistent reaction field (SCRF) technique which supposes that the solute molecule is embedded into a spherical cavity with radius a_0 surrounded and the solvent is represented by a continuous dielectric, characterized by a given dielectric constant (ε). The impacts of solvent effect on the geometries of reactant and transition state as well as the reaction mechanism were systematically studied for the α-cyanoacrylate with water in different dielectric constants of 2.02, 2.38, 7.58 and 12.3. The order of 10^{10} s^{-1} of rate constant calculated in gas phase has been calculated by thermodynamic computation [8–10].

3. Results and discussions

3.1. Experimental results and analysis

3.1.1. Spectral analyses

In IR spectrum, ascription of characteristic absorbing peak of composed PEtCNA is showed as Fig. 1(a) and (b). There exist obvious strong spectrum strips around 2991.2(m, CH_2), 1750(vs, C=O), 1254(vs, C–O) and 2249(m, CN) cm^{-1}, but none at 3129(m, $=CH_2$), 1665 cm^{-1}(w, C=C).

In ^{1}HNMR spectrum as Fig. 2(a) and (b) of $CDCl_3$ solution, proton peak of methylene of main chain is $\delta = 2.5$ (theoretically calculated value $\delta = 1.9$); proton peak of methylene in ester is $\delta = 4.3$ (theoretically calculated value $\delta = 4.1$); proton peak of methyl in ester is $\delta = 1.4$ (theoretically calculated value $\delta = 1.3$). The above results explain that polymerization mechanism is head–tail linkage.

The IR spectrum and ^{1}HNMR spectrum of the PEtCNA indicate that the existence of their major characteristic peak coincide with the anionic polymerization mechanism.

3.1.2. Measuring the molecular weight of PEtCNA

Our experiments prove polymerization in gas can produce poly(ethyl α-cyanoacrylates) with narrow relative molecular weight at room temperature, by using water or sodium hydroxide catalyzed water as initiator, as showed in Table 1, the D is large (1.55, 2.07) because the products do not refine.