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SHORT COMMUNICATIONS

Novel Zwitterionic Alternating Copolymerization of Substituted Acetylenes with 2-Methyl-2-oxazoline

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Spontaneous alternating copolymerization of electrophilic (M_E) with nucleophilic monomers (M_N) *via* zwitterionic intermediates, zwitterionic copolymerization, is very unique since complete alternation of two polar monomers is possible without a catalyst.[1] Since pioneering works on this area were made by Saegusa *et al.*, a wide variety of monomer combinations has been investigated.[1] Not only cyclic monomers including lactones, oxazolines, aziridines but also vinyl monomers[1b] as well as cumulenes[2] undergo zwitterionic alternating copolymerization. This polymerization, however, has not been applied to acetylene derivatives so far in spite of the high reactivity of C-C triple bonds toward various nucleophilic and electrophilic compounds. We demonstrate the first example of the zwitterionic alternating copolymerization of two substituted acetylenes, 4-hydroxybutyl propiolate (**1a**) and 2-hydroxyethyl propiolate (**1b**), with a nucleophilic monomer, 2-methyl-2-oxazoline (**2**) (Scheme 1).

EXPERIMENTAL

General

Molecular weights and distributions were determined by gel permeation chromatography [eluent, tetrahydrofuran (THF); Shodex columns KF-805L, and KF-806L; calibrated by polystyrene standards]. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded with a JEOL EX-400 spectrometer using $CDCl_3$ as a solvent. Acetonitrile and 2-methyl-2-oxazoline were dried over CaH_2 and distilled under nitrogen atmosphere. Nitromethane was dried with P_2O_5 followed by distillation under nitrogen. *N,N*-Dimethylformamide (DMF) was dried with CaH_2 and distilled at reduced pressure. THF was dried from sodium/benzophenone and distilled under nitrogen.

*Preparation of 4-Hydroxybutyl Propiolate (**1a**)*

A benzene solution (60 mL) containing propiolic acid (3.88 g, 55 mmol), 1,4-butanediol (25.0 g, 277 mmol) and *p*-toluenesulfonic acid monohydrate (0.53 g, 2.5 mmol) was refluxed for 10 h. The solution was poured into saturated aqueous $NaHCO_3$, and the organic layer was separated, washed with water several times, and dried over Na_2SO_4. After benzene was removed at reduced pressure, the residue was distilled at reduced pressure. Bp: 93—95℃ (6 mmHg). ^{1}H NMR ($CDCl_3$) δ 1.63—1.70 (m, 2H), 1.73—1.83 (m, 2H), 2.25 (s, 1H), 2.95 (s, 1H), 3.68 (t, 2H, J=8.5 Hz), 4.24 (t, 2H, J=6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 24.7, 28.7, 61.9, 66.1, 74.5, 74.8, 152.8; Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.44; H, 6.97.

*Preparation of 2-Hydroxyethyl Propiolate (**1b**)*

A solution of propiolic acid (7.00 g, 100 mmol) and *p*-toluenesulfonic acid monohydrate (2.60 g, 14 mmol) in ethylene glycol (100 mL) was heated at 60℃ for 24 h. It was then poured into saturated aqueous $NaHCO_3$, and the resulting solution was extracted with ethyl acetate. The organic phase was dried over Na_2SO_4, filtered and condensed. The residue was dissolved with a large amount of water, and the aqueous solution was washed with a small amount of $CHCl_3$. The aqueous solution was extracted with ethyl acetate, and the organic phase was dried over Na_2SO_4, filtered, and concentrated to give **1b** (8.5 g, 74%) as colorless liquid. ^{1}H NMR ($CDCl_3$) δ 2.68 (t, 1H, J=5.8 Hz), 3.02 (s, 1H), 3.87 (dt, 2H, J=5.8, 4.5 Hz), 4.32 (t, 2H, J=4.5 Hz); ^{13}C NMR ($CDCl_3$) δ 60.2, 67.5, 74.2, 75.6, 152.7; Anal. Calcd for $C_5H_6O_3$: C, 52.63; H, 5.30. Found: C, 52.91; H, 5.39.

*Polymerization of ω-Hydroxyalkyl Propiolate (**1**) with 2-Methyl-2-oxazoline (**2**)*

A mixture of **1** (2 mmol) and **2** (2 mmol) was stirred at room temperature for 48 h. The resulting viscous mixture was diluted with THF, and poured into water to precipitate the polymer, which was collected and freeze-dried at reduced pressure. For solution polymerization, 2 mL solvent was used.

RESULTS AND DISCUSSION

Preliminary experiments for the optimization of polymerization conditions using **1a** as an acetylenic monomer indicated polymerization at room temperature in the absence of solvent to give the best yields as well as the molecular weights of copolymers. Bulk copolymerization of **1a** with **2** gave a copolymer with molecular

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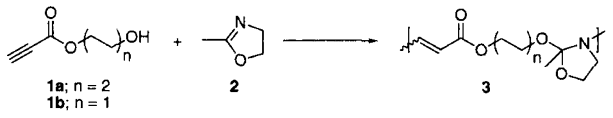


Scheme 1.

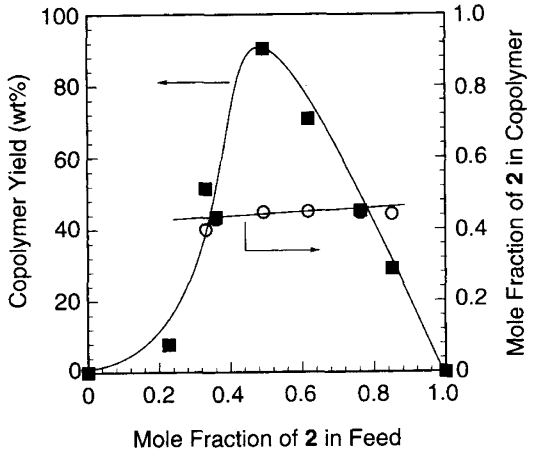


Figure 1. Plots of the copolymer composition (○) and polymer yield (■) *vs.* the mole fraction of **2** in feed for the copolymerization of **1b** with **2**.

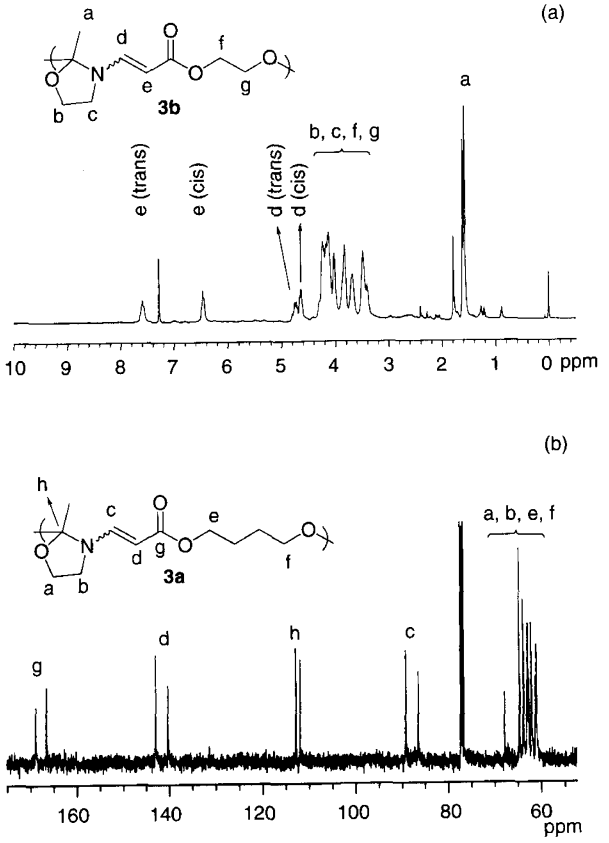


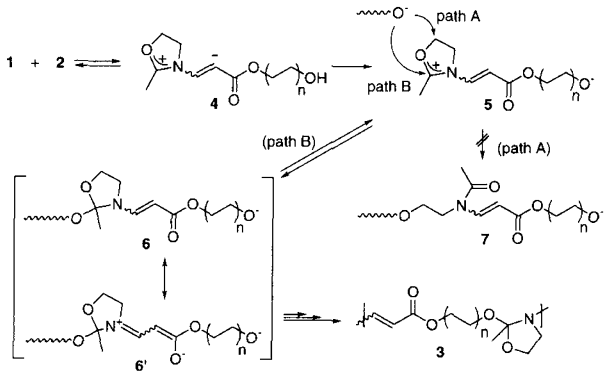
Figure 2. (a) ^{1}H NMR spectrum of the copolymer obtained by the copolymerization of **1b** with **2** and (b) ^{13}C NMR spectrum (expanded) of the copolymer from **1a** with **2** ($CDCl_3$).

weight of 2500 ($M_w/M_n=1.7$) in 78% yield. Polymerization in polar solvents such as acetonitrile, DMF, THF, and nitromethane decreased the yields and molecular weights of the copolymers. The solution polymerization was accompanied by homopolymerization of the individual monomer, in contrast to the zwitterionic copolymerization of oxazolines with 2-hydroxyethyl acrylate, where solution polymerization in polar solvents gives higher yield and molecular weight.[4] Under these optimal conditions, **1b** copolymerized with **2** to give a copolymer with a molecular weight of 1600 ($M_w/M_n=1.7$) in 97% yield.

To confirm the copolymerization mechanism, bulk copolymerizations of **1a** with **2** were carried out by varying the feed ratios of the monomers. As illustrated in Figure 1, no polymer was obtained in the absence of either **1a** or **2**. The homopolymerization of these monomers thus does not occur under the conditions. The yield of the copolymer steeply increased when feed composition approached 1 : 1, and was highest at a 1 : 1 feed ratio. Copolymer compositions calculated by elemental analyses were close to 1 : 1 regardless of the feed composition. These data clearly support that the present polymerization is typical alternating copolymerization.[5]

Characterization of the copolymers was performed by ^{1}H and ^{13}C NMR (Figure 2). Signals observed between 4.5 and 7.8 ppm are assigned as the protons of the double bonds in the main chain (Figure 2a). In addition to the coupling constants of these signals, a comparison of chemical shifts with the expected values calculated using substituent constants gave the assignments of the olefinic signals as shown in Figure 2a. Thus, both *cis* and *trans* geometrical structures are present in the main chain. *Cis/trans* ratios were 48/52 and 57/43 for polymers **3a** and **3b**, respectively. Other signals were assigned as illustrated in Figure 2a. ^{13}C NMR spectra of the produced copolymers gave well resolved signals as demonstrated in Figure 2b, and no carbon signal for the homopolymer of **2** was detected. Several carbons, *i.e.*, carbons c, d, h, and g in polymer **3a**, gave pairs of signals. These peak separations are due to the presence of *cis* and *trans* geometrical structures with respect to the double bonds in the main chain. Low selectivity of the double bond geometry contributed to the observation of more than 6 peaks for carbons a, b, e, and f. The presence of five-membered ring in the main chain was confirmed by the DEPT spectrum of polymer **3b**, in which carbon h was detected as a quaternary carbon.

Generally nucleophiles attack the methylene carbon adjacent to the oxygen atoms of oxazolinium salts to open the ring, giving the corresponding amides. In the homopolymerization of oxazolines, the methylene carbon adjacent to oxygen in the propagating oxazolinium salt is subjected to nucleophilic attack of a monomer, allowing the isomerization of the oxazoline rings to amide groups.[3] Spontaneous alternating copolymerization of **2** with 2-hydroxylethyl acrylate results in the formation of amide groups produced *via* the ring opening of the oxazolinium intermediate.[4] In contrast, alternating co-



Scheme 2.

polymers prepared in the present study involved no amide group, as clearly evident by the absence of amide carbonyl group in the ^{13}C NMR spectra of the copolymers (Figure 2b). No additional carbonyl signal other than those of the ester carbonyl carbons was detected. The observation of no clear ^{1}H signals between 2—3 ppm also denies the presence of the acetamide structure. The oxazoline ring, thus, does not open during the copolymerization and polymers have *N,O,O*-orthoester structures. A plausible polymerization mechanism is illustrated in Scheme 2. The conjugative addition of **2** to the triple bond of **1** results in a zwitterionic species **4**, and the formed carbanion in the zwitterion **4** is subsequently transformed into an alkoxide *via* the proton transfer process to give a zwitterionic intermediate **5**. These reactions are general reactions of the electron-deficient acetylenes with nucleophiles.[6] The alkoxide attacks the carbocation at the 2-position of oxazoline molecule (path B). Repetition of this process leads to copolymer (**3**) having *N,O,O*-orthoester groups in the main chain.

A simple semiempirical calculation of an oxazolinium cation, 2-methyl-2-oxazolinium cation, clearly indicated the enhanced electrophilicity of the carbon at 2-position compared with that at 4-position. Therefore, the nucleophiles kinetically favor attack of the carbon at 2-position (path B). However, in the zwitterionic alternating copolymerization of **2** with 2-hydroxyethyl acrylate, reversibility of this process and the presence of irreversible pathway to form more thermodynamically stable amide groups eventually prefer the ring-opening reaction. Mechanisms for the homopolymerization of oxazolines as well as those for the spontaneous copolymerization of cyclic imino ethers with ω-hydroxyalkyl acrylate are based on this idea. In contrast, zwitterion (**6**) formed by the reaction of two molecules of 5 conjugates with a form **6'**, which thermodynamically promotes path B. Such resonance is not available for copolymerization with ω-hydroxyalkyl acrylate. This resonance effect in the intermediate zwitterionic species excludes path A to provide ring-opened product **7** and results in predominant attack of carbon at 2-position by the nucleophilic site.

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5. As indicated in Figure 1, copolymer compositions were not strictly 1 : 1. One explanation is the effect of terminal groups because zwitterionic copolymerizations generally provide relatively low molecular weight polymers. Another possibility is the presence of side reactions, which may be supported by the presence of undefined signals in ^{1}H NMR around 1 and 2—3 ppm.
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