followed by decarboxylation to yield the acid calixarene.

The typical procedure for the synthesis of **5** is as follows; To a solution containing 0.92 g (1.5 mmole) of **4a** in 20 m*l* of DMSO was slowly added 0.47 g (3.3 mmole) of methyl iodide. After the reaction mixture was stirred for 30 min at the room temperature, 0.4 g (4 mmole) of NaCN was added and the mixture heated for 4 h at 80℃ in an atmosphere of N_2. The solution was cooled, treated with 50 m*l* of ice water, acidified with 2 N HCl, filtered, and air dried. The crude product was purified by column chromatography (eluent, 1 : 1 $CHCl_3$-hexane) to yield 0.50 g (57%) of colorless powder **5a**. ^{1}H-NMR ($CDCl_3$) δ 9.2 ppm (br s, 4, OH), 6.9 and 6.8 (two s, 8, ArH), 5.5-6.0 (m, 2, -CH=), 4.8-5.2 (m, 4, $=CH_2$), 3.3-4.2 (br s, 8, $ArCH_2Ar$), 3.5 (s, 4, $ArCH_2CN$), 3.2 (d, 4, $ArCH_2C=$). IR of **5a** (KBr) 2250 cm^{-1} (-CN, weak). Spectroscopic data of **5b**, **5c**, **5d**, **5e** are listed on the reference[15].

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13. ^{1}H-NMR of **4b** ($CDCl_3$) δ 8.9 (s, 4, OH), 6.9 and 6.7 (two s, 8, ArH), 5.5-6.0 (m, 2, -CH=), 4.7-5.0 (m, 4, $=CH_2$), 3.5-4.2 (br s, 8, $ArCH_2Ar$), 3.3 (s, 4, $ArCH_2N$-), 3.1 (d, 4, $ArCH_2C=$), 2.4 (q, 8, $-NCH_2$-), 1.0 (t, 12, $=CH_3$). ^{1}H-NMR of **4c** ($CDCl_3$) δ 8.9 (br s, 4, OH) 6.9 and 6.7 (two s, 8, ArH), 5.4-6.0 (m, 6, -CH=), 4.8-5.2 (m, 12, $=CH_2$), 3.3-4.2 (br s, 8, $ArCH_2Ar$), 3.3 (s, 4, $ArCH_2N$-), 2.9-3.2 (m, 12, $ArCH_2N$- and $-NCH_2C=$). ^{1}H-NMR of **4d** ($CDCl_3$) δ 7.2 (br s, 4, OH), 6.9 and 6.7 (two s, 8, ArH), 5.5-6.0 (m, 2, -CH=), 4.8-5.2 (m, 4, $=CH_2$), 3.3-4.2 (br s, $ArCH_2Ar$), 3.3 (s, 4, $ArCH_2N$-), 3.2 (d, 4, $ArCH_2C=$), 2.3 (m, 8, $-NCH_2$-), 1.5 (m, 12, $-CH_2CH_2CH_2$-). ^{1}H-NMR of **4e** ($CDCl_3$) δ 9.3 (s, 4, OH), 6.9 and 6.7 (two s, 8, ArH), 5.5-6.0 (m, 2, -CH=), 4.8-5.2 (m, 4, $=CH_2$), 3.5-4.2 (br s, 8, $ArCH_2Ar$), 3.7-3.8 (m, 8, $-CH_2OCH_2$-), 3.3 (s, 4, $ArCH_2N$-), 3.2 (d, 4, $ArCH_2C=$), 2.3-2.6 (m, 8, $-CH_2NCH_2$-).
14. Nucleophiles for **5a**, **5b**, **5c**, **5d**, and **5e** are NaCN, $NaBH_4$, $NaCH(CO_2Et)$ prepared from $CH_2(CO_2Et)$ and Na, NaOEt, and NaN_3.
15. ^{1}H-NMR of **5b** ($CDCl_3$) δ 10.0 (s, 4, OH), 6.7 (s, 8, ArH), 5.5-6.0 (m, 2, -CH=), 4.8-5.2 (m, 4, $=CH_2$), 3.3-4.2 (br s, 8, $ArCH_2Ar$), 3.2 (d, 4, $=CH_2$), 2.1 (s, 6, $-CH_3$). ^{1}H-NMR of **5c** ($CDCl_3$) δ 9.9 (s, 4, OH), 6.9 and 6.8 (two s, 8, ArH), 5.5-6.0 (m, 2, -CH=), 4.8-5.2 (m, 4, $=CH_2$), 3.9 (q, 8, $-OCH_2$-), 3.3-4.0 (br s, 8, $ArCH_2Ar$), 2.9-3.6 (m, 10, $ArCH_2C=$ and $ArCH_2CH$-), 0.9 (t, 12, $-CH_3$). IR of **5c** (KBr) 1720 cm^{-1} (-COO-). ^{1}H-NMR of **5d** ($CDCl_3$) δ 6.9 (br s, 4, OH), 6.9 and 6.7 (two s, 8, ArH), 5.5-6.0 (m, 2, -CH=), 4.8-5.2 (m, 4, $=CH_2$), 4.2 (s, 4, $ArCH_2O$-), 3.3-4.2 (br s, 8, $ArCH_2Ar$), 3.5 (q, 4, $-OCH_2$-), 3.2 (d, 4, $=CH_2$), 1.2 (t, 6, $-CH_3$). ^{1}H-NMR of **5e** ($CDCl_3$) δ 8.7 (br s, 4, OH), 6.9 and 6.7 (two s, 8, ArH), 5.5-6.0 (m, 2, -CH=), 4.0 (s, 4, $ArCH_2N_3$), 3.3-4.2 (br s, 8, $ArCH_2Ar$), 3.2 (d, 4, $ArCH_2C=$). IR of **5e** (KBr) 2100 cm^{-1} ($-N_3$).

Polymerization of Phenylacetylene by Molybdenum Pentachloride/2-Propyn-1-ol Catalyst Systems

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The $MoCl_5$-catalyzed polymerization of some acetylene derivatives such as phenylacetylene,[1,2] 2-hexyne,[3] 2-ethynylthiophene,[4] 1-chloro-2-thienylacetylene,[5] *etc.* have been carried out. In these cases, the cocatalyst (as activator) was mainly restricted to some cases such as organotin- and organoaluminum compounds.[1,3-5] Recently, we found the very active catalytic activity of $MoCl_5$ for the polymerization of $HC{\equiv}CCH_2OH$ to give a quantitative yield of polymer.[6,7] To our knowledge, molybdenum alkoxides such as $Mo(OEt)_5/Al_2O_3/SiO_2$,[8] $Mo(OEt)_2Cl_2/Et_3B$,[9] $Mo(OEt)_2Cl_3/Me_2Al_2Cl_3$,[10] and $Mo(O\text{-}t\text{-}Bu)_2(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)$[11,12] were used as catalyst systems for the olefin metathesis reaction and the metathesis polymerization of cycloolefins.

We now report a cocatalytic effect of $HC{\equiv}CCH_2OH$ for the polymerization of acetylenic monomer, especially phenylacetylene. Unless otherwise specified, the polymerizations

Table 1. Polymerization of Phenylacetylene by $MoCl_5$-$HC{\equiv}CCH_2OH$ Catalyst System[a]

Experiment number	Catalyst system[b] (mole ratio)	Polymer yield[c] (%)	Molecular weight[d] (M_w)
1	$MoCl_5$	34	6850
2	$MoCl_5$-$HC{\equiv}CCH_2OH$ (1 : 1)	43	6580
3	$MoCl_5$-$HC{\equiv}CCH_2OH$ (1 : 3)	54	7030
4	$MoCl_5$-$HC{\equiv}CCH_2OH$ (1 : 5)	58	7200
5	$MoCl_5$-$EtAlCl_2$-$HCl{\equiv}CCH_2OH$ (1 : 2 : 4)	33	6840
6	$Mo(OEt)_5$-$HC{\equiv}CCH_2OH$ (1 : 4)	trace	–
7	WCl_6	84	10800
8	WCl_6-$HC{\equiv}CCH_2OH$ (1 : 4)	8	3160

[a] Polymerized in chlorobenzene at 60℃ for 24 h; $[monomer]_o = 1.0$ M, $[monomer]/[catalyst] = 50$. [b] Mixture of catalyst and cocatalyst was aged at 20℃ for 15 min before use. [c] Methanol-insoluble polymer. [d] Measured by GPC-150C of waters using the calibration curves for polystyrene standard.

were carried out under dry nitrogen atmosphere in chlorobenzene at 60℃, $[monomer]_o = 1.0$ M, monomer to catalyst mole ratio (M/C)=50, for 24 h.

Table 1 shows the results for the polymerization of phenylacetylene by $MoCl_5$ activated by $HC{\equiv}CCH_2OH$. In most cases, $HC{\equiv}CCH_2OH$ activated $MoCl_5$ for the polymerization of phenylacetylene by $MoCl_5$. As the mole ratio of $HC{\equiv}CCH_2OH$ to $MoCl_5$ was increased, the polymer yield was increased, and then over $[HC{\equiv}CCH_2OH]/[MoCl_5]=5$ the polymer yield was decreased. When $EtAlCl_2$, a typical cocatalyst for the polymerization of acetylene derivatives by $MoCl_5$ and WCl_6,[4,5] was used, the catalytic activity was decreased. Fully substituted molybdenum ethoxide, $Mo(OEt)_5$, showed no catalytic activity even when $HC{\equiv}CCH_2OH$ was used as a cocatalyst. When $HC{\equiv}CCH_2OH$ was used as a cocatalyst in the WCl_6-catalyzed polymerization of phenylacetylene, the polymer yield was notably decreased than the polymer yield (84%) obtained by WCl_6 alone. It can be deduced that the oxygen atom of $HC{\equiv}CCH_2OH$ deactivate WCl_6. The deactivation phenomena of WCl_6 by the oxygen atom-containing acetylene monomers was also observed in the polymerization of propiolic acid,[13] dipropargyl ether,[14] and dipropargyl sulfone.[15]

The average molecular weight ($\overline{M}_w$)s of poly(phenylacetylene) prepared by $MoCl_5$-$HC{\equiv}CCH_2OH$ catalyst system were similar to that of poly(phenylacetylene) obtained by $MoCl_5$ alone. These molecular weights were somewhat lower than that ($\overline{M}_w = 10800$) of poly(phenylacetylene) prepared by WCl_6 alone under the same reaction conditions.

The initial purple color of $MoCl_5$ catalyst solution was disappeared as soon as the $HC{\equiv}CCH_2OH$ solution was injected. The resulting poly(phenylacetylene) prepared by $MoCl_5$-$HC{\equiv}CCH_2OH$ was yellow and light-brown colored powder.

The elemental analyses agreed well with the calculated value (*e.g.*, $MoCl_5$-$HC{\equiv}CCH_2OH$ (1 : 5) catalyzed poly(PA), calcd for $(C_8H_6)_n$: C, 94.08%; H, 5.92%. Found: C, 93.21%; H, 5.83%).

The NMR (^1H- and ^{13}C-), IR, UV-visible spectral data were similar to those of poly(phenylacetylene) obtained by $MoCl_5$ and $MoCl_5$-*n*-Bu_4Sn.[16-18] The higher catalytic activity of $MoCl_5$-$HC{\equiv}CCH_2OH$ catalyst system was deduced that the partially substituted molybdenum compounds by $HC{\equiv}CCH_2OH$ are active species though the mechanism is not fully understood.

Further works for the polymerization mechanism and the effect of 2-propyn-1-ol homologues are in progress.

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Reformatsky Reactions of *N*-Alkylidenebenzenesulfenamides

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Among various approaches to the preparation of primary