Palladium-Mediated Polymerization of Alkyl Diazoacetates To Afford Poly(alkoxycarbonylmethylene)s. First Synthesis of Polymethylenes Bearing Polar Substituents

Eiji Ihara,* Nobuyuki Haida, Makoto Iio, and Kenzo Inoue*

Department of Applied Chemistry, Faculty of Engineering, Venture Business Laboratory, Ehime University, 3 Bunkyo-cho, Matsuyama 790-8577, Japan

Received July 22, 2002; Revised Manuscript Received November 4, 2002

ABSTRACT: Polymerization of alkyl diazoacetates [N_2CHCO_2R: R = Et (**1a**) and Me (**1b**)] mediated by $PdCl_2$ in the presence of an amine gave poly(alkoxycarbonylmethylene)s [$(CHCO_2R)_n$: R = Et (**2a,b**), Me (**3a,b**)] bearing an ester group on every carbon atom of their main chains. MALDI−TOF−MS analyses of the polymers **2a** and **3b** indicated that the degree of polymerization of the polymers extended up to nearly 100. The Pd-mediated polymerization of **1a** and **1b** in the presence of pyridine afforded the polymers quantitatively after reprecipitation from $CHCl_3$ into *n*-hexane. A mechanism of the polymerization initiated with a Pd-assisted nucleophilic attack of an amine to the monomers is proposed.

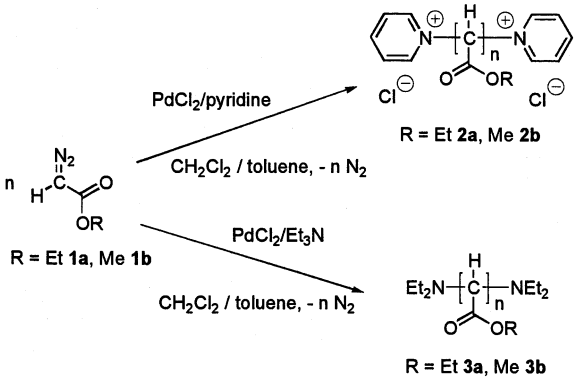
Introduction

Synthesis of polymethylenes $(CRR')_n$ by constructing the polymer backbone from one carbon unit is an attractive method to prepare new polymers which cannot be obtained by any conventional polymerization methodology. Since polymerization of diazoalkanes was reported to give polymethylenes a few decades ago,[1] research of the synthesis of polymethylenes had not been developed until a series of notable studies on living polymethylene syntheses using sulfoxonium ylides as monomers recently reported by Shea and co-workers.[2,3] In contrast to inherently unstable (thus highly reactive) diazoalkanes, diazocarbonyl compounds such as diazoacetates (N_2CHCO_2R) are stable and have been utilized as useful reagents in organic syntheses.[4] However, to our knowledge, polymerization of diazocarbonyl compounds has not been reported to date, although oligomers or polymers derived from them might have been occasionally observed as side products in synthetic reactions using the reagents. On the basis of the high reactivity of diazocarbonyl compounds with transition-metal catalysts,[4] we have been speculating that they can be polymerized by proper choice of catalysts and reaction conditions. Herein, we report that the palladium-mediated polymerization of alkyl diazoacetates N_2CHCO_2R (R = Et, **1a**; Me, **1b**) actually proceeds to give poly(alkoxycarbonylmethylene)s (**2a,b**, **3a,b**) in high yields. Although there has been an important finding that the radical polymerization of dialkyl maleates or dialky fumarates is capable of furnishing polymers bearing an ester group on every main chain carbon atom, which accordingly have the same structure as those of poly(alkoxycarbonylmethylene)s, high-yield syntheses of the polymers by the radical polymerization were achieved only when monomers with sterically bulky ester groups such as *t*-Bu were employed.[5,6]

Results and Discussion

After examining reactions of ethyl diazoacetate **1a** as a monomer with various metal compounds, we have found that the reaction of **1a** with $PdCl_2$ in the presence of an amine such as pyridine and triethylamine (Et_3N) affords a polymeric product (Scheme 1). For example, a

Scheme 1



mixture of **1a** (4.3 mmol), $PdCl_2$ (0.0874 mmol), pyridine (0.9 mmol), and 10 mL of toluene was heated at 55 °C for 17 h with stirring. After volatile substances were removed under reduced pressure, extractive workup of the residue with $CHCl_3$ and aqueous HCl gave viscous oil, from which polymer **2a** (40.6%) was isolated as viscous oil by preparative recycling size exclusion chromatography (SEC). The product exhibited the same resonances in ^1H NMR as those reported for poly(diethyl fumarate)s prepared by radical polymerization of diethyl fumarate,[5] which should have the same main chain structure as that of **2a**. MALDI−TOF−MS analysis provided clear evidence that the monomer unit of **2a** was actually $CHCO_2Et$, which should be generated from the monomer **1a** via C−C bond formation between α-carbons after elimination of N_2. As shown in Figure 1, the MS spectrum of **2a** in linear mode shows peaks in the mass range of m/z = 1500−10 000, which corresponds to degree of polymerization of ca. 20−110. The expansion of the spectrum in Figure 1 shows that a main set of peaks has an interval of m/z = 86 ($CHCO_2$-Et), which indicates that the product has the structure of a polymethylene having ethoxycarbonyl substitutents on all the main chain carbon atoms. Unfortunately, since the MALDI−TOF−MS measurement in reflector mode did not show any peaks derived from the polymer, we cannot characterize the precise chemical structure of the chain ends.

10.1021/ma021169v CCC: $25.00
Published on Web 12/07/2002

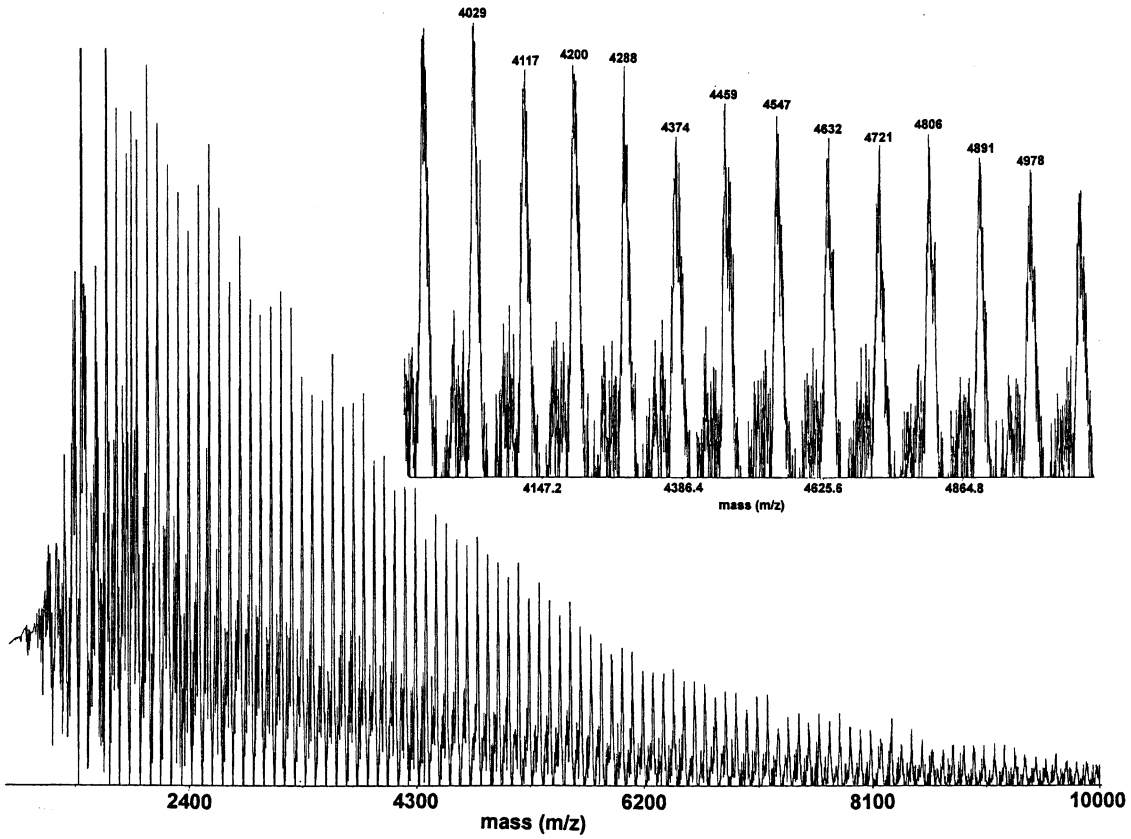


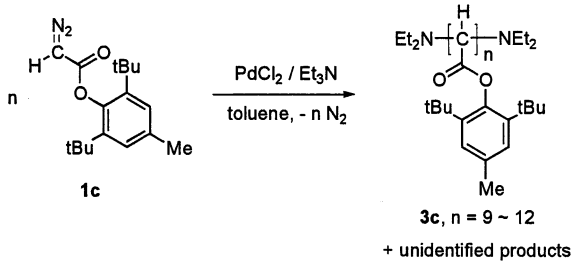
Figure 1. MALDI−TOF−MS spectrum of **2a** in linear mode.

From SEC analysis using a standard poly(methyl methacrylate) (PMMA, number-average molecular weight (M_n) = 2190) and dibutyl sebacate (MW = 314.5) for calibration, the M_n of **2a** was estimated to be 420 (M_w/M_n = 1.87). Although the spreading of peaks in a wide *m*/*z* range in Figure 1 agrees with the broad molecular weight distribution from SEC analysis, the M_n value obtained from SEC analysis seems to be too small. We assume that SEC analysis calibrated with the standard PMMA is not appropriate for the estimation of M_n of **2a**, since the interaction of PMMAs and **2a** with porous polystyrene gel used for the analysis should be quite different. However, keeping the problem in mind, we will use the results from SEC analysis as relative M_n values for comparison in this study.

Poly(methoxycarbonylmethylene) (**3b**) was also obtained in a similar procedure using triethylamine (Et_3N) instead of pyridine. The reaction of methyl diazoacetate **1b** (5.0 mmol) with $PdCl_2$ (0.0998 mmol) and Et_3N (1.0 mmol) in toluene (10 mL) at 55 °C for 14 h gave **3b** as viscous oil in 20.1% yield after purification using the preparative recycling SEC. The product showed broad signals (3.0−3.8 ppm for CH, 3.5−4.0 ppm for OMe) assignable to the protons of the poly(methoxycarbonylmethylene) structure in its ^{1}H NMR spectrum, and the M_n estimated by SEC analysis was 290. The structure of **3b** was clearly confirmed by MALDI−TOF−MS analysis, in which a main set of peaks with an interval of 72 ($CHCO_2Me$) in the mass range of *m*/*z* = 1500−9000 (degree of polymerization = 20 ∼ 125) was observed as shown in Figure 2.

Mechanistic information for the polymerization was obtained from MALDI−TOF−MS analysis of the product prepared from the Pd-mediated reaction of an aryl diazoacetate monomer **1c** [N_2CHCO_2(2,6-*t*-Bu-2,4-Me-C_6H_2)] (Scheme 2). The reaction of **1c** (1.04 mmol) with $PdCl_2$ (0.052 mmol) and Et_3N (1.4 mmol) in toluene (10 mL) at 75 °C for 62 h followed by extractive workup and purification by the preparative recycling SEC gave a solid, which was a mixture of several species at least containing poly(aryloxycarbonylmethylene) (**3c**) as demonstrated by the MALDI−TOF−MS spectrum in Figures 3 and 4. Thus, in the MALDI−TOF−MS spectrum in linear mode of the solid (Figure 3), along with peaks in a low molecular weight region (M_n < 2000), four intense peaks with an interval of *m*/*z* = 260 [$CHCO_2$-(2,6-di-*t*-Bu-4-Me-C_6H_2)] were observed at mass values of *m*/*z* = 2509, 2769, 3029, and 3289. These peaks were also observed in reflector mode of the MS analysis, which enabled us to investigate the precise structure of the polymer chain ends. Figure 4a shows a peak cluster around *m*/*z* = 2769, whose appearance suggested the presence of several species with a few mass (*m*/*z*) difference. We have found that the reasonable structure of the compounds giving these peaks would be a series of derivatives based on a 10-mer of **3c** bearing Et_2N− groups at both chain ends. As shown in Figure 4b, the theoretical isotopic distribution of the 10-mer of **3c** agrees with the higher molecular region of the observed

Scheme 2



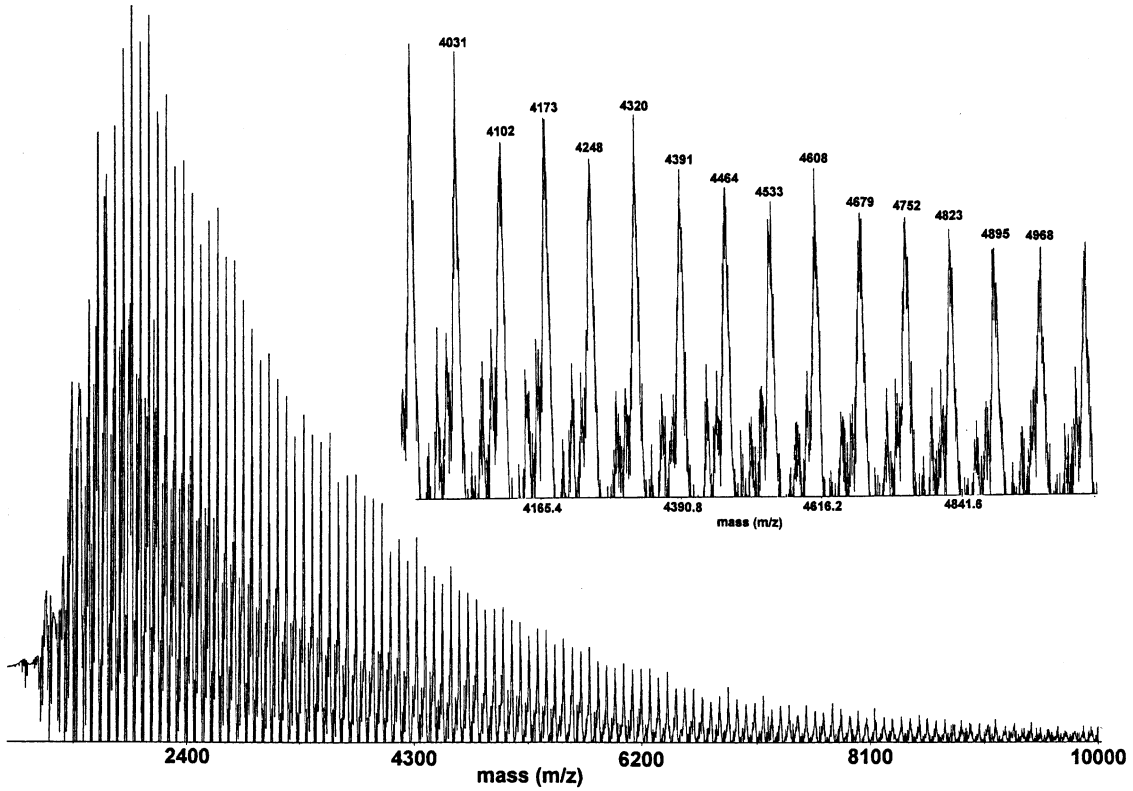


Figure 2. MALDI−TOF−MS spectrum of **3b** in linear mode.

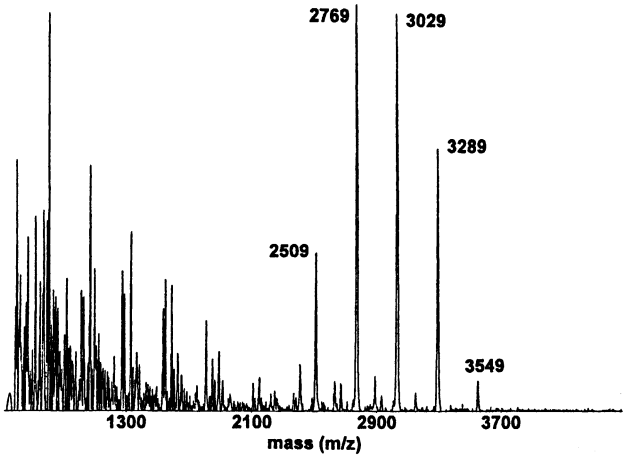


Figure 3. MALDI−TOF−MS spectrum of the product obtained from the Pd-mediated reaction of **1c** in linear mode.

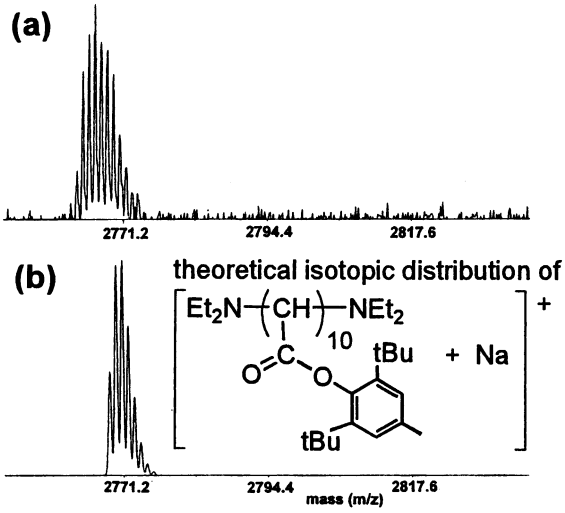


Figure 4. Comparison of one of the peak clusters appeared in the MALDI−TOF−MS spectrum of the product obtained from the Pd-mediated reaction of **1c** in reflector mode (a) and theoretical isotopic distribution of 10-mer of **3c** (b).

peak cluster. Other species included in the peak cluster with lower molecular weights could be generated by elimination of one or two H_2 from the structure of the 10-mer, which would occur during the polymerization or workup with HCl treatment, or by laser irradiation in the MALDI−TOF-MS analysis. On the basis of the result of the MALDI−TOF-MS analysis, we can tentatively propose one of the plausible mechanisms of the palladium-mediated polymerization of diazoacetate monomers initiated with Et_3N as shown in Scheme 3. The initiation will be a nucleophilic attack of Et_3N coordinated on the Pd to the α-carbon atom of the diazoacetate monomer accompanied by elimination of N_2 and formation of the carbon−palladium bond. Then, insertion of a α-carbon of another monomer into the Pd−C bond with elimination of N_2 will be the propagation. The ammonium salt of the chain end would be transformed into a neutral Et_2N- group by Hofmann-type elimination releasing an ethylene molecule. The observation of the presence of the Et_2N- moiety on both chain ends of the polymer suggests that two polymer chains are formed on a palladium center simultaneously, and the final product is given by reductive elimination on the metal center (termination).

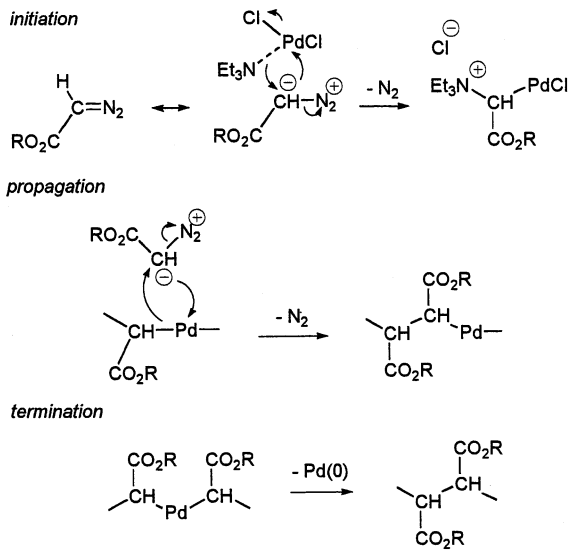
Following the proposed mechanism, the observed values of elemental analysis of the above obtained **2a** agreed with the calculated ones based on the assumptions that (1) a nucleophilic attack of pyridine to an α-carbon of **1a** initiated the polymerization, (2) reductive elimination on Pd was termination, (3) the resulting pyridinium salts at both polymer chain ends remained intact, (4) the average degree of polymerization was 20,

Table 1. Pd-Mediated Polymerization of 1a and 1b in the Presence of Amines in CH_2Cl_2/Toluene at 55 °C[a]

run	monomer (M), mmol	[M]/[$PdCl_2$]	amine	[amine]/[M]	product	yield (%)	M_n[b]	M_w/M_n[b]	elemental analysis[c] found / calcd (n = DP)
1	**1a**, 4.4	51	pyridine	0.50	**2a**	100	700	1.81	C, 54.03; H, 6.38; N, 2.43 C, 55.19; H, 6.55; N, 2.22 (n = 12)
2	**1a**, 4.3	49	pyridine	0.19	**2a**	50	610	1.74	
3	**1a**, 4.4	50	pyridine	0.99	**2a**	100	730	1.80	
4	**1a**, 4.5	103	pyridine	0.50	**2a**	73	750	1.74	
5	**1b**, 5.0	49	pyridine	0.50	**2b**	100	470	1.94	C, 49.49; H, 5.22; N, 2.43 C, 50.40; H, 5.40; N, 2.03 (n = 16)
6	**1a**, 4.7	53	Et_3N	0.49	**3a**	57	420	1.70	C, 51.29; H, 6.05; N, 1.73 C, 53.06; H, 7.79; N, 1.41 (n = 20)
7	**1b**, 5.0	50	Et_3N	0.49	**3b**	56	370	1.81	C, 47.57; H, 5.50; N, 1.99 C, 48.74; H, 6.62; N, 1.67 (n = 20)

[a] All the polymerizations were conducted overnight (14−18 h) in a mixture of CH_2Cl_2 (ca. 5 mL) and toluene (10 mL). [b] M_n and M_w/M_n were obtained by SEC calibration using a standard PMMA and dibutyl sebacate in THF solution. [c] Calculated values were based on the following compositions: $Cl^-[C_5H_5N]^+(CHCO_2R)_n[C_5H_5N]^+Cl^-$; run 1, R = Et, n = 12; run 5, R = Me, n = 16. $(C_2H_5)_2N(CHCO_2R)_nN(C_2H_5)_2\cdot(H_2O)_m$; run 6, R = Et, n = 20, m = 7; run 7, R = Me, n = 20, m = 5.

Scheme 3



and (5) five H_2O molecules were included in one polymer chain. Calcd for $Cl^-[C_5H_5N]^+(CHCO_2Et)_{20}[C_5H_5N]^+Cl^-\cdot 5H_2O$ ($C_{90}H_{140}Cl_2N_2O_{45}$; MW = 2040.99): C, 52.96; H, 6.91, N; 1.37. Found: C, 53.27; H, 6.49; N, 1.64. In a similar manner, the elemental analysis of the aforementioned **3b** can also be reasonably explained by assuming that the polymer with an average degree of polymerization of 25 has neutral Et_2N- groups on both chain ends and five H_2O molecules per polymer chain. Calcd for $(C_2H_5)_2N(CHCO_2Me)_{25}N(C_2H_5)_2\cdot 5H_2O$ ($C_{83}H_{130}N_2O_{55}$; MW = 2035.92): C, 48.97; H, 6.44, N; 1.37. Found: C, 47.93; H, 5.48; N, 0.73.

The purification of **2a,b** and **3a,b** with reprecipitation from $CHCl_3$ into *n*-hexane was effective to obtain the polymers in high yields (Table 1). For example, the reaction of **1a** with $PdCl_2$ and pyridine in a molar ratio of **1a**:$PdCl_2$:pyridine = 1:0.02:0.5 afforded **2a** with SEC-estimated M_n of 700 quantitatively after the reprecipitation (run 1). The use of excess pyridine with respect to **1a** is required because decreasing the amount of pyridine resulted in a lower yield (run 2). On the other hand, the M_n of **2a** slightly increased without decrease of the yield, when the same amount of pyridine with respect to **1a** was employed (run 3). The M_n of **2a** became slightly higher by changing the molar ratio of $PdCl_2$ to **1a** from 0.02 to 0.01, although the yield of **2a** decreased significantly (run 4). Similarly, **2b** was prepared quantitatively by the reaction of **1b** with $PdCl_2$ and pyridine after the reprecipitation (run 5). The use of Et_3N instead of pyridine in the polymerization of **1a** and **1b** with $PdCl_2$ gave **3a** and **3b**, respectively, with lower SEC-estimated M_n's and in lower yields than those obtained by the reaction with pyridine (runs 6, 7).

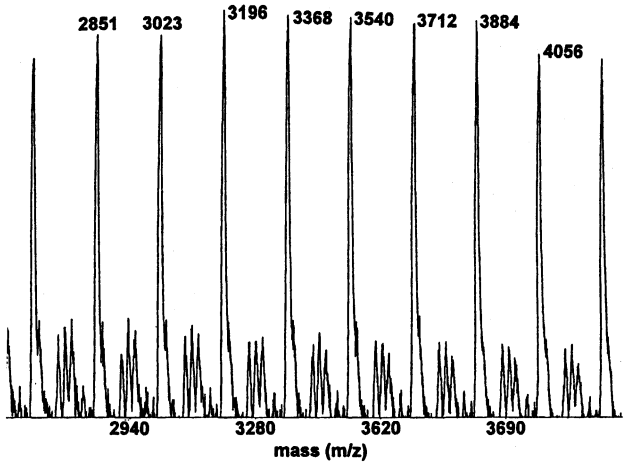
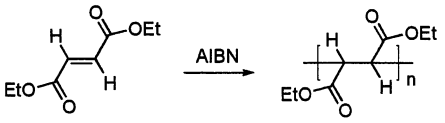


Figure 5. A part of MALDI−TOF−MS spectrum of poly(diethyl fumarate) obtained from radical polymerization in linear mode.

For the purpose of comparison, we carried out a radical polymerization of diethyl fumarate initiated with AIBN.[5] The reaction of the monomer with 0.05 equiv of the radical initiator in toluene at 70 °C for 35 h afforded poly(diethyl fumarate) in 31% yield. SEC analysis indicated the M_n of the polymer estimated by calibration with PMMA standards was 4700 (M_w/M_n = 1.41), which was much higher than those of **2a** obtained by the Pd-mediated polymerization of **1a**. Figure 5 shows a part of MALDI−TOF−MS spectrum of the poly(diethyl fumarate). As expected, the interval of a main set of peaks in the spectrum is m/z = 172 corresponding to the molecular weight of the monomer unit [$(CHCO_2Et) \times 2$], which is twice that in the MS spectrum of **2a** and **3a** in Figure 1. From the difference of the intervals observed in these spectra, we can rule out the possibility that **2a** and **3a** were obtained via radical polymerization of diethyl fumarate or maleate, which might be generated by the reaction of **1a** with $PdCl_2$.

We have demonstrated that alkyl diazoacetates can act as monomers for the Pd-mediated polymerization, which can afford ester-substituted polymethylenes. To our knowledge, this is the first example of the synthesis

Scheme 4



of polymethylenes having polar functional groups. In addition to homopolymerization of various diazocarbonyl compounds, copolymerization with diazoalkanes will be a useful method for preparation of new polymers. For example, random copolymerization of **1a** with diazomethane will provide the polymer whose structure is almost identical to that of random copolymer of ethylene and ethyl acrylate. Various possibilities of application of the polymerization are now being pursued in our laboratory.

Experimental Section

Materials. Diazoacetate monomers **1a,b**[7] and **1c**[8] were prepared according to the literature. $PdCl_2$ (Wako Chemicals, >99%), diethyl fumarate (Wako, >98%), and AIBN (Wako Chemicals, >98%) were used as received. Pyridine (Sigma-Aldrich Japan, 99.5%) and triethylamine (Sigma-Aldrich Japan, 98%) were dried over KOH pellet (Wako, >85%) and used without further purification. Toluene (Sigma-Aldrich Japan, 99%) was dried over sodium (Wako, >98%) and distilled before use. CH_2Cl_2 (Nacalai, 98%), $CHCl_3$ (Sigma-Aldrich Japan, 99%), HCl (Sigma-Aldrich Japan, 35−37%), MeOH (Sigma-Aldrich Japan, 99.5%), Na_2SO_4 (Wako, >99%), *n*-hexane (Sigma-Aldrich Japan, 95%), and benzene (Wako, >99%) were used as received.

Measurement. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker Avance 400 spectrometer using tetramethylsilane (TMS) as an internal standard in chloroform-*d* ($CDCl_3$) at 25 °C. Molecular weights (M_n) and molecular weight distributions (M_w/M_n) were measured by means of size exclusion chromatography (SEC) on a Jasco-Bowin system (ver. 1.50) equipped with a differential refractometer detector using tetrahydrofuran as eluent at a flow rate of 1.0 mL/min and 40 °C, calibrated with a poly(MMA) standard (Shodex M-75, $M_n = 2190$, $M_w/M_n = 1.08$) and dibutyl sebacate (MW = 314.5) for **2a,b** and **3a,b**, and poly(MMA) standards (Shodex M-75, $M_n = 2190-653\,000$, $M_w/M_n = 1.03-1.08$) for the poly(diethyl fumarate) prepared by the radical polymerization. The columns used for the SEC analyses were KF-802 (Shodex; 300 mm × 8 mm i.d., 6 μm average particle size, exclusion molecular weight of 5K for polystyrene) for **2a,b** and **3a,b** and a combination of G6000H_{HR} (TOSOH; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 40M for polystyrene), G4000H_{HR} (TOSOH; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 400K for polystyrene), and G3000H_{HR} (TOSOH; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 60K for polystyrene) for the poly(diethyl fumarate). Purification by preparative recycling SEC was performed on a JAI LC-918RU equipped with a combination of columns of a JAIGEL-3H (600 mm × 20 mm i.d., exclusion molecular weight of 70K for polystyrene) and a JAIGEL-2.5H (600 mm × 20 mm i.d., exclusion molecular weight of 20K for polystyrene) using $CHCl_3$ as eluent at a flow rate of 3.5 mL/min and 25 °C. The sample solution (3 mL containing ca. 0.1 g of the crude product) was injected and recycled before fractionation.

MALDI−TOF−MS analyses were performed on a PerSeptive Biosystems Voyager RP equipped with 1.3 m linear and 2 m reflector flight tubes and a 337 nm nitrogen laser (pulse width, 3 ns). All experiments were carried out at an accelerating potential of 20 kV in both linear and reflector modes under the pressure of ca. $(2-3) \times 10^{-7}$ mmHg. In general, mass spectra from 100 laser shots were accumulated to produce a final spectrum. Angiotensin I (human, MW = 1296.5) (Sigma, 97%) and insulin (bovine pancreas, MW = 5733.50) (Nacalai, 28.0 U/mg solid) were used as internal standards to calibrate the mass scale. A 1.5 μL portion of the mixture consisting of a polymer solution (100 μL, 10 mg/mL in THF), a matrix, 3-indoleacrylic acid (TCI, >97%) for **2a** and **3b**, 1,8-dihydroxy-9(10*H*)-anthracenone (Nacalai, 95%) for **3c** and the poly(diethylfumarate), solution (300 μL, 10 mg/mL in THF), and a cationizing agent, sodium trifluoroacetate (TCI, >98%), solution (100 μL, 10 mg/mL in THF) was deposited onto a sample target plate and allowed to dry in air at room temperature. The theoretical isotopic distribution of 10-mer of **3c** in Figure 4 was obtained using Isotope Calculator program on Data Explorer Software (version 4.0, Applied Biosystems).

Elemental analyses were performed on a YANAKO MT-5 analyzer at Advanced Instrumentation Center for Chemical Analysis in Ehime University.

Pd-Mediated Polymerization of Alkyl Diazoacetates. As a typical procedure for the polymerization of alkyl diazoacetates, the procedure for run 1 in Table 1 using **1a** as a monomer is shown as follows. Under a nitrogen atmosphere, a mixture of $PdCl_2$ (15.5 mg, 0.0874 mmol), pyridine (0.18 mL, 2.2 mmol), and 10 mL of toluene in a Schlenk tube was stirred for 30 min at room temperature. After a solution of **1a** (5.6 mL of 0.79 M solution in CH_2Cl_2, 0.50 g, 4.4 mmol) was added via a syringe, the mixture was stirred for 18 h at 55 °C. After volatile materials were removed under reduced pressure, the residue was extracted by using 60 mL of $CHCl_3$, 20 mL of 1 N HCl/MeOH, 20 mL of 1 N HCl, and 60 mL of water. Removal of the solvent from the organic layer after drying over Na_2SO_4 gave viscous oil, which was purified by reprecipitation from 3 mL of $CHCl_3$ into 100 mL of *n*-hexane. Freeze-drying of the residue using benzene afforded **2a** as a highly viscous oil quantitatively (0.38 g). ^{1}H NMR ($CDCl_3$): δ 0.90−1.50 (OCH_2CH_3), 3.00−3.90 (C*H*), 3.90−4.50 (OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 13.2−14.5 (OCH_2CH_3), 42.0−55.0 (*C*H), 59.0−64.0 (OCH_2CH_3), 166.0−175.0 (*C*=O). Signals for polymer chain end groups could not be identified.

The Pd-mediated polymerization of **1b** was carried out in a similar procedure to give **2b** and **3b**. ^{1}H NMR ($CDCl_3$): δ 3.00−3.80 (C*H*), 3.50−4.00 (OCH_3). ^{13}C NMR ($CDCl_3$): δ 43.0−55.0 (*C*H), 50.0−55.0 (OCH_3), 168.0−175.0 (*C*=O). Signals for polymer chain end groups could not be identified.

The Pd-mediated reaction of **1c** was carried out in a similar procedure where the product was obtained as a mixture including **3c**.

Radical Polymerization of Diethyl Fumarate. Under a nitrogen atmosphere, a mixture of diethyl fumarate (10.0 g, 58.1 mmol) and AIBN (487 mg, 2.97 mmol) in 15 mL of benzene was heated at 70 °C for 35 h with stirring. After the solvent and unreacted monomer were removed under reduced pressure, poly(diethyl fumarate) was obtained in 31.0% yield (3.1 g) by reprecipitation from $CHCl_3$ into *n*-hexane and freeze-drying using benzene. Characterization of the poly(diethyl fumarate)s prepared by this procedure was reported in the literature.[5]

Acknowledgment. Dr. Yukihiro Motoyama (Toyohashi University of Technology) is gratefully acknowledged for his advise on the synthesis of diazoacetate monomers.

References and Notes

(1) (a) Smets, G.; Bourtembourg, A. *J. Polym. Sci., Part A-1* **1970**, *8*, 3251−3258. (b) Imoto, M.; Nakaya, T. *J. Macromol. Sci., Rev. Macromol. Chem.* **1972**, *C7*, 1. (c) Mucha, M.; Wunderlich, B. *J. Polym. Sci., Polym. Phys.* **1974**, *12*, 1993.

(2) (a) Shea, K. J.; Walker, J. W.; Zhu, H.; Paz, M.; Greaves, J. *J. Am. Chem. Soc.* **1997**, *119*, 9049−9050. (b) Shea, K. J.; Busch, B. B.; Paz, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1391−1393. (c) Shea, K. J.; Lee, S. Y.; Busch, B. B. *J. Org. Chem.* **1998**, *63*, 5746−5747. (d) Shea, K. J.; Staiger, C. L.; Lee, S. Y. *Macromolecules* **1999**, *32*, 3157−3158. (e) Zhou, X.-Z.; Shea, K. J. *J. Am. Chem. Soc.* **2000**, *122*, 11515−11516.

(f) Busch, B. B.; Paz, M. M.; Shea, K. J.; Staiger, C. L.; Stoddard, J. M.; Walker, J. R.; Zhou, X.-Z.; Zhu, H. *J. Am. Chem. Soc.* **2002**, *124*, 3636−3646. (g) Busch, B. B.; Staiger, C. L.; Stoddard, J. M.; Shea, K. J. *Macromolecules* **2002**, *35*, 8330−8337.

(3) The anionic oligomerization of arylaziridine hydrazones of aldehydes has been reported to give substituted polymethylenes. Maruoka, K.; Oishi, M.; Yamamoto, H. *Macromolecules* **1996**, *29*, 3328−3329.

(4) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Carbonyl Compound*; John Wiley & Sons: New York, 1998.

(5) Toyoda, N.; Yoshida, M.; Otsu, T. *Polym. J.* **1983**, *15*, 255−260.

(6) (a) Otsu, T.; Toyoda, N. *Polym. Bull. (Berlin)* **1984**, *11*, 453−458. (b) Otsu, T.; Yasuhara, T.; Shiraishi, K.; Mori, S. *Polym. Bull. (Berlin)* **1984**, *12*, 449−456. (c) Otsu, T.; Shiraishi, K. *Macromolecules* **1985**, *18*, 1795−1796. (d) Otsu, T.; Shiraishi, K.; Matsumoto, A. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 885−890.

(7) Searle, N. E. In *Organic Syntheses Collect. Vol. 4*; Rabjohn, N., Ed.; John Wiley & Sons: New York, 1963; pp 424−426.

(8) Doyle, M. P.; Bagheri, V.; Wandless, T. J.; Harn, N. K.; Brinker, D. A.; Eagle, C. T.; Loh, K.-L. *J. Am. Chem. Soc.* **1990**, *112*, 1906−1912.

MA021169V