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Random and Block Copolymerization of Substituted Acetylenes Catalyzed by Tungsten μ-Hydride Complexes

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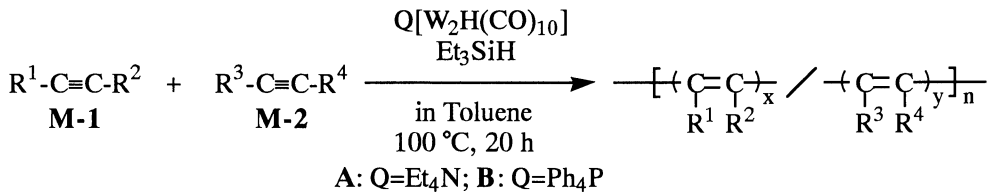
High molecular weight copolymers were obtained from 1-phenyl-1-propyne and monosubstituted acetylenes by coordination polymerization with tungsten μ-hydride complexes as catalysts in toluene as a solvent. The permeability coefficients of N_2 and O_2 through the membranes obtained from phenylacetylene/1-phenyl-1-propyne copolymers were evaluated.

Polyacetylenes have been noted in the view of importance as the functional materials according to their electric conductivity[1] and gas- and liquid-permeabilities.[2] In recent years, several transition metals have been developed for the catalysts to polymerize substituted acetylenes under mild conditions.[3] However, homopolymers obtained by such catalysts have some disadvantages like as low molecular weights (often observed polymerization of monosubstituted acetylenes bearing less hindered alkyl groups) and insolubilities in organic solvents. Copolymerization of substituted acetylenes is one of the most powerful methods to improve the properties of polyacetylenes for the functional materials. In addition, it makes possible to discover new functions in polyacetylenes. For example, the improved ethanol permselectivity at pervaporation was achieved by the copolymerization of 1-trimethylsilyl-1-propyne with F-containing comonomer.[4] There are, nevertheless, few reports on the copolymerization of substituted acetylenes,[5] in which copolymerization of different type of acetylenes resulted in the formation of polymers containing higher reactive monomers predominantly. It is difficult to control the monomer ratios in polymers at will by depending upon ones in feeds. Recently, we reported on the polymerization of substituted acetylenes catalyzed by tungsten μ-hydride complexes to give polyacetylenes with high molecular weights in moderate to good yields.[6] While well-known tungsten catalysts like as tungsten halides are not effective for the polymerization of less hindered monosubstituted acetylenes to produce cyclotrimers and of hindered disubstituted acetylenes to give no polymers, tungsten μ-hydride complexes can polymerize a variety of acetylenes, even 1-octyne and 1-phenyl-1-propyne. Aiming as promoting the usefulness of tungsten μ-hydride complex catalyzed polymerization, we evolve to the copolymerization of substituted acetylenes.

Copolymerization of substituted acetylenes were carried out as follows: the mixtures of two monomers (total 1 mmol) were heated at 100 °C for 20 h with triethylsilane (1 mmol) and tungsten μ-hydride complexes (0.01 mmol) in absolute toluene (0.2 ml) under Ar. The reaction mixture was dissolved in toluene (10 ml) and added dropwise to rapidly stirred methanol (100 ml) while soluble materials were removed by filtration to give a copolymer. The obtained polymers were identified by IR and ^{1}H NMR, and their molecular weights were determined by gel permeation chromatography (GPC),[7] which also indicated the obtained polymers were not the

blends of two homopolymers but copolymers. The results obtained from copolymerization of various acetylenes are shown in Table 1. In the copolymerization catalyzed by WCl_6-Ph_4Sn, the monomer reactivity ratio of 1-phenyl-1-propyne against phenylacetylene is reported to be 0.35.[5d] It is noteworthy that the compositions in the obtained copolymers catalyzed by $Et_4N[W_2H(CO)_{10}]$ were found to be nealy equal to those of monomers in feed. So the copolymers with various ratio of phenylacetylene and 1-phenyl-1-propyne were synthesized in good yields by the way of polymerization of two monomers in arbitrary proportions. Although homopolymers of 1-octyne were viscous oily materials, the copolyacetylenes from 1-octyne and 1-phenyl-1-propyne polymerized by $Et_4N[W_2H(CO)_{10}]$ were obtained as solid substances. The reactivity of 3,3-dimethyl-1-butyne catalyzed by tungsten μ-hydride complex were quite distinct from that catalyzed by WCl_6-Ph_4Sn. With 3,3-dimethyl-1-butyne, phenylacetylene was copolymerized much easily as compared with 1-phenyl-1-propyne (**P-8** *vs.* **P-9**).

Table 1. Random Copolymerization of Substituted Acetylenes Catalyzed by $Et_4N[W_2H(CO)_{10}]$[a]

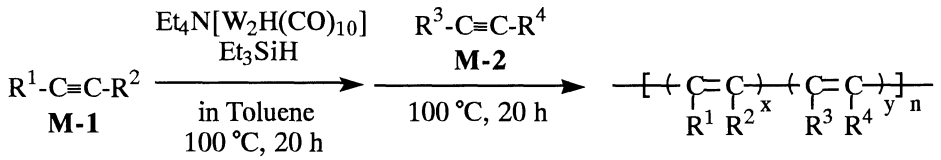


Poly-mer	Cat.	M-1	M-2	M-1/M-2 in feed	Yield[b] w%	M-1/M-2 in polymer	$M_n/10^4$	$M_w/10^4$	M_w/M_n
P-1	A	Ph-C≡C-H	Ph-C≡C-Me	19.7/80.3	63.6	26.5/73.5	8.16	30.9	3.78
P-2[c]	A	Ph-C≡C-H	Ph-C≡C-Me	50.1/49.9	70.5	55.6/44.4	4.25	17.8	4.18
P-3	A	Ph-C≡C-H	Ph-C≡C-Me	79.7/20.3	71.3	84.8/15.2	2.85	5.22	1.83
P-4	B	Ph-C≡C-H	Ph-C≡C-Me	19.0/81.0	68.8	31.4/68.6	10.2	41.5	4.05
P-5	B	Ph-C≡C-H	Ph-C≡C-Me	49.5/50.5	55.6	63.5/36.5	3.65	20.6	5.63
P-6	B	Ph-C≡C-H	Ph-C≡C-Me	80.4/19.6	69.4	86.0/14.0	2.60	5.12	1.97
P-7	A	1-Octyne	Ph-C≡C-Me	20.4/79.6	21.2	26.1/73.9	5.25	22.41	4.27
P-8	A	*t*-Bu-C≡C-H	Ph-C≡C-H	50.6/49.4	59.7	39.5/60.5	3.10	4.79	1.55
P-9	A	*t*-Bu-C≡C-H	Ph-C≡C-Me	50.4/49.6	21.8	89.9/10.1	2.84	4.40	1.55

a) Reaction conditions: Monomer, total 1 mmol; catalyst, 0.01 mmol; triethylsilane, 1 mmol; toluene, 0.2 ml. b) Yield of methanol-insoluble material. c) The quantity of each chemicals was 10 times of that of other entries.

Block copolymerization of substituted acetylenes was also achieved with $Et_4N[W_2H(CO)_{10}]$. To the reaction mixtures of 1 st. polymerization, 2 nd. monomer was added and polymerized at 100 °C for additional 20 h to give block copolymers in high yields. It was confirmed that the obtained polymers were not the blends of two homopolymers but the copolymers by the GPC measurement . Although 1-phenyl-1-propyne or 3,3-dimethyl-1-butyne gave homopolymers with high molecular weights under these conditions, the molecular weight of **P-11**, **P-14**, and **P-15** could not reach that of homopolymers.[8] One reason may be due to the degradation of the formed polymer with the catalyst but further details are not clear.[9]

Table 2. Block Copolymerization of 1-Phenyl-1-propyne and Mono-substituted Acetylenes[a)]



Polymer	M-1	M-2	M-1/M-2 in feed	Yield[b)] w%	M-1/M-2 in polymer	$M_n/10^4$	$M_w/10^4$	M_w/M_n
P-10[c)]	Ph-C≡C-H	Ph-C≡C-Me	49.9/50.1	69.6	59.6/40.4	4.43	22.0	4.96
P-11[c)]	Ph-C≡C-Me	Ph-C≡C-H	50.3/49.7	66.7	34.2/65.8	3.50	13.5	3.87
P-12	1-Octyne	Ph-C≡C-H	48.3/51.7	70.2	41.0/59.0	0.673	2.01	2.99
P-13	1-Octyne	Ph-C≡C-Me	51.1/48.9	37.5	62.8/37.2	1.02	15.1	14.8
P-14	*t*-Bu-C≡C-H	Ph-C≡C-H	49.8/50.2	59.8	35.1/64.9	2.31	3.66	1.58
P-15	*t*-Bu-C≡C-H	Ph-C≡C-Me	48.9/51.1	16.2	85.8/14.2	1.99	8.32	4.19

a) See footnote a) in Table 1. b) Yield of methanol-insoluble material. c) The quantity of each chemicals was 10 times of that of other entries.

Table 3 lists N_2 and O_2 permeability coefficients of four polyacetylene membranes. Copolymer (300 mg) was dissolved in toluene (8 ml), the solution was cast on a poly(tetrafluoroethylene) sheet, and the solvent was evaporated over a period of 24 h to form membranes with 120-180 μm thickness. Samples for gas permeability measurement were circular pieces of 22 mm diameter. Gas permeabilities were measured using ordinary vacuum method. The initial pressure of the downstream side was 0.04 mmHg, and the pressure increase was measured with Pirani gauge. Permeability coefficient, P in cm^3 (STP) • cm • cm^{-2} • s^{-1} • $cmHg^{-1}$, was calculated from the slope in a time-pressure curve (dp/dt) at a steady state. Very interestingly, every copolymer membrane produced

Table 3. Gas Permeability Coefficients P[a)] of Random and Block Copolymers of 1-phenyl-1-propyne and Phenylacetylene

Polymer[b)]	$P_{N2}/10^{-10}$	$P_{O2}/10^{-10}$	P_{O2}/P_{N2}
P-2	1.07	6.45	6.01
P-10	1.18	6.62	5.62
P-11	1.32	7.34	5.55
PPP[c)]	0.863	4.06	5.33

a) Units are cm^3 (STP) • cm • cm^{-2} • s^{-1} • $cmHg^{-1}$. b) See Tables 1 and 2.
c) Poly(1-phenyl-1-propyne); M_n=1.64×10^5, M_w=3.57×10^5, M_w/M_n=2.17.

from phenylacetylene and 1-phenyl-1-propyne shows higher permeability coefficients than that from poly(1-phenyl-1-propyne). Further more, copolymers are superior in separation factor P_{O2}/P_{N2} to homopolymer, and P_{O2}/P_{N2} of random copolymer **P-2** is the highest value among those of various copolymers.

In conclusion, we have shown that the random- and block-copolymerizations of substituted acetylenes catalyzed by triethylsilane and tungsten μ-hydride complexes provide copolymers in good yields with high molecular weights. The compositions of the obtained copolymer from phenylacetylene and 1-phenyl-1-propyne were nearly equal to the ratio of monomers in the feed. And gas permeabilities and separation factors of the obtained copolymers were superior to that of homopolymer.

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7) Gel permeation chromatography was carried out with a TOSOH HLC-802A instrument using THF as an eluent, equipped with four columns of TSK gels G5000H6, G4000H6, G3000H6, and G2000H6. Standard polystylenes were used for calibration.

8) Moleculer weights of homopolymers polymerized under these conditions are as follows; Poly(1-phenyl-1-propyne): M_n=1.72×10^5, M_w=3.39×10^5, M_w/M_n=1.98. Poly(*tert*-3,3-dimethyl-1-butyne): M_n=5.35×10^4, M_w=1.26×10^5, M_w/M_n=2.36.

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