SHORT COMMUNICATION

Hydrogenation of Alternating Butadiene–Methyl Methacrylate Copolymer

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Electron-donating and -accepting monomer pairs often give alternating copolymers. The addition of Lewis acids such as zinc chloride and ethylaluminum chlorides enables monomer pairs, which otherwise given random copolymers, to give alternating copolymers.¹ Random and alternating copolymers show different physical properties and certain alternating copolymers have proved to be useful materials.^{2,3}

It is yet difficult, however, by directly copolymerizing three monomers to obtain a ternary alternating copolymer in which three monomer units are linked in a definite sequence.

In this communication, we describe an indirect synthesis of an alternating ethylene–ethylene–methyl methacrylate copolymer by hydrogenating the alternating butadiene–methyl methacrylate copolymer. Its characterization and physical properties are also given.

Hydrogenation of diene polymers to give new binary alternating copolymers has been recently reported.^{4,5}

EXPERIMENTAL AND RESULTS

Preparation of Alternating Butadiene–Methyl Methacrylate Copolymer

According to Furukawa *et al.*'s procedure,⁶ butadiene and methyl methacrylate were alternatingly copolymerized. In a nitrogen-purged glass ampoule, purified butadiene and methyl methacrylate were taken at -78°C . Ethylaluminum sesquichloride and vanadyl chloride solutions in hexane were added. The ampoule was sealed off and allowed to stand at 0°C . The copolymerization mixture was poured into methanol containing 1% hydrochloric acid and a trace of *tert*-butylcatechol. The precipitated copolymer was twice reprecipitated from benzene into methanol and freeze-dried from benzene. The copolymer samples were stored under nitrogen to avoid gel formation. The molecular weight of the copolymer sample used for the following experiments was 1.5×10^5 as estimated by gel-permeation chromatography. The copolymer structure was confirmed by infrared (IR) and ^1H nuclear magnetic resonance (NMR) spectra. The butadiene units were essentially of 1,4-*trans* configuration.

Hydrogenation of Alternating Butadiene–Methyl Methacrylate Copolymer

The copolymer sample (1.5 g) dissolved in tetrahydrofuran (50 ml) was magnetically stirred with platinum black⁷ (65 mg). Tiny hydrogen bubbles were passed into the suspension for 4 days. Methanol was added to the solution separated from the settled catalyst. The quantitatively recovered copolymer was freeze-dried from benzene as a white

Figure 1. IR spectrum of alternating butadiene-methyl methacrylate copolymer (before hydrogenation), 0.1 mm chloroform solution.

Figure 2. IR spectrum of alternating ethylene-ethylene-methyl methacrylate copolymer (after hydrogenation), 0.1 mm chloroform solution.

Figure 3. ¹H NMR spectrum of alternating butadiene-methyl methacrylate copolymer (before hydrogenation), deuteriochloroform solution at 60°C.

rubbery solid.

Alternating butadiene-methyl acrylate and -acrylonitrile copolymers were prepared in the same way.

Characterization and Physical Properties of Alternating Ethylene-Ethylene-Methyl Methacrylate Copolymer

Figures 1–4 show the IR and ¹H NMR spectra of the copolymers before and after the hydrogenation. After the hydrogenation, absorptions due to the carbon-carbon double bond in the butadiene unit disappear and methylene absorptions are observed. Since the alternating structure before hydrogenation has been well established by

Furukawa *et al.*,⁶ the hydrogenated copolymer must have the expected alternating ethylene-ethylene-methyl methacrylate structure. The proton noise decoupled ¹³C NMR spectrum of the hydrogenated copolymer in Figure 5 shows seven peaks and therefore clearly demonstrates this structure. Assignment was done by the proton off resonance decoupling technique. The three CH₂ peaks were tentatively assigned according to their distances from the COOH₃ group.

The alternating ethylene-ethylene-methyl methacrylate copolymer is soluble in benzene, chloroform, tetrahydrofuran and insoluble in methanol, ether, petroleum ether, and acetonitrile. From the tetrahydrofuran solution, an almost transpar-

Figure 4. ^1H NMR spectrum of alternating ethylene-ethylene-methyl methacrylate copolymer (after hydrogenation), deuteriochloroform solution at 60°C .

Figure 5. Proton noise decoupled ^{13}C NMR spectrum of alternating ethylene-ethylene-methyl methacrylate copolymer, deuteriochloroform solution at room temperature.

ent film can be cast. A tensile experiment on this film showed that the copolymer is a soft and tough material like an ethylene-vinyl acetate copolymer and breaks at 300% elongation. Differential scanning calorimetry showed a weak endothermic peak at 90°C . X-Ray diffraction pattern showed peaks at $2\theta = 16.1^\circ$, 19.8° , and 23.4° . Both results indicate that the copolymer is partially crystalline.

Hydrogenation of the alternating butadiene-methyl acrylate copolymer gave an alternating ethylene-ethylene-methyl acrylate copolymer. Hy-

drogenation of the alternating butadiene-acrylonitrile copolymer under the same conditions was unsuccessful, probably because of the interference of the nitrile group.⁸

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