First Synthesis of Poly(acylmethylene)s via Palladium-Mediated Polymerization of Diazoketones

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Received August 19, 2004; Revised Manuscript Received December 15, 2004

ABSTRACT: Palladium-mediated polymerization of diazoketones (**1a**, **2a**, **3a**, **4a**, and **6a**) proceeded to give poly(acylmethylene)s (**1b**, **2b**, **3b**, **4b**, and **6b**), in which all of the main chain carbons had acyl groups. The structures of the novel polymers were characterized by NMR spectroscopy, elemental analyses, and molecular weight measurements (GPC and VPO), where the results of the elemental analyses suggested incorporation of a small amount of azo group (-N=N-) into the main chain (ca. one -N=N- per polymer chain). The presence of a C=C double bond adjacent to the carbonyl carbon in the monomers was required for the polymerization to proceed. Palladium-mediated copolymerizations using a variety of combinations of diazoketones and ethyl diazoacetate, **8**, as comonomers proceeded to give various poly(substituted methylene)s.

Introduction

Vinyl polymerizations, which generally produce polymers whose main chains are composed of carboncarbon (C-C) single bonds, such as polyethylene, polypropylene, polystyrene, poly[alkyl (meth)acrylate], are one of the most important methods for polymer synthesis. While the vinyl polymerization is so-called "poly(substituted ethylene) synthesis", where the polymer main chain is constructed from two carbon units (e.g., -CH₂-CXY-), the C-C backbone with the same composition can also be constructed from one-carbon units (e.g., $-CH_2$ and -CXY -). This strategy, which should be called as "poly(substituted methylene) synthesis", will be an attractive method to prepare new polymers that cannot be synthesized by vinyl polymerization, if we can find appropriate compounds that can serve as monomers for the polymerization (Scheme 1).

Since it was reported that poly(substituted methylene)s could be obtained by polymerization of diazo-alkanes a few decades ago,¹ the chemistry of "poly-(substituted methylene) synthesis" had not been developed until Shea and co-workers disclosed that sulfoxonium ylides efficiently served as monomers for "poly(substituted methylene) synthesis" initiated with oraganoboranes to give polymers with narrow molecular weight distributions (MWD) and controlled molecular weights.² We have found and reported that alkyl diazoacetates can be polymerized to give poly(alkoxycarbonylmethylene)s via Pd-mediated polymerization releasing dinitrogen.³ We proposed that the propagation of the polymerization was an insertion of the monomer into a Pd-C bond of the propagating chain end. That is the first example of the synthesis of poly(substituted methylene)s with polar substituents, although syntheses of polymers with the same structure have been established with the radical polymerization of dialkyl maleates or dialkyl fumarates in a series of pioneering studies by Otsu and co-workers.4,5







Herein, as an extension of the polymerization of diazocarbonyl compounds, we describe Pd-mediated polymerization of diazoketones to afford poly(acylmethylene)s, which are novel polymers that cannot be obtained by any conventional methods for polymer synthesis.

Results and Discussion

Palladium-Mediated Polymerization of (E)-1-Diazo-3-nonen-2-one (1a). We have found that po-

			·			(m+) 0110			
									elemental analysis
	monomer (M),				temp,	yield			found
run	mmol	initiator (M)	[I]/[M]	solvent	°C.	(%)	$M_{ m n}{}^b$	$M_{ m w}/M_{ m n}^b$	calcd for $Cl(monomer unit)_m(-N=N-)_n Cl \cdot (H_2O)_p, M_n$
1	1.82	$PdCl_2$	100	toluene	40	45.8	2370	1.42	C, 72.87; H, 9.55; N, 1.40
2	1.81	$PdCl_2(MeCN)_2$	100	toluene	40	49.6	2480	1.53	C, 73.23; H, 9.80; N, 1.40 ($m/n = 17.0:1.25$, $p = 3$, $M_n = 2460$) C, 72.60; H, 9.55; N, 1.16
									C, 73.44; H, 9.91; N, 1.12 ($m/n = 17.0.1.0$, $p = 3$, $M_n = 2450$)
\mathfrak{Z}_{c}^{c}	2.42	$PdCl_2(MeCN)_2$	100	toluene	40	22.0	2020	1.42	C, 69.60; H, 9.02; N, 2.78
	60 1		000	401.000	01	2 V V	0200	<i>3</i> 6 1	C, 70.10; H, 9.45; N, 3.22 $(m/n = 15.0:1.5, p = 6, M_n = 2070)^d$
4	00'T	Fu2(uDa)3(UIIUI3)	700	allanton	40	44.0	0707	06.1	C, 12.20 ; II, 3.43 ; IV, 1.33 C. 72.82 ; H. 10.03 ; N. 1.57 ($m/n = 18.0$; 1.5 , $p = 6$, $M_n = 2560)^e$
ũ	1.82	$PtCl_2$	100	toluene	40	14.5	2440	1.26	C, 67.45; H, 8.78; N, 2.56
									C, 67.74; H, 9.53; N, 3.19 ($m/n = 11.0.2.0$, $p = 6$, $M_n = 1650$)
9	1.81	$PdCl_2(MeCN)_2$	100	toluene	80	36.8	2400	1.49	
7	1.83	$PdCl_2(MeCN)_2$	100	toluene	0	14.9	1800	1.39	
80	1.83	$PdCl_2(MeCN)_2$	200	toluene	40	30.9	2170	1.45	
6	1.83	$PdCl_2(MeCN)_2$	50	toluene	40	42.3	1820	1.48	
10	1.83	$PdCl_2(MeCN)_2$	100	THF	40	39.0	2250	1.42	C, 71.03; H, 9.45; N, 1.58
									C, 71.43; H, 9.74; N, 1.74 ($m/n = 16.0:1.5$, $p = 5$, $M_n = 2330$)
11	1.83	$PdCl_2(MeCN)_2$	100	MeCN	40	24.1	2020	1.38	C, 70.50; H, 9.20; N, 2.60
									C, 70.33; H, 9.65; N, 2.60 ($m/n = 14.0:2.0, p = 5, M_n = 2060$)
12	1.82	$PdCl_{2}(MeCN)_{2}$	100	DMF	40	22.3	1420	1.36	C, 67.38; H, 8.73; N, 4.22
61	60 1	(IND-IN) IDEA	100	-4-4	01	0 1 0	0100	10 F	C, 67.01; H, 9.37; N, 4.34 $(m/n = 10.0:2.5; p = 5, M_n = 1520)$
61	1.00	rau12(1MIGUIN)2	TUU	eunyi acetate	40	0.10	0017	1.00	O, 10.07; II, 9.24; N, 1.40 C 70 77; H 9 75; N 1 41 ($m/n = 13.0.1.0$ $n = 5.M_{\odot} = 1900$)
14	1.82	$PdCl_{2}(MeCN)_{2}$	100	CH ₂ Cl ₂	40	33.4	2220	1.30	C, 72.21; H, 9.43; N, 1.93
				1					C, 72.51; H, 9.72; N, 1.76 ($m/n = 16.0.1.5$, $p = 3$, $M_n = 2330$)
^a Solven	t = 10 mL; poly	merization period $= 13$ l	n. $^{b} M_{\rm n}$ and	$M_{\rm w}/M_{ m n}$ were obtain	ned by GP(C calibratio	n using a s	standard PM	(MA and dibutyl sebacate in THF solution. c Pyridine (1.24 mmol)
was used a	is an additive. d	Calculated values were b	ased on the	e following composit	ion: Cl-[C	${}_{5}H_{5}N]^{+}$ (mo	nomer uni	$t_m(N=N)_n[C]$	$^{6}_{5}H_{5}N]^{+}CI^{-i}(H_{2}O)_{p}$. e Calculated values were based on the following
compositio	n: (HO)(monom	ler unit) _m (N=N) _n (OH)·(F)	$[_{2}O)_{p}.$						

 $Table \ 1. \ Polymerization \ of \ (E) \cdot 1 \cdot Diazo-3 \cdot nonen-2 \cdot one \ (1a) \ Initiated \ with \ Transition \ Metal \ Compounds^{c}$

Scheme 3. One of Possible Mechanisms for Polymerization of Diazoketone with PdCl₂



lymerization of a diazoketone, (E)-1-diazo-3-nonen-2-one **1a**, initiated with $PdCl_2$ ([**1a**]/[PdCl_2] = 100:1) at 40 °C in toluene for 13 h proceeds to give poly[(E)-2-octenoy]methylene] (1b) in 45.8% yield after purification with preparative recycling gel permeation chromatography (GPC) (Scheme 2, run 1 in Table 1). Compared to poly-(alkoxycarbonylmethylene)s obtained with the PdCl₂/ pyridine system,³ whose GPC-estimated M_n 's using poly(methyl methacrylate) (PMMA) standards were below 1000, the M_n of 1b (2370) is much higher. However, probably because of the low solubility of PdCl₂ in toluene, reproducibility of the polymerization is rather low with respect to the yield and $M_{\rm n}$ of the resulting 1b's. Thus, we employed the acetonitrile (MeCN) adduct of PdCl₂, PdCl₂(MeCN)₂, with higher solubility in organic solvents than PdCl₂, as an initiator. As shown in run 2, $PdCl_2(MeCN)_2$ afforded 1b with a yield and M_n both comparable to those with PdCl₂ in run 1 with higher reproducibility, as expected.

In a previous paper describing the polymerization of alkyl diazoacetates with PdCl₂/amine systems,³ we proposed that the polymerization should be initiated by a nucleophilic attack of amine to the α -carbon of the monomer, accompanied by release of dinitrogen from the monomer and formation of a palladium-carbon bond. Propagation should be the insertion of another monomer into the Pd-C bond with release of dinitrogen, and the polymerization should be terminated by reductive elimination of two propagating chains on the same palladium center, furnishing a poly(alkoxycabonylmethylene) with amine-derived groups at both chain ends. The mechanism was supported by the observation of poly(aryloxycarbonylmethylene)s with amino groups at both chain ends by matrix-assisted laser desorption ionization timeof-flight mass spectrometry (MALDI-TOF-MS) analyses.³ In addition, because the intervals of the signals in the mass spectra were not the m/z values of [CHC- $(=0)OR \times 2$] but those of CHC(=0)OR, we can rule out the possibility of the formation of the polymers via Pdcatalyzed dimerization forming dialkyl fumarate or maleate followed by radical polymerization of the diesters.3

On the other hand, in the polymerization with $PdCl_2$ -(MeCN)₂ in the absence of amines, we initially assumed that chlorides on the Pd center would initiate the polymerization instead of amines, as shown in Scheme 3. However, because the results in run 2 ([1a]/[PdCl₂]

Scheme 4. Proposed Mechanism for Incorporation of Azo group into the Polymer Main Chain



= 100, yield = 49.6%, $M_n = 2480$) indicate that ca. 2.8 polymer chains were produced by one PdCl₂ molecule, there should be a chain-transfer mechanism, where polymerization is reinitiated with a nucleophile other than Cl⁻ on the Pd center. Thus, our tentative explanation for this polymerization behavior is that (1) the Pd-(0) species generated by the reductive elimination would be oxidized to Pd(II) in situ and (2) in the presence of the Pd(II) species, some weak nucleophiles such as H₂O, MeCN, and monomer **1a** would initiate the polymerization, generating the propagating species with Pd-C bonds. Although the actual mechanism for the initiation is not clear at present, we are trying to elucidate it by finding well-defined Pd complexes that can polymerize diazocarbonyl compounds in a controlled manner.

The elemental analyses of 1b obtained in Table 1 indicated the presence of a small amount of nitrogen in the polymers. The origin of the nitrogen cannot be explained by the initiation with MeCN coordinated to the Pd center, because **1b** obtained with PdCl₂ alone (run 1) contained a similar amount of nitrogen as in run 2, and the nitrogen contents in some cases are too much to be rationalized by the presence of MeCN-derived chain ends (eg. runs 11 and 12). Among the compounds used in run 1 (1a, PdCl₂, toluene), the only compound containing nitrogen is the monomer. Accordingly, the most plausible mechanism for the incorporation of nitrogen that we can think of is described in Scheme 4, where the migration of the propagating chain end to the Pd-coordinated monomer occurs at the terminal nitrogen instead of at the α -carbon, resulting in the incorporation of an azo group into the main chain. Although we do not have any direct evidences of the presence of the azo group in the main chain so far, we are currently trying to elucidate the issue by using the polymers with higher nitrogen contents obtained with other systems for poly(substituted methylene) synthesis.

In Table 1, on the assumption that the polymers have chlorides at both chain ends and azo groups in their main chain, calculations were carried out to find the structures of the polymers that agreed well with the results of the elemental analyses. As a result, M_n values comparable to those from GPC were obtained and the presence of nearly one -N=N- unit per polymer chain on average was suggested for runs 1 and 2. Although the assumption with respect to the presence of Cl at both chain ends cannot be correct on the basis of the aforementioned discussion, we believe that the method for the calculation is somewhat useful in order to estimate the structure of the poly(acylmethylene)s obtained in this study.

As the other initiating systems using Pd compounds, PdCl₂/pyridine and Pd₂(dba)₃(CHCl₃) (dba = dibenzylideneacetone) were examined. The PdCl₂/pyridine system, which gave the best results for the polymerization of alkyl diazoacetates,³ afforded **1b** in lower yield and with lower M_n than those of **1b** obtained with PdCl₂-(MeCN)₂ (run 3). The higher N content of **1b** in run 3



Figure 1. ¹H NMR spectrum of 1b (run 2 in Table 1).

can be reasonably attributed to the presence of pyridinium groups at both chain ends.³ As for the polymerization with Pd₂(dba)₃(CHCl₃) giving a similar result to that with PdCl₂(MeCN)₂ because the propagation via zero-valent Pd does not seem to be feasible, we suppose that the Pd might be oxidized to form divalent species, which should mediate the polymerization. Because one possible mechanism for the initiation in this case is that a small amount of H₂O existing as impurity would initiate the polymerization instead of Cl, resulting in the formation of **1b** with hydroxy groups at both chain ends, calculated values of elemental analyses for the polymer (run 4) were obtained on the basis of the OHteminated structure, where a good agreement was observed between the calculated and found values. At any rate, our mechanistic assumption for the chain transfer via Pd(0) species can be supported by the observation of the efficient initiation with Pd₂(dba)₃- $(CHCl_3)$.

We have examined various late-transition-metal halides other than Pd for the initiation of **1a** under the same conditions as run 2. Among the metal halides examined (FeCl₃, RuCl₃, CoCl₂, RhCl₃, NiBr₂, and PtCl₂), only PtCl₂ afforded poly(acylmethylene) **1b** in lower yield and with a higher N content than those in run 2 (run 5), whereas the other metal halides did not afford polymeric products.

From the investigation described above, we have concluded that the use of $PdCl_2(MeCN)_2$ is most appropriate for the polymerization of **1a**. Then, we tried to examine the effects of other polymerization conditions on the polymerization behavior using $PdCl_2(MeCN)_2$. Raising the reaction temperature to 80 °C decreased the polymer yield (run 6); the polymerization at 0 °C afforded a polymer with a lower M_n in lower yield (run 7). Whereas lowering the [M]/[I] ratio from 100 to 50



decreased the M_n of the resulting **1b**, raising the [M]/[I] ratio to 200 was not effective to obtain **1b** with a higher M_n (runs 8 and 9). Various organic solvents other than toluene can be used for the polymerization. As summarized in runs 10–14, the polymerizations in THF, MeCN, DMF, ethyl acetate, and dichloromethylene all afforded polymers in lower yield and with lower M_n 's than those of **1b** obtained in toluene. It should be noted that the degree of N incorporation into the polymer depends on the solvent employed, where the use of highly polar solvents such as MeCN and DMF resulted in the higher N incorporation.

Figure 1 shows a representative ¹H NMR spectrum of **1b** (run 2). Along with the signals for the alkyl group at 0.6–2.4 ppm, two broad signals appear at 5.9–6.6 and 6.6–7.2 ppm, both corresponding to the vinyl proton signals of the monomer **1a** at 5.99 and 6.81 ppm. The correlation between the two vinyl H signals of **1b** was observed in a H–H cosy measurement. The methine H attached to the main-chain carbons seems to appear as very broad signals in a wide range of the spectrum, whereas the signal for poly(alkoxycarbonylmethylene) was observed at 3.0–3.9 ppm as a broad peak.^{3,5}

Palladium-mediated Polymerization of (*E*)-1-Diazo-4-phenyl-3-butene-2-one (2a). Another α,β unsaturated diazoketone, (*E*)-1-diazo-4-phenyl-3-butene-2-one (2a) can be transformed into poly[(*E*)-3-phenyl-2-propenoylmethylene] (2b) (Scheme 5) by the reaction with 1 mol% of PdCl₂(MeCN)₂ in toluene, as shown in runs 1 and 2 in Table 2. The GPC-estimated M_n of 2b is lower than that of 1b under the same condition, and the yield of 2b is significantly higher at 80 °C than at 40 °C. The elemental analyses of 2b's reveal that they also contain nitrogen, but the contents are much lower than those in 1b. Calculation based on the assumption that the polymers have two chlorides at both chain ends reveals that less than one azo group exists per polymer chain on average. The ¹H NMR spectrum of 2b (run 1)

Table 2. Polymerization of Diazoketones Initiated with PdCl₂(MeCN)₂ in Toluene^a

						elemental analysis
	monomer (M),	temp,	yield			found
run	mmol	°C	(%)	$M_{ m n}{}^b$	$M_{ m w}/M_{ m n}{}^b$	calcd for $Cl(monomer unit)_m(-N=N-)_nCl\cdot(H_2O)_p, M_n$
1	2a , 1.76	40	44.9	1720	1.27	C, 78.12; H, 5.53; N, 0.69
						C, 77.98; H, 5.56; N, 0.61 ($m/n = 12.0:0.4$, $p = 2$, $M_n = 1810$)
2	2a , 1.77	80	63.3	1740	1.26	C, 79.64; H, 5.57; N, 0.67
						C, 79.53; H, 5.34; N, 0.62 ($m/n = 12.0:0.4$, $p = 0$, $M_n = 1810$)
3^c	2a , 5.24	80	62.8	1610	1.30	C, 79.80; H, 5.64; N, 0.64
						C, 79.34; H, 5.33; N, 0.50 ($m/n = 11.0:0.3$, $p = 0$, $M_n = 1670$)
4	3a , 2.11	80	25.2	420	1.43	C, 75.24; H, 5.12; N, 0.69
						C, 75.14; H, 4.73; N, 0.68 ($m/n = 8.0:0.5$, $p = 0$, $M_n = 1020$)
5	4a + 5a , 1.96	40	13.4	890	1.29	C, 67.42; H, 9.69; N, 1.56
						C, 67.58; H, 10.23; N, 1.41 ($m/n = 7.0:0.5$, $p = 1.5$, $M_n = 970$)
6	6a + 7a , 1.75	40	15.6	650	1.30	C, 75.11; H, 6.63; N, 1.12
	,					C, 75.46; H, 6.33; N, 0.73 ($m/n = 6.0:0.25, p = 0, M_n = 960$)

^{*a*} Toluene = 10 mL; polymerization period = 13 h. ^{*b*} M_n and M_w/M_n were obtained by GPC calibration using a standard PMMA and dibutyl sebacate in THF solution. ^{*c*} M_n determined by VPO is 1500.



Figure 2. ¹H NMR spectrum of 2b (run 1 in Table 2).





is shown in Figure 2, where signals for protons on C= C double bonds should be included in the Ph-H proton signals at 6.0-8.2 ppm and that for C-H on the main chain appears at 2.2-4.5 ppm as a very broad peak.

Because M_n values of poly(substituted methylene)s determined by GPC based on PMMA standards may not be reliable, M_n measurement of **2b** was carried out by vapor pressure osmometry (VPO). Preparation of **2b** for the VPO measurement was conducted under the same condition as in run 2 except that the polymerization scale was three times larger (run 3). The M_n for the polymer determined by the VPO measurement in CHCl₃ at 45 °C was 1500, which was slightly shorter than those estimated with GPC (1610) and elemental analyses (1670). However, the comparison of the M_n values suggests that, at least for **2b**, we can estimate M_n by GPC and elemental analysis.

Palladium-Mediated Polymerization of 2-Diazoacetophenone (3a), 1-Diazo-2-octanone (4a), and 1-Diazo-4-phenyl-2-butanone (6a). 2-Diazoacetophenone 3a can be polymerized to give poly(benzoylmethylene) 3b (Scheme 6) under the same conditions employed for the polymerization of 2a (run 4 in Table 2). GPC-estimated M_n of 3a (420) was much lower than those of 1a and 2a, which can be ascribed to the high steric crowding around the Pd center during propagation and/or in the resulting poly(benzoylmethylene) backbone, owing to the presence of a phenyl group directly attached to the carbonyl carbon.

Next, we attempted to polymerize 1-diazo-2-octanone (4a), which can be prepared from 2-octanone as a mixture with 3-diazo-2-octanone (5a). The reaction of the mixture of 4a and 5a ([4a]/[5a] = 10.0:1.0) with PdCl₂(MeCN)₂ in toluene at 40 °C afforded poly(heptanoylmethylene) (4b) in 13.4% yield after the purification with the recycling preparative GPC (run 5). The minor component 5a did not participate in the polymerization because no signal assignable to the acyl carbon appeared in the ¹³C NMR (DEPT) spectrum of the product. From the same steric reason as mentioned for **3a**, we suppose that the reactivity of **5a** for the polymerization should be quite low. Similarly, we investigated the reactivity of 1-diazo-4-phenyl-2-butanone (**6a**), which is a saturated counterpart to **2a** and is obtained as a

Scheme 7. Copolymerization of Diazocarbonyl Compounds with PdCl₂(MeCN)₂. I





Scheme 8. Copolymerization of Diazocarbonyl Compounds with PdCl₂(MeCN)₂. II

mixture with **7a**. Again, the reaction of a mixture of **6a** and **7a** ([**6a**]/[**7a**] = 10.4:1.0) with $PdCl_2(MeCN)_2$ in toluene at 40 °C afforded poly(4-phenyl-2-propenoyl-methylene) (**6b**) in 15.6% yield, whose ¹³C NMR (DEPT) spectrum did not exhibit any acyl-carbon signal (run 6). Although the reason for the lower yield of **4b** and **6b** compared to **1b** and **2b** is not clear at present, the distinct difference of the polymerization behaviors indicates that the presence of a C=C bond adjacent to the carbonyl group of the diazoketones is required for the polymerization to proceed.

6a

Copolymerization with Various Combinations of Diazocarbonyl Compounds. Pd-mediated copolymerizations with various combinations of diazoketones **1a, 2a, 3a, 4a**, and **6a** and ethyl diazoacetate **8** (Schemes 7 and 8) were examined to obtain a variety of poly(substituted methylene)s. Copolymerization of diazoketones **1a** and **2a** proceeded to give copolymers with monomer unit compositions roughly corresponding to the feed ratio of the monomers (runs 1 and 2, Table 3). Copolymerizations between the diazoketones (**1a** and **2a**) and ethyl diazoacetate (**8**) were also possible, affording poly(substituted methylene)s bearing both acyl and ethoxycarbonyl groups on the main chain (runs 3 and 4). As a representative example, Figure 3 shows the ¹H NMR spectrum of the copolymer obtained from 2a and 8 (run 4), where broad signals for 2b and poly-(ethoxycabonylmethylene) are observed. Because the copolymer exhibited an unimodal GPC trace, we can conclude that the product is not a mixture of 2b and poly(ethoxycabonylmethylene), but a copolymer of 2a and 8, although we do not have any information on the sequential distribution of the repeating units in the main chain. Similar characteristics in ¹H NMR and GPC traces were observed for all the products obtained in Table 3. The composition of the repeating units in these copolymers can be determined from the integral ratio of the signals in their ¹H NMR spectra, with which the results of elemental analyses agree well throughout Table 3.

In runs 5–9, we examined copolymerizations of diazoketones including **3a**, **4a**, and **6a**, which gave polymers with relatively low M_n (<1000) in their homopolymerizations. With **3a** and **6a**, copolymerization with

								composition in	
	monomer 1,	monomer 2,						copolymer	elemental analysis
	(M1)	(M2)		temp	yield			M1:M2	found
run	mmol	mmol	[M1]:[M2]	°°	(%)	M_{n}^{b}	$M_{ m w}/M_{ m n}^b$	$(^{1}H NMR)$	calcd for $\operatorname{Cl(M1)}_x(\operatorname{M2})_y(-\operatorname{N=N-})_z\operatorname{Cl}(\operatorname{H_2O})_p, M_{\operatorname{n}}$
1	la,	2a,	3:1	80	36.4	1780	1.26	3.92:1	C, 74.13; H, 8.26; N, 0.95
	1.46	0.49							C, 73.85; H, 8.84; N, 1.12 ($x/y/z = 10.0:2.5:0.75$, $p = 2$, $M_n = 1830$)
2	1a,	2a,	1:3	80	44.0	1570	1.32	1:2.28	C, 76.20; H, 6.37; N, 0.90
	1.31	0.44							C, 76.91; H, 6.51; N, 0.84 ($x/y/z = 3.0.8.0.0.5$, $p = 2$, $M_n = 1650$)
က	1a,	Ś	3:1	40	57.4	096	1.60	1.90:1	C, 67.04; H, 8.78; N, 1.68
	1.47	0.48							C, 67.21; H, 8.72; N, 1.78 ($x/y/z = 6.0:3.0:0.75$, $p = 0$, $M_n = 1180$)
4	2a,	Ś	3:1	80	44.0	1400	1.28	1.61:1	C, 73.57; H, 5.75, N, 0.85
	1.47	0.48							C, 72.86; H, 5.60; N, 0.89 ($x/y/z = 8.0:4.0:0.5$, $p = 0$, $M_n = 1580$)
5 L	la,	За,	3:1	80	24.9	1690	1.23	7.66:1	C, 72.73; H, 8.54; N, 1.25
	1.35	0.46							C, 73.03; H, 9.22; N, 1.15 ($x/y/z = 11.0.1.5.0.75$, $p = 2$, $M_n = 1790$)
9	la,	6a + 7a,	3:1	40	26.8	1610	1.41	7.94:1	C, 70.86; H, 8.50; N, 1.66
	1.30	0.45							C, 70.92; H, 9.32; N, 1.61 ($x/y/z = 10.0:1.25:1.0$, $p = 4$, $M_n = 1660$)
7	2a,	$4\mathbf{a} + 5\mathbf{a}$,	3:1	80	41.3	1410	1.29	2.93:1	C, 76.46; H, 6.30; N, 0.73
	1.34	0.45							C, 76.19; H, 6.62; N, 0.78 ($x/y/z = 9.03.0.0.5$, $p = 2$, $M_n = 1760$)
00	3a,	óc	1:3	80	64.2	540	1.34	1:4.67	C, 59.28; H, 6.28; N, 0.87
	0.49	1.44							C, 59.02; H, 6.37; N, 0.61 ($x/y/z = 4.0:20.0:0.5$, $p = 0$, $M_n = 2280$)
6	$\mathbf{6a} + \mathbf{7a},$	œ	1:3	40	56.6	630	1.30	1:5.95	C, 59.03; H, 6.58; N, 1.20
	0.49	1.50							C, 58.70, H, 6.66; N, 1.34 (<i>x</i> / <i>y</i> / <i>z</i> = 3.0.18.0.1.0, $p = 0, M_n = 2090$)
a Tolt	iene = 10 mL: no	lymerization perio	d = 13 - 16 h.	M_n and M	1/M. were	obtained]	by GPC calibr	ation using a star	dard PMMA and dibutyl sebacate in THF solution.

Macromolecules, Vol. 38, No. 6, 2005

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Figure 3. ¹H NMR spectrum of a copolymer from **2a** and **8** (run 4 in Table 3).

1a proceeded to give copolymers with $M_n = \sim 1700$, although the contents of the repeating units derived from 3a and 6a in the products are much lower than expected from the feed ratios (runs 5 and 6). On the other hand, 4a efficiently participated in the copolymerization with 2a, affording a copolymer with the composition nearly expected from the monomer feed ratio (run 7). Copolymerization of diazoacetate 8 with 3a and 6a also proceeded to give copolymers with low M_n 's (runs 8 and 9).

Conclusions

We have demonstrated that Pd-mediated polymerization of diazoketones can afford poly(acylmethylene)s bearing acyl groups on all the main-chain carbon atoms. The poly(acylmethylene)s are novel polymers that cannot be prepared by any conventional methods for polymer synthesis. With the ability to afford a variety of poly(substituted methylene)s as described in this study, we believe that Pd-mediated polymerization of diazocarbonyl compounds will be one of the general methods for polymer synthesis.

Experimental Section

Materials. Toluene, THF, and MeCN were dried over sodium, Na/K alloy, and calcium hydride (CaH₂), respectively, and distilled before use. Ethyl acetate and methylene chloride were dried over CaH₂ and used without further purification. Pyridine (Wako, 99%) was dried over CaH2 and distilled before use. 1,1,1,3,3,3-Hexamethyldisilazane (TCI, >96%) and 2,2,2trifluoroethyl trifluoroacetate (Aldrich, 99%) were dried over CaH₂ and used without further purification. Et₃N was dried over KOH and used without further purification. PdCl₂ (Aldrich, 99%), dimethylformamide (Wako, >99.5%), (E)-3-nonen-2-one (TCI, >96%), 4-phenyl-2-butanone (TCI, > 95%), and *n*-butyllithium (*n*BuLi, Kanto Chemical, 1.60 M in *n*-hexane) were used as received. Diazoketone monomers 2a,6 3a,6 4a + 5a,6 ethyl diazoacetate 8,7 methanesulfonyl azide,6 PdCl₂-(MeCN)₂,⁸ and Pd₂(dba)₃(CHCl₃)⁹ were prepared according to the literature.

Measurements. ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a Bruker Avance 400 spectrometer using tetramethysilane as an internal standard in chloroform-d (CDCl₃) at 50 °C for polymers and at room temperature for **1a** and **6a**.

Molecular weights (M_n) and molecular weight distributions (M_w/M_n) were measured by means of gel permeation chromatography (GPC) 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 at 40 °C, calibrated with a poly(MMA) standard (Shodex M-75, $M_n = 2190$, $M_w/M_n = 1.08$) and dibutyl sebacate $(M_w = 314.5)$. The column used for the GPC analyses was KF-802 (Shodex; 300 mm × 8 mm i.d., 6 μ m average particle size, exclusion molecular weight of 5K for polystyrene). 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 70K for polystyrene) and a JAIGEL-2H (600 mm × 20 mm i.d., exclusion molecular weight

of 20K for polystyrene) using $\rm CHCl_3$ 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.

The vapor pressure osmometry measurement for **2b** was carried out on a Gonotec Osmomat 070 in chloroform at 45 °C. The cell constant for the measurement was determined with benzil (TCI, >99.9%). Three solutions of **2b** in CHCl₃ with different concentrations (2.9256, 9.0392, and 17.9792 g/kg CHCl₃) were used for the measurement.

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

Preparation of (E)-1-diazo-3-nonen-2-one (1a). A solution of 1,1,1,3,3,3-hexamethyldisilazane (7.90 mL, 6.05 g, 37.5 mmol) in 35 mL of THF was placed in a round-bottomed flask and was cooled to 0 °C. nBuLi (1.60 M in hexane, 23.4 mL, 37.5 mmol) was added to the solution by a syringe at 0 °C, and the mixture was stirred at 0 °C for 10 min. Then, the mixture was cooled to -78 °C, and a solution of (*E*)-3-nonen-2-one (5.70 mL, 4.80 g, 34.3 mmol) in 35 mL of THF was added dropwise at -78 °C from an addition funnel. After the mixture was stirred at -78 °C for 30 min, 2,2,2-trifluoroethyl trifluoroacetate (5.50 mL, 8.04 g, 41.0 mmol) was added at that temperature. After the resulting mixture was stirred at -78 °C for 10 min, it was warmed to room temperature and subjected to extraction with Et₂O (50 mL) and 1 N aqueous HCl solution (100 mL). The aqueous phase was extracted with 50 mL of Et₂O, and the combined organic phase was washed with 100 mL of saturated aqueous NaCl solution. After volatiles were removed from the organic phase under reduced pressure, the resulting oil was dissolved in 30 mL of MeCN and transferred to a round-bottomed flask. After water (0.62 g, 34 mmol) and Et₃N (5.19 g, 51.3 mmol) were added, a solution of methanesulfonyl azide (6.21 g, 51.3 mmol) in 20 mL of MeCN was added dropwise from an addition funnel. After the resulting solution was stirred at room temperature for 6 h, the residue was diluted with 50 mL of Et₂O and washed with 300 mL of 5% NaOH solution and 100 mL of saturated aqueous NaCl solution, dried over Na₂SO₄, filtered, and concentrated to afford an oil. The oil was diluted with 150 mL of ethyl acetate, passed through a short column of silica gel (ca. 50 g), concentrated, and dried under reduced pressure to afford 5.59 g (98.2%) of 1a as a reddish brown oil: ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3) \delta 6.81 \text{ (dt}, J = 7.5 \text{ and } 15.2 \text{ Hz}, 1 \text{ H}, -\text{CH} =$ $CH-CH_2-$), 5.99 (d, J = 15.6 Hz, 1 H, -C(=O)-CH=CH-), 5.34 (s, 1 H, N₂CH–), 2.19 (dt, J = 7.0 and 7.6 Hz, 2 H, =CH-C H_2 -C H_2 -), 1.46 (m, 2 H, -C H_2 -), 1.31 (m, 4 H, $-CH_2-$), and 0.89 (t, J = 7.0 Hz, 3 H, $-CH_3$); ¹³C NMR (100 MHz, CDCl₃) δ 184.7 (C=O), 145.2 (-CH=CH-CH₂-), 127.1 (-C(=O)-CH=CH-), 54.8 (N₂CH-), 32.0 (=CH-CH₂-CH₂-), $31.1 (-CH_2-)$, $27.6 (-CH_2-)$, $22.2 (-CH_2-)$, and 13.7 $(-CH_3)$. The assignment of the ¹³C NMR was confirmed by HMQC measurement. Anal. Calcd for C₉H₁₄N₂O: C, 65.03; H, 8.49; N, 16.85. Found: C, 64.61; H, 8.60; N, 15.78.

Preparation of 1-Diazo-4-phenyl-2-butanone (6a) and 3-Diazo-4-phenyl-2-butanone (7a). A mixture of 6a and 7a was prepared from 4-phenyl-2-butanone in 77.3% yield in a similar procedure to that for **1a**, except that diisopropylamine was used in place of 1,1,1,3,3,3-hexamethyldisilazane. The ratio of 6a/7a was determined to be 10.4:1 on the basis of the integral ratio of the ¹H NMR spectrum of the mixture, where the methyl signal at 2.25 ppm was used for 7a. ¹H NMR (400 MHz, CDCl₃) for **6a**; δ 7.17-7.29 (m, 5 H, Ph-H), 5.19 (s, 1 H, N₂CH-), 2.94 (t, J = 7.6 Hz, 2 H, PhCH₂), 2.62 (br-s, 2 H, -C(=O)-CH₂-); ¹³C NMR (100 MHz, CDCl₃) for **6a**; d 193.7 (C=O), 140.4 (Ph-ipso), 128.3 (Ph), 128.1 (Ph), 126.0 (Ph), 54.4 $(N_2CH-), 42.1 (-C=0)-CH_2-, 30.7 (-CH_2-Ph)$. The assignment of the $^{13}\mathrm{C}$ NMR was confirmed by HMQC and HMBC measurements. Anal. Calcd for C₁₀H₁₀N₂O: C, 68.95; H, 5.79; N, 16.08. Found: C, 68.51; H, 5.99; N, 14.92.

Pd-Mediated Polymerization of Diazoketone. As a typical procedure for the polymerization of diazoketones, the procedure for run 2 in Table 1 is described as follows. Under a nitrogen atmosphere, a solution of PdCl₂(MeCN)₂ (4.7 mg,

0.018 mmol) in 5 mL of toluene was placed in a Schlenk tube. After a solution of **1a** in 5 mL of toluene was added at room temperature, the mixture was warmed to 40 °C using an oil bath and stirred for 13 h at that 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 CHCl₃ were added to the residue. The CHCl₃ phase was separated using a separatory funnel, and the aqueous phase was extracted with 30 mL of CHCl₃. The combined CHCl₃ phase was washed with 50 mL of 1 N HCl aqueous solution and 50 mL of water, dried over Na₂SO₄, filtered, and concentrated under reduced pressure to afford a crude product. Purification with preparative recycling GPC gave **1b** (0.149 g, 49.6%) as a highly viscous oil.

Other homopolymerizations and copolymerizations of diazocarbonyl compounds in Tables 1-3 were carried out in similar procedures. ¹H NMR (400 MHz, CDCl₃, ppm) for 1b: 6.6-7.2 (br, 1 H, -COCHCHCH2-), 5.9-6.6 (br, 1 H, -CO-CHCHCH₂-), 1.0-2.4 (br, 8 H, -CHCH₂CH₂CH₂CH₂CH₃), 0.6-1.0 (br, 3 H, -CH₂CH₂CH₃), 2b: 6.0-8.2 (br, 7 H, -COCHCHAr-H), 2.2-4.5 (br, 1 H, polymer main chains), **3b**: 6.3–8.3 (br, 5 H, *H*-Ar), **4b**: 1.1–3.2 (br, 10 H, -COCH₂- $CH_2CH_2CH_2CH_2CH_3$), 0.75–1.05 (br, 3 H, – $CH_2CH_2CH_3$), 6b: 6.7-7.6 (br, 5 H, H-Ar), 1.6-3.5 (br, 4 H, -COCH₂CH₂-Ar). For 1b, 3b, 4b, and 6b, the signals drived from CH on the main chain cannot be identified, probably because of the broadness of the peaks. In ¹H NMR spectra of the copolymers obtained in Table 3, the appearances of the two sets of broad signals derived from each monomer unit are the same as those in their homopolymers.

Acknowledgment. This research was supported by Mitsubishi Chemical Corporation Fund, the Inamori Foundation, and Grant-in-Aid (No. 15036251, for Scientific Research on Priority Areas "Reaction Control of Dynamic Complexes", No. 15350071, and No. 16655047) from Ministry of Education, Culture, Sports, Science and Technology, Japan.

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MA048293U