Free-radical polymerization of tetraethyl (2,3-dimethylenebutane-1,4-diyl)bis(phosphonate)

Katsuhiko TAKENAKA*, Mayumi ARIMOTO, Hiroki TAKESHITA, Masamitsu MIYA, and Tomoo SHIOMI

Department of Materials Science and Technology, Nagaoka University of Technology, 1603–1 Kamitomioka, Nagaoka, Niigata 940–2188, Japan

*Corresponding Author: ktakenak@vos.nagaokaut.ac.jp

Received October 24, 2012; Accepted April 19, 2013
©2013 The Society of Rubber Science and Technology, Japan

Abstract Free-radical polymerization of tetraethyl (2,3-dimethylenebutane-1,4-diyl)bis(phosphonate), a 1,3-butadiene derivative containing two diethyl phosphonate functions in a molecule, was carried out under various conditions. When polymerization was performed in benzene at 60°C for 21 h with using 1 mol% of 2,2’-azobisisobutyronitrile as an initiator, sticky polymer was obtained in 70% yield without forming gel. Number average molecular weight of the polymer thus obtained was estimated to be 69,000 by SEC based on polystyrene calibration using N,N-dimethylformamide as an eluent. The rate of polymerization was found to be proportional to 0.5 and 1.5 power of the initiator and the monomer concentration, respectively. The overall activation energy of polymerization was determined to be 91.4 kJ/mol. The microstructure of the polymer was exclusively 1,4- but both E and Z configurations were contained. Glass transition temperature of the polymer was –18°C. Monomer reactivity ratio of the monomer with styrene as comonomer was determined to be r_E=0.15, r_Z=6.1.

Keywords Tetraethyl (2,3-dimethylenebutane-1,4-diyl)bis(phosphonate), 1,3-butadiene derivative, radical polymerization, kinetics; microstructure, copolymerization

Introduction

There have been many reports on the free-radical polymerization of vinyl monomers1). Although there are some limitations, this polymerization mechanism is also applicable to a variety of 1,3-dienyl monomers containing functional groups. The polymerizations of 1,3-butadiene derivatives containing cyanomethyl2,3), N,N-dialkylaminomethyl4,5) and 4-ethoxy-4-oxobutyl6) groups have been reported. Though an appropriate methylene spacer was introduced between the functional groups and the polymerizable dienyl function in these cases, it is also possible to introduce functional groups directly onto butadienyl group. Free-radical polymerization of 1,3-butadiene derivatives containing dialkylamide7–9), triethoxymethyl10), and triethoxyxysilyl11) groups were reported.

Among variety of functional groups, phosphonic acid ester is one of the most attractive functional groups. Phosphorus containing polymers found applications in many fields. Dental adhesives, ion-exchange resins, and flame retardants are just some of the more common applications12–15). Although many reports concerning the polymerization of vinyl, allyl, styryl, and methacrylate type monomers containing this functions16) are known, there were few report on the polymerization of 1,3-butadiene derivatives containing phosphoric ester function.

In our previous report, we have discussed the free-radical polymerization behavior of diethyl (2-methylenebut-3-en-1-yl)phosphonate, 1, a 1,3-butadiene derivative containing one phosphoric ester group on the side chain17). Sticky polymer was obtained in moderate yield by bulk and solution polymerization in benzene. However, thermal polymerization and Diels-Alder dimerization of 1 was hard to avoid even in the solution polymerization. Microstructure was a mixture of 1,4-E, 1,4-Z, and vinyl structures.

On the other hand, 1,3-butadine derivative having bulky substituents on 2- and 3- position are reported to
give polymer of high 1,4-structure. If so, introduction of the second phosphonate ester group to 1 may be useful to give polymer of highly controlled microstructure. In this paper, we would like to report the free-radical polymerization of tetraethyl (2,3-dimethylenebutane-1,4-diyl) bis(phosphonate), 2, a 1,3-butadiene derivative containing two diethyl phosphonate functions in a molecule.

**Experimental**

**Materials**

Absolute THF (BHT free grade) was purchased from Kanto Chemical Co. Ltd. Diethyl ether was dried with CaH₂ and distilled under nitrogen atmosphere. Zinc-copper couple was prepared from zinc dust and copper sulfate according to the reported procedure. Triethyl phosphite was distilled from CaH₂ under reduced pressure. 2,3-Dimethyl-1,3-butadiene (Aldrich), bromine, N-bromosuccinimide, benzoyl peroxide were used as received.

**Synthesis of monomer and model compounds**

Tetraethyl (2,3-dimethylenebutane-1,4-diyl)bis(phosphonate), 2, was prepared via 3 steps from 2,3dimethyl-1,3-butadiene as shown in scheme 2.

1,4-Dibromo-2,3-bisbromomethyl-2-butene: Starting from 30 g (0.37 mol) of 2,3-dimethyl-1,3-butadiene, 92.3 g (0.23 mol) of tetrabromide was obtained after recrystallization from ethyl acetate. mp: 160°C. 1H NMR: δ 4.14 (s, 8H, CH₂), 13C NMR: δ 27.8 (CH₂), 137.1 (C=), MS (EI): 400 (M +), 319 (M-Br +), 239 (M-2Br+), 159 (M-3Br+).

2,3-Bisbromomethyl-1,3-butadiene: 2,3-Bisbromomethyl-1,3-butadiene was prepared according to the reported procedure with modification. A 3L three-neck round-bottomed flask equipped with overhead stirrer and thermometer was filled with nitrogen atmosphere. Triethyl phosphite was distilled from CaH₂ under reduced pressure. 2,3-Dimethyl-1,3-butadiene (Aldrich), bromine, N-bromosuccinimide, benzoyl peroxide were used as received.

2,3-Bisbromomethyl-1,3-butadiene: 2,3-Bisbromomethyl-1,3-butadiene was prepared according to the reported procedure with modification. A 3L three-neck round-bottomed flask equipped with overhead stirrer and thermometer was filled with nitrogen atmosphere. Triethyl phosphite was distilled from CaH₂ under reduced pressure. 2,3-Dimethyl-1,3-butadiene (Aldrich), bromine, N-bromosuccinimide, benzoyl peroxide were used as received.

2,3-Bisbromomethyl-1,3-butadiene was prepared according to the reported procedure with modification. A 3L three-neck round-bottomed flask equipped with overhead stirrer and thermometer was filled with nitrogen atmosphere. Triethyl phosphite was distilled from CaH₂ under reduced pressure. 2,3-Dimethyl-1,3-butadiene (Aldrich), bromine, N-bromosuccinimide, benzoyl peroxide were used as received.

Tetraethyl (2,3-dimethylenebutane-1,4-diyl)bis(phosphonate): In a 100 mL round-bottomed flask equipped with reflux condenser, 2,3-bisbromomethyl-1,3-butadiene (4.82 g, 20.1 mmol), triethyl phosphite (10.22 g, 61.6 mmol) and hydroquinone (1.0 g 9 mmol) were added and refluxed for 1 h. The progress of the reaction was monitored by gas chromatography. After reaction, residual metallic compound was removed by hot filtration and the filtrate was washed with water. The resulting organic layer was dried with anhydrous magnesium sulfate. After usual workup, aimed product was isolated by recrystallization at 5°C. Yield: 20 g, 69%, mp 57°C. 1H NMR: δ 4.17 (s, 4H, Br-CH₂), 5.51, 5.54 (2s, 4H, =CH₂) 13C NMR: δ 32.7 (Br-CH₂), 140.7 (C=CH₂), 119.2 (C=CH₂), MS (EI): 240 (M⁺), 159, 161 (M-Br⁺), 79 (M-2Br⁺).

**Scheme 2**

(E)- and (Z)-(E)- mixture of tetraethyl (2,3-dibutyl but-2-ene-1,4-diyl)bis(phosphonate): Low molecular weight model compounds that imitate the 1,4-structure of poly(2) were prepared according to scheme 3. Bromination of 2,3-dibutyl-1,3-butadiene gave 1,4-addition product exclusively. Although the initial product was a...
mixture of geometric isomers (major: minor = 87:13), the major isomer was isolated by recrystallization from pentane. The absolute configuration of this isomer determined by X-ray structural analysis was (E). Since the configuration should not change by the following Arbuzov reaction, it gives model compounds imitating the 1,4-structure of the polymer. 1,4-(E)-Mixture of tetraethyl (2,3-dibutylbut-2-ene-1,4-diyl)bis(phosphonate): In a round-bottomed flask equipped with condenser, (E)-5,6-bisbromomethyl-5-decene (0.72 g, 2.2 mmol) and triethyl phosphate (1.6 g, 9.6 mmol) were charged under nitrogen atmosphere, and heated to 100°C for 3 h. The progress of the reaction was monitored by gas chromatography. After complete consumption of starting dibromide was confirmed, residual triethyl phosphate and other volatile compound were evacuated under vacuum. Then aimed product was isolated as colorless liquid by distillation under vacuum.

(E)-5,6-Bisbromomethyl-5-decene: To the stirred mixture of n-propylmagnesium bromide (100 mmol) and THF solution of Li₂CuCl₄ (0.1 mmol), 2,3-bisbromomethyl-1,3-butadiene (4.8 g, 20 mmol) in 60 mL of THF was added dropwise at 0°C. After addition, the reaction mixture was stirred at 20°C for additional 4 h, and quenched with HClaq. It was extracted three times with ether. After usual workup, 2,3-dibutyl-1,3-butadiene was isolated as colorless liquid by distillation under reduced pressure. Yield 50%, bp. 60°C/3 mm Hg. ¹H NMR: δ 4.98, 4.84 (2s, 4H, =CH₂), 2.15 (t, 4H, J=6.0 Hz, =C-CH₂), 1.35 (m, 4H, =C-CH₂ CH₃), 1.26 (m, 4H, CH₃-CH₂), 0.83 (t, 6H, J=6.88 Hz, CH₃), ¹³C NMR: δ 147.9 (=C), 111.2 (=CH₂), 33.9 (=C-CH₂), 30.8 (=C-CH₂-CH₂), 22.6 (CH₃-CH₂), 13.9 (CH₃)

(E)-5,6-Bisbromomethyl-5-decene: In a two-necked flask equipped with pressure-equalizing dropping funnel and condenser, CCl₄ (100 mL) solution of 2,3-dibutyl-1,3-butadiene (4.33 g, 26 mmol) was charged to 0°C. Bromine (7.77 g, 3.6 mmol) in 50 mL of CCl₄ was slowly added and stirred for 1 h at that temperature. Then the reaction mixture was added to aqueous solution of sodium thiosulfate and extracted two times with CCl₄. The combined organic layer was dried with anhydrous MgSO₄. After usual workup, colorless crystal was obtained as a mixture of geometric isomers, (E) and (Z). The major component (87%) was isolated by recrystallization from pentane. Yield 32%, mp. 52°C. The geometry of the purified crystal was determined to be (E) by X-ray structural analysis at −180°C. ¹H NMR: δ 3.99 (s, 4H, Br-CH₂), 2.24 (t, 4H, J=7.59 Hz, =C-CH₂) 1.45 (m, 4H, =C-CH₂-CH₂), 1.35 (m, 4H, CH₂-CH₃), 0.91 (t, 6H, J=7.19 Hz, CH₃), ¹³C NMR: δ 137.7 (=C), 32.0 (Br-CH₂), 30.9 (=C-CH₂-CH₂), 30.8 (=C-CH₂-), 22.9 (CH₃-CH₂), 13.9 (CH₃)

(E)-tetrachloro (2,3-dibutylbut-2-ene-1,4-diy)bis(phosphonate): In a round-bottomed flask equipped with condenser, (E)-5,6-bisbromomethyl-5-decene (0.72 g, 2.2 mmol) and triethyl phosphate (1.6 g, 9.6 mmol) were charged under nitrogen atmosphere, and heated to 100°C for 3 h. The progress of the reaction was monitored by gas chromatography. After complete consumption of starting dibromide was confirmed, residual triethyl phosphate and other volatile compound were evacuated under vacuum. Then aimed product was isolated as colorless liquid by distillation under vacuum.

¹H NMR: δ 4.02 (pent, 8H, J=7.0 Hz, ³¹⁷P-D-C-H=7.0 Hz, O-CH₂), 2.56 (d, 4H, J=19.2 Hz, P-CH₂), 2.19 (t, 4H, J=7.3 Hz, =C-CH₂-CH₂), 1.20–1.30 (m, 8H, =C-CH₂-CH₂-CH₂), 1.24 (t, 12H, J=7.00 Hz, OCH₂-CH₂), 0.83 (t, 6H, J=7.1 Hz, CH₃), ¹³C NMR: δ 128.0 (=C), 61.6 (O-CH₂), 32.2 (P-CH₂), 30.1 (=C-CH₂-CH₂), 28.6 (=C-CH₂-CH₂), 22.6 (CH₂-CH₂-CH₂), 16.4 (O-CH₂-CH₂), 14.0 (CH₃), ³¹P NMR: δ 28.6

(E),(Z)-Mixture of tetrachloro (2,3-dibutylbut-2-ene-1,4-diyl)bis(phosphonate) was prepared by photoisomerization of (E)-5,6-bisbromomethyl-5-decene followed by the reaction with triethyl phosphate. Photoisomerization was carried out in a quartz test tube. A 0.45 g of (E)-5,6-bisbromomethyl-5-decene, 1 drop of thiophenol was dissolved in 2 mL of hexane and charged in a quartz test tube under nitrogen atmosphere. It was stand still for 24 h under irradiation of UV light by high-pressure mercury lamp. After isomerization, hexane was removed under reduced pressure and Arbuzov reaction was carried out same as the case of (E) isomer.

³¹P NMR: δ 28.6 (E) isomer, 28.9 (Z) isomer

Free-radical polymerization
Polymerization was carried out in a sealed glass tube in benzene using AIBN as an initiator. After polymerization, the reaction mixture was poured into large excess of hexane to precipitate polymer. It was purified by reprecipitation additional two times by benzene/hexane, and freeze-dried from benzene solution. For the measurement of the rate dependence on monomer and initiator concentra-
tion and temperature, aimed amount of AIBN and 2 were weighed in a 5 mL volumetric flask and diluted with benzene. Then the solution was split into small ampoules and polymerized under different conditions. Conversion was determined by $^1$H NMR measurement.

**Measurements**

$^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded by a JEOL JNM-AL-400 spectrometer in CDCl$_3$. The solvent peak was used as a reference for $^1$H and $^{13}$C measurement. In the case of $^{31}$P measurement, chemical shift of trimethylphosphite was used as external reference. Gas chromatograph-mass spectrum (GC-MS) was measured by Shimadzu GCMS-QP2010Plus with EI mode. UV spectrum of the monomer was recorded on JASCO V-660 spectrophotometer. Size exclusion chromatography (SEC) was obtained at 40°C with a TOSOH HLC-8020 instrument equipped with two polystyrene gel columns (TOSOH TSKgel GMH$_{w}$t-M (7.8 mm×30 cm)) with refractive index detector. $N,N$-Dimethylformamide (DMF) was a carrier solvent at the flow rate of 1 mL/min. Calibration curve was made to values with standard polystyrene samples. The glass transition temperatures of the polymer were determined with Perkin Elmer PYRIS 1 differential scanning calorimeter (DSC) at a heating rate of 20°C/min with nitrogen purge. Single crystal X-ray structural analysis was done on Rigaku Saturn724 diffractometer at −180°C using multi-layer mirror monochromated Mo Kα radiation ($\lambda$=0.71075 Å).

**Results and Discussion**

In our previous paper, we have reported the free-radical polymerization behavior of diethyl 2-methylene-3-butenylphosphonate, 1, a 1,3-butadiene derivative containing one diethyl phosphonate function in the monomer unit 17). Since this monomer had strong tendency to undergo thermal polymerization and Diels-Alder dimerization, free-radical polymerization of 2 under similar condition was performed to check the effect of the second diethyl phosphonate group.

When bulk polymerization of 2 was carried out with using 1 mol% of AIBN at 60°C for 21 h, approximately 30% of monomer was consumed to give sticky polymer. The number average molecular weight of the polymer was estimated to be 67,000 based on SEC measurement in DMF. The monomer consumption is slightly slower than that of 1 where 47% of monomer was consumed under the identical condition. On the other hand, 69% of 2 was consumed in the solution polymerization in benzene. This might be the viscosity effect of the polymerization mixture. Since bulk monomer of 2 is highly viscous even at the polymerization temperature, it might have lowered the initiation efficiency by the cage effect, resulting in the low conversion.

Table 1 shows result of solution polymerization of 2 under various conditions. When benzene solution of 2 was heated at 60°C for 21 h in the absence of AIBN, neither polymerization nor Diels-Alder dimerization took place. In the case of previously reported polymerization behavior of 1, monomer consumption by thermal polymerization or Diels-Alder dimerization was hard to suppress even in a dilute solution in benzene. Bulky substituents on C2 and C3 position of the monomer might have reduced not only polymerizability but also Diels-Alder dimerization reactivity by making the butadienyl skeleton have out-of-planar conformation as shown in scheme 4.

Similar low polymerizability was reported for 2,3-di-tert-butyl-1,3-butadiene22). However, if the dihedral angle of butadienyl skeleton C$_1$=C$_2$−C$_3$=C$_4$ is as large as 90°, it may cause the lack of conjugation resulting in the short UV absorption wave length, less than 200 nm. The actual $\lambda$$_{max}$ of 2 was 230, which is slightly shorter than that of 1,3-cyclohexadiene having planar s-cis dienyl skeleton and close to that of 1,3-butadiene in s-trans conformation. Therefore 2 should behave as conjugated monomer.

As can be seen from the table, molecular weight of the resulting polymer decreased with the increase of initiator concentration and elevation of the polymerization tem-

| Table 1. Free-radical polymerization of 2 in benzene$^a)$. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| AIBN mol%      | Temperature °C  | Time h          | Conversion %    | Mn$^b)$ kg/mol  | Mw/Mn           |
| 0              | 60              | 21              | 0               | –               | –               |
| 0.1            | 60              | 21              | 35              | 446             | 1.22            |
| 0.1            | 80              | 5               | 60              | 159             | 1.98            |
| 1              | 60              | 21              | 69              | 69              | 1.85            |
| 1              | 80              | 5               | 57              | 46              | 1.84            |
| 1.9            | 60              | 21              | 85              | 46              | 2.34            |
| 1.9            | 80              | 5               | 79              | 13              | 2.10            |

a) $[2]=1.0$ mol/L in benzene
b) Measured by SEC using DMF as eluent and based on polystyrene calibration.
perature, showing the ordinary free-radical polymerization behavior. Resulting poly(2) was sticky solid at room temperature. Table 2 summarizes the solubility of the resulting polymers. Solubility of poly(1) and polyisoprene are also shown in the table as a reference. It is obvious that both poly(1) and poly(2) are soluble in variety of polar solvent such as water, methanol, and DMF but insoluble in non-polar aliphatic hydrocarbon solvent. Though poly(1) and poly(2) was soluble in THF, they were not eluted from SEC column using THF as an eluent, presumably due to adsorption to polystyrene gel. If DMF was used as an eluent, ordinary chromatograms were obtained.

As we discuss in the later section, the microstructure of poly(2) was exclusively 1,4-structure. The glass transition temperature of poly(2) was −18°C, which is higher than that of poly(1).

### Kinetics of Homopolymerization

Through the study of diene polymerizations, the Diels-Alder dimerization and thermal polymerization are not favorable since they may increase the apparent rate of monomer consumption and make the analysis of the polymerization kinetics complicated. In the previous paper, it was very difficult to determine the accurate rate equation of polymerization of 1 because of thermal polymerization. As mentioned in the previous section, AIBN-initiated polymerization of 2 in benzene was not accompanied by thermal polymerization. Therefore we have checked the polymerization rate dependence on the initiator concentration, monomer concentration, and polymerization temperature.

Table 3 summarizes the result of free-radical polymerization of 2 in benzene at low conversion. Conversion was determined by 1H NMR analysis of the polymerization mixture. In this region, conversion was found to be proportional to the reaction time. The rate of polymerization ($R_p$) was determined by the slope of the time-conversion curves.

The dependences of $R_p$ on the initiator and monomer concentrations were investigated at 60°C. Figure 1 and 2 show the double logarithmic plot of $R_p$ vs. AIBN and 2 concentrations, respectively. As can be seen, these plots showed good linearity. Thus the rate of polymerization can be expressed.
Based on the slopes of the plots. Though the rate dependence of the initiator concentration obeys the usual free-radical polymerization kinetics, slightly higher dependence on the monomer concentration was observed. One of the likely explanations for this rate dependence would be partial primary radical termination reaction.

The effect of the polymerization temperature on $R_p$ was examined in the range of 50–80°C. The Arrhenius plot is shown in Figure 3. From the slope of the Arrhenius plot, the overall activation energy of polymerization ($E_a$) was calculated to be 91.7 kJ/mol. In the presence of initiator, the overall activation energy is given by

$$E_a = E_p/2 + E_t/2$$

where $E_p$, $E_t$, and $E_i$ are the activation energies of initiation, propagation, and termination steps, respectively. Using the literature value of 128 kJ/mol for $E_p$, one can calculate $E_p - E_i/2$ as 27.2 kJ/mol.

**Microstructure of poly(2)**

Through the study of the diene polymerization, control and analysis of the microstructure of the polymer obtained is of considerable interest because the physical properties of the polydiienes strongly depends on the microstructure. In this study, the microstructure of the resulting polymer was analyzed by $^1$H and $^{31}$P NMR.

Figure 4 shows the $^1$H NMR spectrum of the polymer obtained at 60°C. In the aliphatic proton region, four individual signals were clearly observed at 1.2, 2.2, 2.8, and 4.0 ppm. Methyl and methylene protons of phosphonic ester group were observed around 1.2 and 4.0 ppm, respectively. Allylic methylene protons in main chain and methylene protons adjacent to phosphonate group were observed at 2.2 and 2.8 ppm, respectively. The relative integrated intensity of these signals were found to be $I_{1.2} : I_{2.2} : I_{2.8} : I_{4.0} = 12 : 4 : 4 : 8$. On the other hand, no signals were observed in the olefinic proton region. These results strongly indicate that the poly(2) obtained in this study is composed of 1,4-structure exclusively.

Further information on the geometry of monomer unit, 1,4-$E$ and $Z$, was provided by $^{31}$P NMR analysis. Figure 5 shows $^{31}$P NMR spectra of poly(2) with and without proton decoupling. In the proton coupled spectrum, broad signals centered at 27.8 and 28.5 ppm were observed. Proton decoupled spectrum of the same sample indicated that the each of the broad signals were convoluted signals of different chemical shifts, indicating that phosphorous atoms in the different magnetic environment present in the polymer. The assignment of proton coupled signals at 27.8 and 28.5 ppm was attempted by comparing their chemical shifts with those of well-defined low molecular weight model compounds. Figure 6 shows proton decoupled $^{31}$P NMR spectra of ($E$)-tetaethyl (2,3-dibutylbut-2-ene-1,4-diy)bis(phosphonate) and the mixture of ($E$) and ($Z$) isomers. As we have described in the experimental section,
the geometry of these model compounds were determined by X-ray structural analysis of the intermediate compound, 5,6-Bisbromomethyl-5-decene. As can be seen, (E) isomer gives signal at 28.6 ppm whereas the mixture of isomers give signals at 28.6 and 28.9 ppm, indicating that signal attributable to (E) configuration appears slightly higher field than (Z) isomer. Applying this relation to poly(2), broad signals at 27.8 and 28.5 can be assigned to 1,4-(E) and (Z) configurations, respectively. From the relative integrated intensity of these signals, it was found that 1,4-(Z) structure, a cis-1,4 structure of main chain, predominates than 1,4-(E) in poly(2) obtained in this study. This is in contrast to the results of poly(1) where 1,4-(Z), a trans-1,4-structure of main chain, slightly predominates. Bulky two diethyl phosphonate groups might have lead the formation of less hindered cis-1,4 configuration.

The copolymerization of styrene (St) with 2 as comonomer was carried out in bulk at 60°C with using AIBN as an initiator. Polymerization time was set to 30–180 min depending on the feed monomer ratio. Rate of polymerization was slow at high 2 feed ratio. Conversion and the copolymer composition were determined by 1H NMR spectroscopy.

Figure 7 shows the copolymerization composition curve. As can be seen, the curve for the copolymerization with St is concave downward in the entire range of feed monomer ratio. The monomer reactivity ratios (r_{st}, r_2) were determined by Kelen-Tudos method\(^{23}\). From the copolymerization with St, defining 2 as M_2, these values were determined to be r_{st}=0.15 and r_2=6.10. Alfrey-Price’s Q-e values were determined to be Q=5.4 and e=−0.54 using these monomer reactivity ratios. The Q value of 2 is much larger than that of 2,3-dimethyl-1,3-butadiene, 1.42, whereas the e values of these monomers do not differ so much\(^{24}\). The two phosphonate group on the butadienyl skeleton may have contributed conjugation by hyper conjugation through methylene groups.
Conclusion

1,3-Butadiene derivative containing two diethylphosphonate groups, tetraethyl (2,3-dimethylenebutane-1,4-diyl)bis(phosphonate), was synthesized and its free-radical polymerization behavior was studied. Sticky polymer was obtained in moderate yield using AIBN as an initiator by solution polymerization in benzene. Microstructure of the polymer was exclusively 1,4- where both 1,4-\(E\) and \(Z\) configurations were incorporated. Copolymerization with styrene.

References and Notes

1) Moad, G., Solomon, D.: “The Chemistry of Free Radical Polymerization, 2nd fully revised edition” Elsevier, London, pp. 1–9 (2006).
2) Jing, Y., Sheares, V.: Macromolecules, 33, 6255–6261 (2000).
3) Jing, Y., Sheares, V.: Macromolecules, 33, 6262–6268 (2000).
4) Sheares, V. V., Wu, L., Li, Y., Emmick, T.: J. Polym. Sci. Part A: Polym. Chem., 38, 4070–4080 (2000).
5) Sheares, V. V., Wu, L.: J. Polym. Sci. Part A: Polym. Chem., 39, 3227–3238 (2001).
6) Beery, M. D., Rath, M. K., Sheares, V.: Macromolecules, 34, 2469–2475 (2001).
7) Yaegashi, T., Takeshita, H., Takenaka, K., Shioi, T.: J. Polym. Sci. Part A: Polym. Chem., 41, 1545–1552 (2003).
8) Yaegashi, T., Yodoya, S., Nakamura, M., Takeshita, H., Takenaka, K., Shioi, T.: J. Polym. Sci. Part A: Polym. Chem., 42, 999–1007 (2004).
9) Takenaka, K., Matsui, M., Takeshita, H., Miya, M., Shioi, T.: e-Journal Soft Mater., 5, 1–8 (2009).
10) Takenaka, K., Hanada, K., Shioi, T.: Macromolecules, 32, 3875–3877 (1999).
11) Takenaka, K., Kawamoto, S., Miya, M., Takeshita, H., Shioi, T.: Polym. Int., 59, 891–895 (2010).
12) Quittmann, U., Lecamp, L., El Khatib, W., Youssef, B., Bunel, C.: Macromol. Chem. Phys., 202, 628–635 (2001).
13) Moszner, N., Salz, U., Zimmermann, J.: Dental Materials, 21, 895–910 (2005).
14) Egawa, H., Nonaka, T., Maeda, H.: J. Appl. Polym. Sci., 30, 3239–3247 (1985).
15) Ebdona, J. R., Priceb, D., Hunta, B. J., Josepha, P., Fengge Gaob, Milnesb, G. J., Cuniliffe, L. K.: Polym. Degrad. Stab., 69, 267–277 (2000).
16) David, G., Negrell-Guirao, C., Iftene, F., Boutevin, B., Chougrani, K.: Polym. Chem., 3, 265–274 (2012).
17) Takenaka, K., Nishida, T., Takeshita, H., Miya, M., Shioi, T.: Kobunshi Ronbunshu, 66: 61–68 (2009).
18) Kondo, J., Takagi, M., Asani, R.: Kobunshi Ronbushu, 46: 769–774 (1989).
19) Lambert, J. B., Koeng, F. R., Hamersma, J. W.: J. Org. Chem., 36, 2941–2947 (1971).
20) Cope, A. C., Kagan, F.: J. Am. Chem. Soc., 80, 5499–5502 (1958).
21) Gaoni, Y., Sadeh, S.: J. Org. Chem., 45, 870–881 (1980).
22) Huyser, E. S., Siegert, F. W., Sinnige, H. J. W., Wynberg, H.: J. Org. Chem., 31, 2437–2441 (1966).
23) Kelen, T., Tudos, S.: Macromol. Sci. Chem., A9, 1–27 (1975).
24) Brandrup, J., Immergut, E. H., Eds., Polymer Handbook 3rd Ed, Wiley, New York, 1975, pII-268.