Palladium-mediated Polymerization of Diazoacetamides

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Palladium-mediated polymerization of diazoacetamides bearing various substituents **1–4** is described. Homopolymerization of monomers with *n*-hexyl or 4-*n*-octylphenyl group on the nitrogen afforded polymers [poly(*N*-substituted carbamoyl-methylene)], whose all the main chain carbons have *N*-substituted carbamoly groups. Elemental analysis of the products indicated incorporation of azo group in the main chain. Copolymerization of diazoacetamides **1–4** with a diazoketone, (*E*)-1-diazo-4-phenyl-3-buten-2-one **5**, proceeded efficiently, giving poly(substituted methylene)s with a variety of *N*-substituted carbamoyl groups in their side chains.

KEY WORDS: Poly(subsutituted methylene) Synthesis / Diazoacetamide / Poly(*N*-substituted carbamoylmethylene) / Copolymerization /

Poly(substituted methylene) synthesis (PSMS) is a method for preparing C-C main chain polymers, constructing the main chain from one carbon unit. As an example for PSMS, we and other groups have demonstrated that B,[1] Al,[2] Cu,[3] Pd,[4] an Rh[5]-mediated polymerizations of diazocarbonyl compounds are effective to afford polymers or oligomers bearing various polar substitutents on their main chain carbons. Whereas diazoacetates and diazoketones have been utilized as diazocarbonyl compounds in these studies,[1–5] further extension of the range of the available monomers will broaden the generality of the polymerization, providing a variety of repeating unit structures resulting from the monomers. In that context, expecting the formation of polymers incorporating *N*-substituted carbamoyl-methylene as repeating units, we have tried to examine the reactivity of diazoacetamides with various substituents, which have not been used as monomers for any kind of polymerization so far, whereas the synthesis of poly(*N*,*N*-dimethylcarb-amoylmethylene) has been achieved by transformation of poly(di-*t*-butyl fumarate), and its unique miscibility with commodity polymers has been revealed.[6] The results of Pd-mediated polymerization of some diazoacetamides will be presented in this paper.

EXPERIMENTAL

Materials

Toluene and THF were dried over sodium and Na/K alloy, respectively, and distilled before use. *n*-Hexylamine (Nacalai, 98%), isopropylamine (Nacalai, 99%), 4-*n*-octylaniline (TCI, > 95%), *N*,*N*′-dicyclohexycarbodiimide (DCC) (Nacalai, 99%) were used as received. Et₃N (Nacalai, 99%) was dried over CaH₂, and used without further purification. Diazoacetamide **4**,[7a] (*E*)-1-diazo-4-phenyl-3-buten-2-one **5**,[10] succinimidyl diazoacetate,[7a] glyoxylic acid tosylhydrazone,[11] and PdCl₂(MeCN)₂,[12] were prepared according to the literatures.

Measurements

¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a Bruker Avance 400 spectrometer using tetra-methylsilane as an internal standard in chloroform-*d* (CDCl₃) at room temperature (monomers) or 50 °C (polymers).

Molecular weights (M_n) and molecular weight distributions (M_w/M_n) were measured by means of gel permeation chromatography (GPC) on a Jasco-ChromNAV system equipped with a differential refractometer detector using tetrahydrofuran as eluent at a flow rate of 1.0 mL/min at 40 °C, calibrated with poly(MMA) standards. The column used for the GPC analyses was a combination of Styragel HR4 (Waters; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 600 K for polystyrene) and Styragel HR2 (Waters; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 20 K for polystyrene), and poly(MMA) standards (Shodex M-75, $M_n = 200000$, $M_w/M_n = 1.05$, $M_n = 47300$, $M_w/M_n = 1.02$, $M_n = 21700$, $M_w/M_n = 1.02$, $M_n = 5220$, $M_w/M_n = 1.06$, $M_n = 2190$, $M_w/M_n = 1.08$) and dibutyl sebacate ($M_w = 314.5$) were used for the calibration.

Purification by preparative recycling GPC was performed on a JAI LC-918R equipped with a combination of columns of a JAIGEL-3H (600 mm × 20 mm i.d., exclusion molecular weight of 70 K for polystyrene) and a JAIGEL-2H (600 mm × 20 mm i.d., exclusion molecular weight of 20 K for polystyrene) using CHCl₃ as eluent at a flow rate of 3.8 mL/min at 25 °C. The sample solution (3 mL containing *ca.* 0.3 g of the crude product) was injected and recycled before fractionation.

Elemental analyses were performed on a YANAKO MT-5 analyzer at Integrated Center for Science (INCS) in Ehime University.

Preparation of *N*-*n*-Hexyl Diazoacetamide 1 and *N*-Iso-propyl Diazoacetamide 3

Caution: Although we have not experienced any explosions of diazocarbonyl compounds or their derivatives in our series of the studies, extra care should be taken for handling them because they could be potentially explosive.

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Diazoacetamide **1** and **3** were prepared following the procedure reported by Badet, B *et al.*[7a] As an example, the procedure for **1** is described as follows. Under a nitrogen atmosphere, a THF (30 mL) solution of succinimidyl diazoacetate (1.50 g, 8.20 mmol) was placed in a Schlenk tube. After *n*-hexylamine (2.20 mL, 16.7 mmol) was added dropwise, the mixture was stirred at room temperature for 2 h. After the volatiles were removed under reduced pressure, the product was purified by chromatography on silica gel with ethyl acetate as eluent to give **1** as a yellow solid (1.23 g, 89.0%). The yield for **3** (a yellow solid) was also 89.0%.

1: ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.30 (s, 1H, -NH-), 4.75 (s, 1H, N$_2$CH-), 3.27 (s, 2H, -NH-CH_2-), 1.50 (m, 2H, -NH-CH$_2$CH_2-), 1.30 (m, 6H, -(CH$_2$)$_3$-CH$_3$), 0.89 (t, 3H, -CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 165.9 (C=O), 46.9 (CN$_2$), 40.1 (-NH-CH$_2$-), 31.5 (-NH-CH$_2$CH$_2$-), 29.9 (-NH-CH$_2$CH$_2$CH$_2$-), 26.6 (-CH$_2$CH$_2$CH$_3$), 22.6 (-CH$_2$CH$_3$), 14.0 (-CH$_3$). Anal. Calcd for C$_8$H$_{15}$N$_3$O: C, 56.78; H, 8.93; N, 24.83. Found: C, 56.59; H, 8.94; N, 24.29.

3: ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.18 (s, 1H, -NH-), 4.73 (s, 1H, N$_2$CH-), 4.09 (s, 1H, -NH-CH(CH$_3$)$_2$), 1.16 (d, J = 6.8, 6H, -CH(CH_3)$_2$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 165.2 (C=O), 46.9 (CN$_2$), 41.9 (-NH-CH(CH$_3$)$_2$), 22.9 (-CH(CH$_3$)$_2$). Anal. Calcd for C$_5$H$_9$N$_3$O: C, 47.23; H, 7.13; N, 33.05. Found: C, 47.31; H, 7.02; N, 32.32.

Preparation of *N*-(4-*n*-Octyl)phenyl Diazoacetamide 2

Diazoacetamide **2** was prepared following the reported procedure.[7b] Under a nitrogen atmosphere, a THF (100 mL) solution of glyoxylic acid tosylhydrazone (6.00 g, 24.8 mmol) was placed in a round bottomed flask equipped with a dropping funnel and a three-way cock, and was cooled to 0 °C. After 4-*n*-octylaniline (5.2 mL, 23 mmol) was added, a THF (30 mL) solution of DCC (5.20 g, 25.2 mmol) was added dropwise from the dropping funnel for 30 min at 0 °C. The mixture was warmed to room temperature and stirred for 12 h. After the precipitated urea was removed by filtration, the volatiles were removed under reduced pressure. The product was purified by chromatography on silica gel with an eluent (EtOAc:CH$_2$Cl$_2$ = 1:6) to give *N*-4-*n*-octylphenylamide derivative of glyoxylic acid tosylhydrazone in a 49.0% yield. The product (4.70 g, 11.0 mmol) was placed in a round bottomed flask and dissolved with 60 mL of MeCN under a nitrogen atmosphere. After Et$_3$N (3.1 mL, 22 mmol) was added, the mixture was stirred for 2 h at room temperature. After the precipitate was removed by filtration and the volatiles were removed under reduced pressure, the product was purified by chromatography on silica gel with an eluent (EtOAc:hexane = 1:2) to give **2** as a yellow solid (1.75 g, 58.0%).

^{1}H NMR (400 MHz, (CD$_3$)$_2$SO) δ 9.63 (s, 1H, -NH-), 7.44 (d, J = 7.6 Hz, 2H, Ar-H), 7.07 (d, J = 8.4, 2H, Ar-H), 5.47 (s, 1H, N$_2$CH-), 3.37 (s, 2H, -C$_6$H$_4$CH_2-), 1.52 (m, 2H, -C$_6$H$_4$CH$_2$CH_2-), 1.25 (m, 10H, -(CH$_2$)$_5$-), 0.85 (t, J = 12.8 Hz, 3H, -CH$_3$); ^{13}C NMR (100 MHz, (CD$_3$)$_2$SO) δ 163.3 (C=O), 137.3 (Ar), 136.6 (Ar), 128.4 (Ar), 118.6 (Ar), 47.8 (CN$_2$), 34.6 (-C$_6$H$_4$CH$_2$-), 31.3 (-C$_6$H$_4$CH$_2$CH$_2$-), 31.1

(-C$_6$H$_4$CH$_2$CH$_2$CH$_2$-), 28.9 (-C$_6$H$_4$CH$_2$CH$_2$CH$_2$CH$_2$-), 28.7 (-CH$_2$CH$_2$CH$_2$CH$_3$), 28.7 (-CH$_2$CH$_2$CH$_3$), 22.1 (-CH$_2$CH$_3$), 13.9 (-CH$_3$). Anal. Calcd for C$_{16}$H$_{23}$N$_3$O: C, 70.30; H, 8.48; N, 15.37. Found: C, 70.22; H, 8.40; N, 15.28.

Pd-mediated Polymerization of Diazoacetamides

As a typical procedure for the polymerization of cyclic diazocarbonyl compounds, the procedure for run 3 in Table I is described as follows.

Under a nitrogen atmosphere, a suspension of PdCl$_2$(MeCN)$_2$ (6.0 mg, 0.023 mmol) in toluene (5 mL) was placed in a Schlenk tube. After a toluene (5 mL) solution of a mixture of **1** (0.196 g, 1.16 mmol) and **5** (0.199 g, 1.16 mmol) was added to the suspension at room temperature, the resulting mixture was heated to 80 °C and stirred for 14 h at the temperature. After the volatiles were removed under reduced pressure, 20 mL of 1 N HCl/MeOH, 20 mL of 1 N HCl aqueous solution, and 30 mL of CHCl$_3$ were added to the residue. After the organic layer was separated, the aqueous layer was extracted with 30 mL of CHCl$_3$. The combined organic layer was washed with 50 mL of 1 N HCl aqueous solution and 50 mL of H$_2$O, dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure to afford a crude product. Purification with preparative recycling GPC gave the copolymer (100 mg, 32.0%) as a dark brown solid.

Other polymerizations in Table I were carried out in similar procedures.

Poly**1'**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.8–3.6 (-NH-CH_2-), 1.4–2.0 (-NH-CH$_2$CH_2-), 1.1–1.4 (-[CH$_2$]$_3$-), 0.8–1.0 (CH$_3$). Poly**2'**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.7–7.8 (-C$_6$H$_4$-), 2.3–2.7 (-Ar-CH$_2$-), 1.5–1.8 (-Ar-CH$_2$CH_2-), 1.1–1.5 (-[CH$_2$]$_5$-), 0.8–1.0 (-CH$_3$). Poly(**1'**-*ran*-**5'**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.0–8.0 (C$_6$H$_5$-CH=CH-), 4.0–5.7 (main chain CH), 2.7–3.6 (-NH-CH_2-), 1.0–2.0 (-[CH$_2$]$_4$-), 0.6–1.0 (-CH$_3$). Poly(**2'**-*ran*-**5'**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.0–7.8 (C$_6$H$_5$-CH=CH-), 3.2–5.5 (main chain CH), 2.2–2.8 (-Ar-CH$_2$-), 1.4–1.9 (-Ar-CH$_2$CH_2-), 1.0–1.4 (-[CH$_2$]$_5$-), 0.7–1.0 (-CH$_3$). Poly(**3'**-*ran*-**5'**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.1–7.9 (C$_6$H$_5$-CH=CH-), 4.4–5.7 (main chain CH), 3.8–4.4 (-CH[CH$_3$]$_2$), 0.3–2.0 (-CH[CH_3]$_2$). Poly(**4'**-*ran*-**5'**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.0–8.0 (C$_6$H$_5$-CH=CH-), 4.3–5.7 (main chain CH), 2.4–4.0 (-CH$_2$-[CH$_2$]$_3$-CH$_2$-), 0.6–2.4 (-CH$_2$-[CH_2]$_3$-CH$_2$-). Signals for NH for all the polymers and main chain CH signals for poly**1'** and poly**2'** could not be identified.

RESULTS AND DISCUSSION

Hompolymerization of Diazoacetamides 1–4

According to the procedures reported in the literatures,[7] we prepared four diazoacetamides **1–4**, three (**1–3**) of which are new compounds. Among the four diazo compounds, **1** and **2** could be transformed into homopolymers by the reaction with PdCl$_2$(MeCN)$_2$, whereas **3** and **4** with relatively bulky substituents at the amide-*N* did not give polymeric products under the same condition, probably because steric congestion around Pd-center during propagation[4a,b] is too severe for **3** and

Table I. Polymerization of Diazoacetamides **1,2** and Copolymerization of Diazoacetamides **1–4** with (*E*)-1-Diazo-4-phenyl-3-buten-2-one **5**[a]
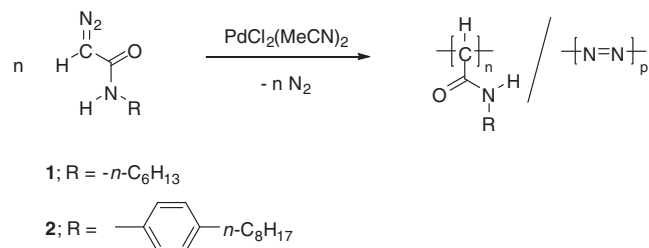
run	monomer 1, (M1) mmol	monomer 2, (M2) mmol	feed ratio [M1]:[M2]	yield[b] (%)	M_n[c]	M_w/M_n[c]	composition in copolymer M1′:M2′[d] (^{1}H NMR)	elemental analysis found calcd for Cl(M1′)$_m$(M2′)$_n$(-N=N-)$_p$Cl, M_n
1	**1**, 2.31	—	—	10.7	990	1.12	—	C, 62.94; H, 9.61; N, 12.13 C, 61.54; H, 9.68; N, 12.05 (*m/p* = 7.0:1.2, M_n = 1090)
2	**1**, 1.54	**5**, 0.77	2:1	28.7	1050	1.20	2.5:1	
3	**1**, 1.16	**5**, 1.16	1:1	31.5	1260	1.31	1.3:1	C, 67.76; H, 7.34; N, 11.15 C, 66.51; H, 7.47; N, 11.15 (*m/n/p* = 5.0:4.0:3.3, M_n = 1440)
4	**1**, 0.77	**5**, 1.54	1:2	39.2	1270	1.29	1:1.8	
5	**2**, 2.31	—	—	9.1	1890	1.10	—	C, 75.77; H, 9.18; N, 7.70 C, 73.62; H, 8.88; N, 7.60 (*m/p* = 7.2:1.5, M_n = 1880)
6	**2**, 1.54	**5**, 0.77	2:1	43.7	1420	1.23	4.3:1	
7	**2**, 1.16	**5**, 1.16	1:1	35.1	1440	1.25	2.6:1	
8	**2**, 0.77	**5**, 1.54	1:2	31.3	1520	1.32	1:0.8	C, 74.19; H, 7.41; N, 7.45 C, 73.04; H, 7.41; N, 7.48 (*m/n/p* = 3.7:3.3:2.2, M_n = 1520)
9	**3**, 1.54	**5**, 0.77	2:1	25.7	650	1.48	2.6:1	
10	**3**, 1.16	**5**, 1.16	1:1	26.6	750	1.51	1.6:1	
11	**3**, 0.77	**5**, 1.54	1:2	34.7	1020	1.43	1:1.4	C, 69.01; H, 5.88; N, 9.19 C, 66.65; H, 6.12; N, 8.73 (*m/n/p* = 3.3:4.0:1.5, M_n = 1010)
12	**4**, 1.54	**5**, 0.77	2:1	52.5	450	1.61	2.0:1	
13	**4**, 1.16	**5**, 1.16	1:1	41.3	720	1.44	1.1:1	C, 69.50; H, 6.34; N, 8.05 C, 66.58; H, 6.48; N, 7.85 (*m/n/p* = 3.1:2.5:0.8, M_n = 840)
14	**4**, 0.77	**5**, 1.54	1:2	49.0	840	1.44	1:1.8	

[a]([M1] + [M2])/[PdCl$_2$(MeCN)$_2$]) = 100, toluene = 10 mL; polymerization period = 14 h; polymerization temperature = 80 °C.
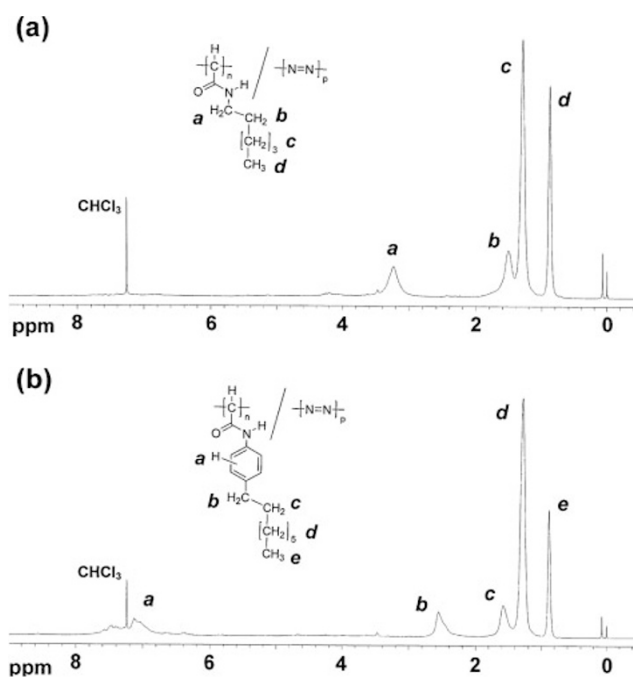[b]Yield (%) = 100 × (the weight of the product after purification with the recycling GPC − the weight of N contained in the product calculated from the result of elemental analysis)/(total amount monomers − the weight of N contained in the monomers). For the copolymer samples without elemental analysis data, the yield was calculated on the assumption that [M1′]:[-N=N-] is the same as that obtained by elemental analysis for other sample with the same comonomer combination but a different feed ratio.
[c]M_n and M_w/M_n were obtained by GPC calibration using standard PMMAs in THF solution.
[d]M1′ = repeating unit derived from M1.

1; R = -*n*-C$_6$H$_{13}$

2; R = ⟨phenyl⟩-*n*-C$_8$H$_{17}$

Scheme 1. Pd-mediated Polymerization of Diazoacetamides **1,2**.

(a)

(b)

Figure 1. ^{1}H NMR spectra of polymers from **1** (a) and **2** (b) (runs 1 and 5, respectively, Table I).

4 (Scheme 1). For example, when the reaction of **2** with 1 mol % of PdCl$_2$(MeCN)$_2$ was conducted in toluene at 80 °C for 14 h, a polymeric product was obtained, whose GPC-estimated M_n (based on PMMA standards) was 1890 (run 5 in Table I). ^{1}H NMR spectrum for the product shown in Figure 1(b) exhibits broad signals assignable to each H in the amide-substituent (-C$_6$H$_4$-*n*-C$_8$H$_{17}$) of **2**, which apparently suggests the progress of the Pd-mediated polymerization of **2** in the similar manner as diazoacetates and diazoketones,[4] although the main chain CH and NH peaks cannot be identified in the spectrum probably due to broadening of the signals. The result of the elemental analysis for the sample indicates that its N content (7.70%) is significantly higher than that expected for

the polymer obtained *via* complete removal of N_2 from the monomer (N = 5.71%). Accordingly, the partial incorporation of azo group should occur during the polymerization as proposed in the Pd-mediated polymerization of diazoketones.[4b] On the assumption that Cl derived from the initiator attached to both chain ends,[4b] the calculated values based on the composition with 17.2 mol % of the azo group agree with the observed values as listed in Table I. The degree of the azo-incorporation is much higher than that observed for the Pd-mediated polymerization of diazoketones (< 5 mol %).[4b] Similarly, homopolymerization of **1** proceeded to give a polymer, whose GPC-estimated M_n was 990 and azo content in the main chain determined from elemental analysis was 14.6 mol % (run 1). Figure 1(a) shows the ^{1}H NMR spectrum for the product, which exhibits broad signals derived from the *N*-hexyl side chain. The much lower M_n of poly**1′** (**1′** = repeating unit derived from **1**) compared to poly**2′** may indicate that the presence of π-electrons in the vicinity of diazocarbonyl moiety plays an important role for the polymerization to proceed, as demonstrated in the Pd-mediated polymerization of various diazoketones.[4b] Although the yields for the homopolymerizations were rather low (*ca.* 10%), these results demonstrate that polymers whose all the main chain carbons bear *N*-substituted carbamoyl group can be obtained by the Pd-mediated polymerization of some diazoacetamides.

Copolymerization of Diazoacetamides (1–4) with (*E*)-1-Diazo-4-phenyl-3-buten-2-one (5)

Next, we examined copolymerization of diazoacetamides **1–4** with (*E*)-1-diazo-4-phenyl-3-buten-2-one **5**, whose homopolymerization mediated by $PdCl_2(MeCN)_2$ in toluene at 80 °C has been demonstrated to afford polymers with M_n = 1740 in a 63.3% yield.[4b] As summarized in Table I, all the four diazo compounds **1–4** can be copolymerized including **3** and **4**, which did not afford polymers for their homopolymerization as described above (Scheme 2). For example, a mixture of **1** and **5** in a 1:1 molar ratio was reacted with $PdCl_2(MeCN)_2$ ([Pd] × 100 = [**1**] + [**5**]) in toluene at 80 °C for 14 h, giving a polymeric product whose GPC-estimated M_n calibrated with PMMA standards was 1260 (run 3). As shown in Figure 2, the ^{1}H NMR spectrum for the product exhibits broad signals assignable to each H in the repeating units of **1** and **5**. In this case, broad signals that should be ascribed to main chain C-Hs for **1′** and/or **5′** are observed at 4.0–5.7 ppm. The composition of the two repeating units can be calculated from the integral ratio between the broad signals for CH_3 at 0.6–1.0 ppm (**1′**) and $C_6H_5CH{=}CH$ at 6.0–8.0 ppm (**5′**), to be [**1′**]:[**5′**] = 1.3:1.[8]

As listed in Table I, the observed values for the elemental analysis of the product agree with the calculated values for the structure with the composition of [**1′**]:[**5′**] = 1.3:1 and M_n = 1440. The calculation was also based on the assumption that the polymer has Cl at both chain ends and the azo content in the main chain is 26.8 mol %. On the basis of the composition, the yield of the polymer is 31.5%. In a similar manner, copolymerization with feed ratios of [**1**]:[**5**] = 2:1 and 1:2 proceeded to give copolymers with compositions corresponding to the
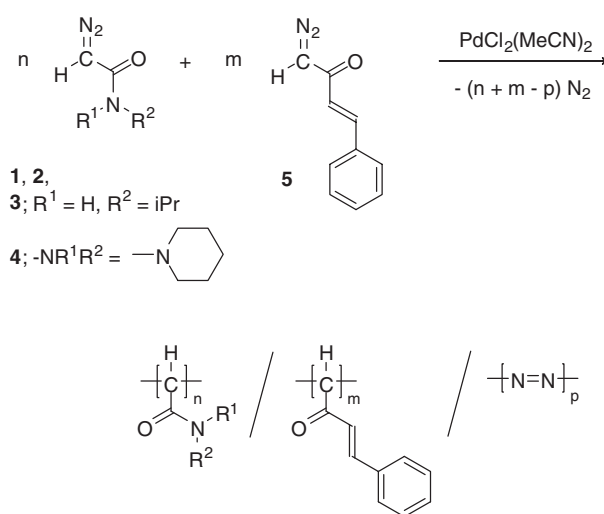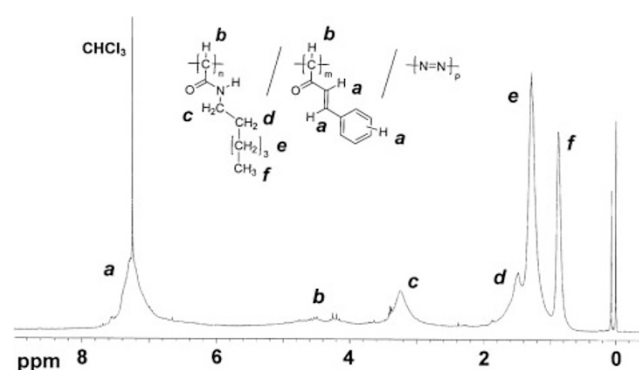

Scheme 2.

Figure 2. ^{1}H NMR spectrum of a copolymer from **1** and **5** (run 3, Table I).

feed ratios (runs 2 and 4). Reflecting the low reactivity of **1** compared to **5** toward homopolymerization, the M_ns and yields of the resulting poly(**1′**-*ran*-**5′**) were lower than those of the poly**5′** obtained under the same condition.

When **2** was used as a diazoacetamide for the copolymerization with **5**, the composition of **2** in the resulting copolymer is much higher than that expected from the feed ratio, which clearly indicates the higher relative reactivity of **2** than **5** in the copolymerization, whereas the composition of the copolymers changed corresponding to the feed ratio (runs 6–8). In addition, M_ns of poly(**2′**-*ran*-**5′**)s are much higher than those of poly(**1′**-*ran*-**5′**)s in runs 2–4. The high reactivity of **2** could again be ascribed to the presence of the aromatic ring in the monomer structure. The copolymerization with [**2**]:[**5**] = 1:2 gave a copolymer, whose observed elemental analysis values agreed with the calculated values for the structure with a NMR-determined composition and GPC-estimated M_n (run 8).

The non-homopolymerizable diazoacetamides **3** and **4** could be used for the copolymerization with **5** (runs 9–14). The progress of the copolymerization of **3** and **4** with **5** supports our assumption mentioned above that the monomers cannot be homopolymerized because of the steric reason derived from

their substituents although the diazocarbonyl groups have potential to be polymerized. However, probably because the monomer structures of **3** and **4** with bulky substituents may be sterically unfavorable for the Pd-centered propagating center even in the copolymerization, the M_ns of the copolymers are relatively low, and they become lower with the increase of the feed ratio of **3** and **4**. On the other hand, the composition of the copolymers corresponds to the monomer feed ratio, indicating that the relative reactivity of **3** and **4** is close to that of diazoketone **5**. The repeating unit structure derived from **3** is of interest because it could be regarded as poly(substituted methylene) analogue of poly(*N*-isopropylacrylamide), whose unique thermo-responsive property has been well known.[9] The compositions for those copolymers obtained from **3** and **4** were also determined from ^{1}H NMR and elemental analyses.

CONCLUSIONS

We have demonstrated that diazoacetamides can be polymerized to give polymers having *N*-substituted carbamolymethylene as a repeating unit. Although the M_ns of the resulting polymers are rather low, the polymer structures with *N*-substituted carbamolymethylene repeating units obtained here are unprecedented and would be expected to have unique properties.

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