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Polymerization of 1,3-Dienes with Functional Groups. 1. Free-Radical Polymerization of 2-Triethoxymethyl-1,3-butadiene

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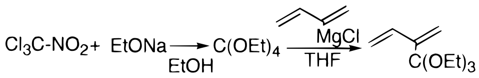
ABSTRACT: Free-radical polymerization behavior of 2-triethoxymethyl-1,3-butadiene, a potential precursor for poly[2-(ethoxycarbonyl)-1,3-butadiene], whose carboxyl group was masked as an ortho ester, was investigated. When polymerization was carried out in bulk at 60 °C for 50 h with using 1 mol % of 2,2′-azobisisobutyronitrile as an initiator, viscous polymer was obtained in 36% yield without forming gel. The resulting polymer containing an ortho ester function was soluble in common organic solvents, including methanol. It can readily be converted to carboxylic ethyl ester by adding small amount of dilute hydrochloric acid. The microstructure of the resulting polymer with ethyl ester group was predominantly a 1,4-*E*, cis-1,4 structure about the main chain.

Introduction

There have been many reports on the free-radical polymerization of vinyl monomers.[1] Although this polymerization mechanism is applicable to a variety of monomers; however, polymerization of 1,3-butadiene derivatives containing functional groups is still quite limited. This was presumably due to the fact that functional groups directly attached to the polymerizable 1,3-butadienyl skeleton often affect the stability and the polymerizability of the dienes. As a matter of fact, nonfunctional alkyl-, phenyl-, and halogen-substituted butadienes were reported to give high polymers by free-radical polymerization.[2] On the other hand, some functional groups, especially those substituted at the 2 position of the butadienyl frame, decrease the stability of the monomer. To our knowledge, 1,3-butadiene derivatives having a carboxyl group and its ester at the 2 position have not been isolated whereas its isomer, ethyl 2,4-pentadienoate, was synthesized and polymerized under ordinary reaction condition.[3] 2-Cyano-1,3-butadiene is reported to dimerize upon heating under polymerization conditions.[4] These reactions are presumably due to the high tendency of the reactants to form Diels−Alder dimers, which is caused by the electron-withdrawing character of the functional group. One of the methods to overcome this difficulty would be the transformation of such functional groups to the other group, which is inert during the polymerization. We chose here an ortho ester function, the trialkoxymethyl group, as a suitable masking group of carboxyl group. This protecting group is known to be stable under basic and neutral conditions whereas it can readily be hydrolyzed to carboxylic ester under mild acidic condition.[5] There have been a few examples where the ortho ester was applied for polymer syntheses. Padis and Hall have reported the free-radical polymerization of methacrylates containing bicyclic ortho ester group.[6] Ishizone et al. used the same protecting group for the anionic polymerization of styrene derivatives containing three hydroxyl groups in each of the monomer units.[7] The bicyclic ortho esters are reported to be more stable than acyclic ortho esters such as the triethoxymethyl group.[5] Because polydienes are potentially to be cross-linked under acidic conditions, the protecting group should be cleaved with as mild of conditions as possible. From this point of view, we employed the triethoxymethyl group as a protecting group for the carboxyl function. In this paper, the free-radical polymerization behavior of 2-triethoxymethyl-1,3-butadiene, **1**, and the microstructure of the resulting polymer will be described.

Scheme 1



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Experimental Section

Synthesis of 2-Triethoxymethyl-1,3-butadiene. 2-Triethoxymethyl-1,3-butadiene was prepared as shown in Scheme 1. Tetraethyl orthocarbonate was prepared according to the reported procedure.[8] In a three-necked round-bottomed flask equipped with a mechanical stirrer, dropping funnel, and reflux condenser, 12 g (62.8 mmol) of tetraethyl orthocarbonate and dry tetrahydrofuran (THF, 12 mL) were charged under nitrogen atmosphere. A THF solution of 2-(1,3-butadienyl)magnesium chloride (250 mmol, 160 mL) was added dropwise at 55−65 °C in 1 h. The reaction mixture was further stirred at that temperature for 48 h. After removing ca. 100 mL of THF under reduced pressure, the reaction mixture was poured into ice-cooled aqueous ammonium chloride and extracted three times with ether. Then the combined organic layer was washed with water and dried with anhydrous magnesium sulfate. The title compound was isolated as a colorless liquid by distillation under reduced pressure. (Bp 45 °C/3 mmHg, Yield 44%). ^{1}H NMR: δ 1.16 (t, 9H, J = 7.0 Hz, $-CH_3$), 3.39 (q, 6H, J = 7.0 Hz, $-CH_2$), 5.08 (d, 1H, J = 11.2 Hz, $-CH{=}CH_2$), 5.45, 5.56 (2s, 2H, $-C{=}CH_2$), 5.68 (d, 1H, J = 17.6 Hz, $-CH{=}CH_2$), 6.23 (dd, 1H, J = 11.2, 17.6 Hz, $-CH{=}CH_2$). ^{13}C NMR: δ 14.9 ($-CH_3$), 57.2 ($-OCH_2$), 112.8 (${=}C-C-O$), 116.1 ($-CH{=}CH_2$), 118.6 ($-C{=}CH_2$), 133.8 ($-CH{=}CH_2$), 142.3 ($-C{=}CH_2$).

IR (NaCl plate): 2979, 2932, 2894 (aliphatic C−H stretch), 1593 (C=C, stretch), 1113−1048 (C−O−C, stretch), 922 (=C−H, out-of-plane, deformation).

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Free-Radical Polymerization. Free-radical polymerization of 2-triethoxymethyl-1,3-butadiene was performed in sealed glass tube in bulk with an appropriate amount of azobisisobutyronitrile (AIBN) as an initiator. The reaction mixture was degassed three times by the freeze−thaw method and sealed under vacuum. It was allowed to stand still in an oil bath for an appropriate time for polymerization. Then it was diluted with benzene, and the amount of residual monomer was measured by gas chromatography. Before reprecipitation, ethanol and a few drops of dilute hydrochloric acid were added to the polymerization mixture to convert the ortho ester function to the carboxylic ester. The polymer thus obtained was precipitated thrice from benzene into ethanol.

Measurements. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ with a JEOL EX-400 spectrometer in the Fourier transform mode. IR spectra were recorded with a Shimadzu DR-8000 spectrophotometer. Size-exclusion chromatography was performed with a Tosoh HLC-8020 instrument at 40 °C with the differential refractive index detector. THF was used as an eluent at the flow rate of 1 mL/min. Two polystyrene gel columns (TSK-gel GMH_{HR}-M, 7.8 mm i.d. × 30 cm), calibrated with standard polystyrene samples, were used.

Results and Discussion

Synthesis of 2-Triethoxymethyl-1,3-butadiene. Although several methods have been reported on the synthesis of acyclic ortho ester up to now, nucleophilic substitution of tetraalkyl orthocarbonate with Grignard reagent is one of the simplest ways. This method is useful if the selectivity of the substitution reaction is high enough to give a monosubstituted product, i.e., an ortho ester. Chichibabin emphasized[9] that short reaction times and relatively low reaction temperatures are essential if the reaction is to yield ortho esters rather than acetal, disubstituted product. In light of these reports, 2-(1,3-butadienyl)magnesium chloride was allowed to react with a 2 times excess amount of tetraethyl orthocarbonate in THF at −30 to 0 °C for 24 h. Surprisingly no reaction took place under the reaction conditions employed. It was necessary to use a 4 times excess amount of Grignard reagent at 50−60 °C to obtain the desired ortho ester compound in moderate yield. No disubstituted product was formed, even in the presence of excess Grignard reagent. This indicates that the nucleophilicity of the 2-(1,3-butadienyl)magnesium chloride is very low, presumably because of the resonance structure of butadienyl anion and steric hindrance.

Homopolymerization. Free-radical homopolymerization was performed in sealed glass-tubes. Because the monomer synthesized in this study always contained a few percentage of tetraethyl orthocarbonate, the amount of the monomer consumed was measured by gas chromatography (GC) using this impurity as the internal standard.

The result of bulk polymerization was summarized in Table 1. When the monomer was heated in bulk at 60 °C for 20 h without using initiator, no monomer was consumed. Neither polymer nor Diels−Alder product was formed at all, indicating that 2-triethoxymethyl-1,3-butadiene has low thermal polymerizability. It is also notable that a Diels−Alder reaction did not take place in this system. In a previous paper, we reported that trialkoxysilyl-1,3-butadiene, a silicon analogue of the monomer used in this study, had a strong tendency to form Diels−Alder dimers under similar polymerization conditions.[10] The substituent directly attached to the polymerizable group might have affected the reactivity of dienyl group.

Table 1. Free-Radical Polymerization of 2-Triethoxymethyl-1,3-butadiene in Bulk at 60 °C

AIBN (× 10^{-2} mol/L)	**1** (mol/L)	time (h)	conv. (%)	M_n (× 10^4)	M_w/M_n
0	4.50	20	0		
4.60	4.50	5	3.9	1.0	2.6
4.60	4.50	30	22	2.4	1.8
4.60	4.50	50	36	2.1[a]	3.5[a]
0.92	4.50	30	7.0	1.9	3.0
2.30	4.50	20	45	1.3	1.8

[a] Measured in the carboxylic ester form after hydrolysis of the ortho ester.

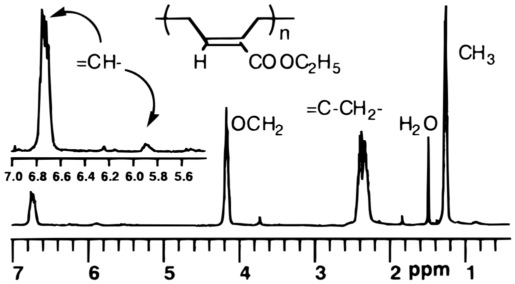

Figure 1. ^{1}H NMR spectrum of poly[2-(ethoxycarbonyl)-1,3-butadiene].

Free-radical polymerization proceeded smoothly when heated with an appropriate amount of AIBN at 60 °C. Although the polymerization was carried out in bulk, the rate of polymerization was extremely slow, and only 36% of the monomer was consumed in 50 h. The amount of the monomer consumed agreed well with the value calculated from the polymer yield. This indicates that low-molecular-weight oligomers such as the Diels−Alder dimer were not formed during the course of polymerization. No gelation was observed even at high conversion. Because the resulting polydienes containing the triethoxymethyl function was soluble in most of the common organic solvents, a sticky polymer was isolated after hydrolysis to carboxylic ethyl ester form.

Microstructure of Resulting Polymers. In the study of diene polymerization, control and analysis of the microstructure of the resulting polymer is of considerable interest because the physical properties of polydienes strongly depend on the microstructure. In this study, the mode of the monomer addition (1,4, 1,2, or 3,4) and the geometry of the repeating unit (1,4-*E* or 1,4-*Z*) were analyzed by NMR.

Figure 1 shows the ^{1}H NMR spectrum of the resulting polymer in carboxylic ethyl ester form. As can be seen, methyl and methylene proton signals attributable to ethyl ester were clearly observed at 1.2 and 4.1 ppm, respectively. Methylene protons in the main chain adjacent to the carbon−carbon double bond were also observed around 2.3 ppm. In the olefinic region, two signals were observe at 5.8 (minor) and 6.7 ppm (major). The relative integrated intensity of these signals was $I(1.2)/I(4.1)/I(2.3)/I(5.8 + 6.7) = 3:2:4:1$. This clearly indicates that the resulting polymer has exclusively 1,4-structure. The two signals in the olefinic region may be attributable to the geometric isomers 1,4-*E* and 1,4-*Z*. The assignment of these signals was carried out by

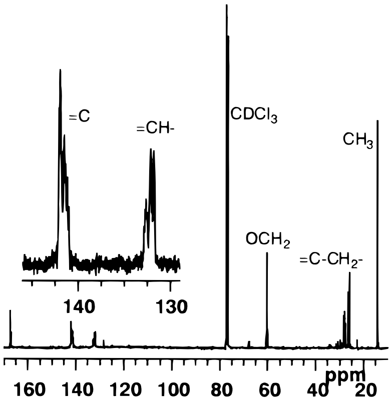

Figure 2. ^{13}C NMR spectrum of poly[2-(ethoxycarbonyl)-1,3-butadiene].

comparing the chemical shifts with those of *E*- and *Z*-ethyl 2-propyl-2-propenoate, which imitate the 1,4-*E* and 1,4-*Z* structures of the polymer chain, respectively. The olefinic proton of the former isomer resonates at 6.7 ppm, and the latter resonates at 5.8 ppm. These chemical shifts were assigned by differential nuclear Overhauser effect (NOE) spectra because the model compounds were obtained as a mixture of two geometric isomers.[11]

As can be seen in Figure 1, the 1,4-*E*, the cis-1,4 structure of main chain, predominates in the polymers obtained in this study. The relative intensity of olefinic proton signals at 6.7−5.8 ppm was 95:5, indicating that 95% and 5% of the cis and trans 1,4 structures, respectively, were included in the polymer. A similar tendency was observed in the free-radical polymerization of 1,3-dienes containing bulky substituents on the 2 position of the butadienyl skeleton such as 2-tributylstannyl-1,3-butadiene[12] and 2-triisopropoxysilyl-1,3-butadiene.[10] In either case, the steric hindrance might have controlled the microstructure as pointed out in a literature.[13]

Figure 2 shows ^{13}C NMR spectra of the polymer. A quaternary carbon signal attributable to ortho ester was not observed around 110 ppm whereas a carbonyl signal appears at 167 ppm, indicating the complete hydrolysis of the ortho ester to the carboxylic ester. In the olefinic carbon region, methine and quaternary carbons of the main chain were observed around 132 and 143 ppm, respectively. In the aliphatic region, methylene carbons of the main chain were observed at 25−29 ppm. It should be noted that these signals show complicated splitting although the geometry of the monomer unit is almost uniform as described above. One of the likely explanation for this is that the splitting is caused by the irregular addition of a monomer to the propagating radicals, i.e., 1,4 addition or 4,1 addition. The mode of monomer addition will be discussed separately in the near future.

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