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Synthesis of alkoxycarbene-containing polymers and their application as polymeric catalysts for phenylacetylene polymerization

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Summary

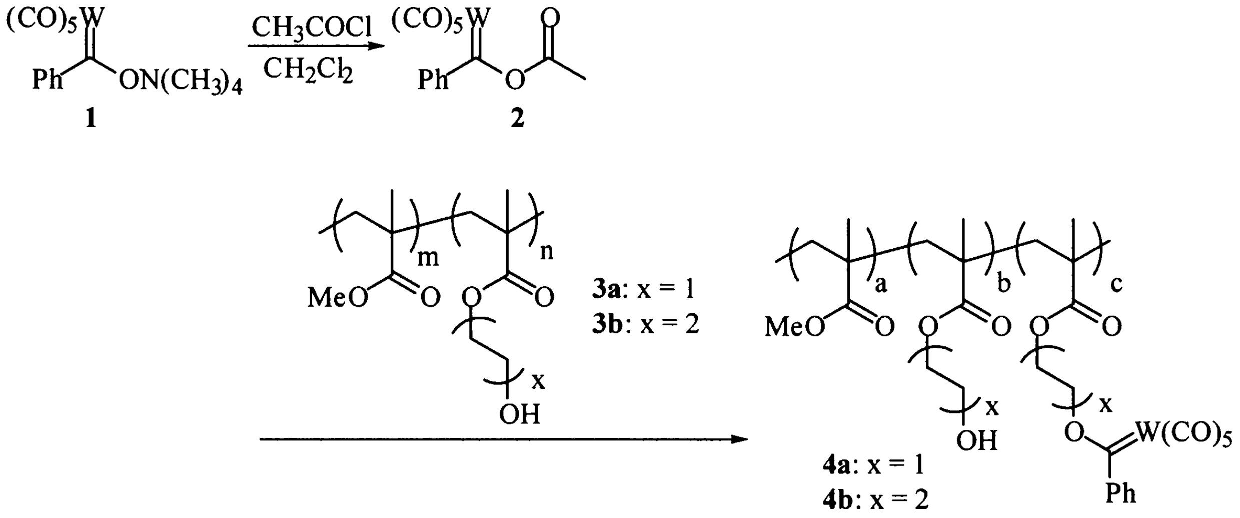
Polymers having Fischer-type alkoxycarbenes in the side chain were synthesized by the reaction of pendant hydroxy groups with pentacarbonyltungsten acetoxyphenylcarbene [$(CO)_5W{=}C(Ph)O_2CCH_3$, **2**]. Namely, copolymers of methyl methacrylate with 4-hydroxybutyl methacrylate [poly(MMA-*co*-HBMA), **3b**] were prepared and subjected to the reaction with **2** derived from tetramethylammonium salt of pentacarbonyltungsten hydroxyphenylcarbene [$(CO)_5W{=}C(Ph)ON(CH_3)_4$, **1**] with acetyl chloride. Soluble copolymers (**4b**) with pendant metal-carbene segments were obtained, and ^{1}H NMR and UV spectroscopic analyses indicated that the metal-carbene moiety was introduced onto 20-70% of hydroxy groups of the copolymers. In contrast, the introduction of carbene moiety into a copolymer of MMA with 2-hydroxyethyl methacrylate [poly(MMA-*co*-HEMA), **3a**] was unsuccessful because no reaction with **2** took place. The formed polymer (**4b**) served as a polymeric catalyst for the polymerization of phenylacetylene under the photo-irradiation.

Introduction

One of the recent focuses is placed on the metal-carbene complexes because they nicely induce many kinds of reactions and polymerizations [1]. It is unfortunate that synthesis of metal-carbene containing polymers is quite limited despite the prospect that they act as a new class of reactive polymers [2]. These backgrounds stimulated us to synthesize metal-carbene containing polymers, and we recently reported the polycondensation of difunctional Fischer-type alkoxycarbenes with diamines to the polymers with aminocarbenes in the main chain [3]. Although this approach readily allows the formation of stable organometallic polymers, unsatisfactory reactivity of aminocarbenes would inhibit their application as polymeric catalysts or reagents [4]. Therefore, the synthesis of a polymer containing alkoxycarbenes which are more reactive than aminocarbenes is advantageous for the production of carbene-based reactive polymers. Furthermore, the ability of alkoxycarbenes to initiate the metathesis polymerizations of cyclic olefins and acetylenes [5] would permit the use of such polymers as polymeric catalysts.

An early attempt for the access to the alkoxycarbene containing polymer has been reported by Macomber et al. who demonstrated the polymerization of pentacarbonyltungsten niethoxyvinylcarbene [$(CO)_5W{=}C(OCH_3)CH{=}CH_2$]. Although this is undoubtedly the most direct approach to the metal-carbene containing polymer, isolation of extremely unstable monomers is required, and the resulting polymer is insoluble unless the carbene unit is oxidatively cleaved [2]. On the basis of these

Scheme 1



backgrounds, we now report a new convenient method for the preparation of a polymer with alkoxycarbenes in the side chain. Our strategy includes the reaction of alcohols with acetoxycarbenes, which serves as a convenient approach to alkoxycarbenes [6]. We investigated the reaction of pentacarbonyltungsten acetoxyphenylcarbene (**2**) with pendant hydroxy groups of copolymers of methyl methacrylate (MMA) with either 2-hydroxyethyl methacrylate [poly(MMA-*co*-HEMA), (**3a**)] or 4-hydroxybutyl methacrylate [poly (MMA-*co*-HBMA), (**3b**)] (Scheme 1). Application of the formed metal-carbene containing polymer (**4**) as a polymeric catalyst for the polymerization of phenylacetylene is also described.

Results and discussion

Acetoxycarbenes are readily formed in situ by the reaction of acetyl chloride with ammonium salts of hydroxycarbenes as shown in Scheme 1 [6]. The acetoxycarbenes are sequentially reacted with alcohols to produce the corresponding alkoxycarbenes in good yield. This reaction is generally performed in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$. Because the homopolymers of HEMA and HBME are insoluble in such solvents, we employed the copolymers with MMA. These copolymers were readily prepared by the typical radical polymerization technique in toluene at 80°C by using AIBN as an initiator. Introduction of the carbene moiety was carried out by the addition of acetyl chloride to the solution of **1** in CH_2Cl_2 at -20°C, which was followed by the addition of a CH_2Cl_2 solution of **3**. The results are summarized in "Table 1.

The carbene-containing polymer **4a** was not attainable from **3a** because the reaction of **3a** with **2** did not take place under the conditions where alkoxycarbenes are readily obtained from low molecular weight alcohols (runs 1 and 2). The use of trifluoromethanesulfonyl chloride instead of acetyl chloride gave a similar result (run 3). The reaction in the presence of *N,N*-dimethylaminopyridine (DMAP) which often enhances the nucleophilicity of alcohols also led to an unsuccessful result because the reaction of **2** with DMAP dominated over the desired reaction (run 4). This can be explained by the low nucleophilicity of hydroxy group of **3a**. In contrast, the reaction of **2** with **3b** smoothly took place, giving the corresponding carbene-containing polymer (**4b**) (runs 5 and 6). **4b** was readily isolated by the reprecipitation into hexane. Conversion of approximately 70% of hydroxy group into the alkoxycarbene moiety was possible

Table 1. Synthesis of alkoxycarbene-containing polymers (**4**) by the reaction of **2** with **3**.

run	3			time (h)	4	
		m:n	M_n $(M_w/M_n)^a$		a:b:c^b	M_n (M_w/M_n)
1	**3a**	90:10	6600 (2.01)	1	90:10:0	nd^c
2				2	90:10:0	nd^c
3^d				2	90:10:0	nd^c
4^e				2	90:10:0	nd^c
5	**3b**	90:10	9000 (2.16)	2	90:8:2	10300 (2.02)
6				24	90:4:6	10900 (1.97)
7		73:27	10200 (2.44)	2	73:9:18	12900 (2.09)

[a] Estimated by GPC (THF, PSt). [b] Determined by ^{1}H NMR. [c] Not determined. [d] CF_3SO_2Cl was used instead of acetyl chloride. [e] In the presence of *N,N*-dimethylaminopyridine.

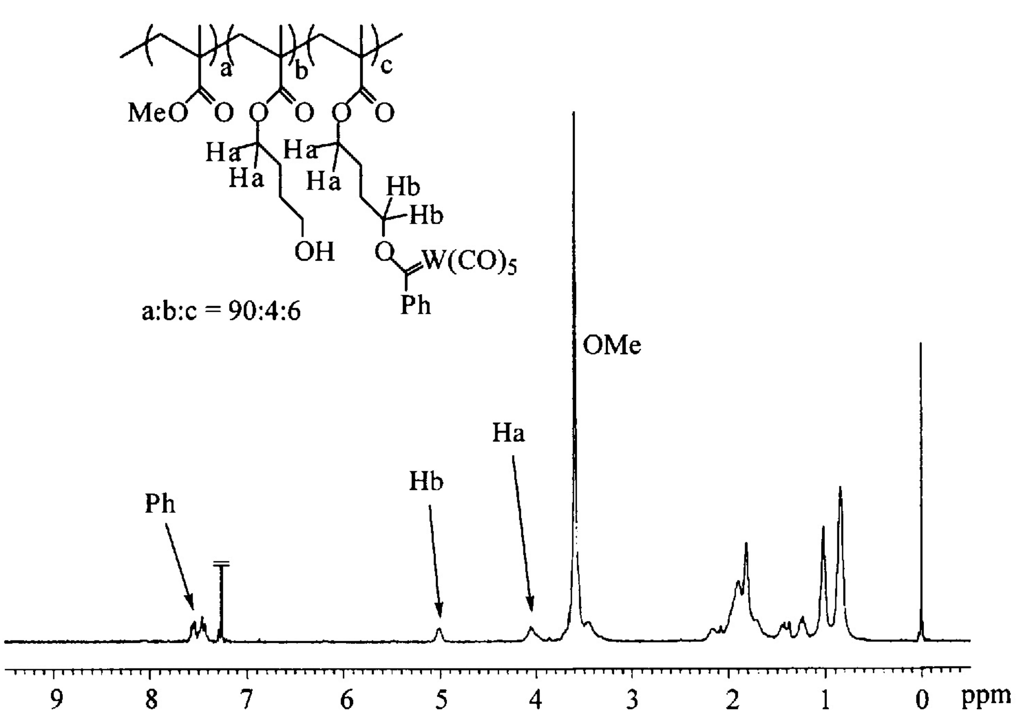


Figure 1. ^{1}H NMR spectrum of **4b** (run 6 in Table 1, in $CDCl_3$, rt).

(run 7). Increase in the molecular weight distribution was not observed after the reaction, which indicates the absence of the reaction between the polymer chains.

Characterization of **4b** was carried out by ^{1}H NMR and UV-vis spectroscopic analyses. In the ^{1}H NMR spectrum (Figure 1), the aromatic protons and methylene protons adjacent to the alkoxycarbene groups (Hb) were observed at δ 7.4 and 5.0, respectively. The integration of the signals readily gave the degree of the introduction of carbene unit. In contrast to the absence of an absorption of **3b** in UV-visible region, **4b** exhibited absorption maxima around 250 and 400 nm, which were also observed in the UV spectrum of the corresponding low molecular weight tungsten carbene complex

Table 2. Polymerization of phenylacetylene in toluene.[a]

run	catalyst	conv. (%)[b]	yield (%)[c]	M_n (M_w/M_n)[d]
1	**5**	9	6	11300 (3.20)
2[e]	**5**	nd[f]	37	37000 (3.10)
3[g]	**5**	42	34	29700 (2.96)
4[g]	**4b** (a:b:c = 90:8:2, M_n = 10300)	4	nd[f]	nd[f]
5[g]	**4b** (a:b:c = 90:4:6, M_n = 10900)	11	nd[f]	nd[f]
6[g]	**4b** (a:b:c = 73:9:18, M_n = 12900)	8	nd[f]	nd[f]

[a] 50°C, 24h; [M] = 1.0 M, [W] = 20 mM. [b] Determined by GC. [c] Methanol-insoluble part. [d] Estimated by GPC (PSt, THF). [e] Bulk polymerization. [f] Not determined. [g] UV-irradiated.

[$(CO)_5W=C(Ph)OCH_3$, **5**]. The results of UV titration of the pendant carbene unit well agreed with those estimated by ^{1}H NMR spectroscopy. **4b** was soluble in most of organic solvents such as toluene, chloroform, and THF and stable enough to be treated under air.

As mentioned above, Fischer-type tungsten alkoxycarbene **5** works as catalyst for the polymerization of cycloolefins and substituted acetylenes [5], which would enable the produced polymer to function as a polymeric catalyst for the acetylene polymerization. Thus, we investigated the polymerization of phenylacetylene with **4b** and its model compound **5**, and the results are listed in Table 2. Polymerization of phenylacetylene with **5** in toluene provided only a low yield of the polymer (run 1), which stems from the low catalytic activity of **5**. A moderate yield of the polymer was only accessible when the polymerization was carried out in bulk (run 2). These results are consistent with the previous results [5d]. On the contrary, we found that the photo-irradiation remarkably enhances the activity of **5**, which led to a moderate yield of the polymer even by the solution polymerization (run 3) [7]. Based on these results, the polymerization of phenylacetylene with **4b** was carried out in toluene under photo-irradiation (runs 4-6). Although the conversion of the monomer is not of satisfaction similarly to the general feature of polymer-supported catalysts, ^{1}H NMR of the product clearly supported the formation of poly(phenylacetylene). Namely, the signals attributed to the phenyl and vinyl protons of poly(phenylacetylene) were clearly observed. The presence of the signals due to the unreacted carbene moieties in the ^{1}H NMR spectrum of the product means that a part of carbene species contributed to the polymerization. GPC profile of the prepolymer **4b** did not shift toward high molecular weight region after the polymerization of phenylacetylene, and a shoulder due to the formed poly(phenylacetylene) was observed in the GPC curve of **4b**. This reveals that the poly(phenylacetylene) chain does not graft to **4b**.

In summary, we demonstrated an alternative and convenient approach to a polymer with metal-carbene moiety in the side chain through the polymer reaction. Relatively high degree of introduction of metal-carbene moiety was attainable, and the resulting polymer has proven to work as a polymeric catalyst for the polymerization of phenylacetylene under photo-irradiation.

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Experimental

Materials. All the solvents used were distilled by the standard procedures. Acetyl chloride was distilled from P_20_5. **1** [6c] and **4** [8] were prepared by the reported manners. 4-Hydroxybutyl methacrylate was prepared by the condensation of methacrylic acid with a large excess of 1,4-butandiol in the presence of *p*-toluenesulfonic acid in toluene followed by the chromatographic purification (SiO_2, hexane-ether). **3a** and **3b** were synthesized by the standard radical polymerization technique by using toluene as a solvent and AIBN as an initiator at 80°C for 5h.

M*easurements.* The molecular weights of the polymers were estimated by gel permeation chromatography (THF as an eluent, polystyrene standards). IR spectra, UV-visible spectra, and NMR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer, a Shimadzu UV-2200 spectrophotometer, and a JEOL GSX-270 spectrometer, respectively. Gas chromatographic analyses were carried out with a Shimadzu GC-8A gas chromatograph.

*Reaction of **2** with **3**.* The procedure for run 5 (Table 1) is described as a typical example. Into a solution of **1** (250 mg, 0.5 mmol) in CH_2Cl_2 was added dropwise acetyl chloride (39 mg, 0.5 mmol) at -20°C to form **2**. After stirring the solution for 40 min, a CH_2Cl_2 solution (7 mL) of **3b** (530 mg, 0.5 mmol of hydroxy group) was slowly added to the solution containing **2**. The resulting mixture was stirred for 2h at rt. After filtration, the filtrate was poured into a large amount of hexane to give **4b** (500 mg).

*Polymerization of phenylacetylene with **4b**.* Following is the procedure for run 6 in Table 2. A THF solution (3 mL) containing **4b** (131 mg), phenylacetylene (306 mg, 3 mmol), and bromobenzene (standard) was photo-irradiated with a 450W high pressure Hg lamp at >300 nm at rt for 24h. The resulting solution was poured into a large excess of hexane to precipitate the product.

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