10 and 11, and introducing them to eq 9, we obtain eq 12.

$$k_{12}[\mathrm{m_1\cdot}][\mathrm{M_2}] = k_{21}[\mathrm{m_2\cdot}][\mathrm{M_1}] \qquad (10)$$

$$R_\mathrm{i} = R_\mathrm{t} = k_{\mathrm{t}11}[\mathrm{m_1\cdot}]^2 + 2k_{\mathrm{t}12}[\mathrm{m_1\cdot}][\mathrm{m_2\cdot}] + k_{\mathrm{t}22}[\mathrm{m_2\cdot}]^2 \qquad (11)$$

$$(R_\mathrm{i} = \text{initial rate})$$

$$R_\mathrm{p} = \frac{R_\mathrm{i}^{1/2}k_{21}(k_{11}[\mathrm{M_1}] + 2k_{12}[\mathrm{M_2}])[\mathrm{M_1}]}{(k_{\mathrm{t}11}k_{21}^2[\mathrm{M_1}]^2 + 2k_{\mathrm{t}12}k_{12}k_{21}[\mathrm{M_1}][\mathrm{M_2}] + k_{\mathrm{t}22}k_{12}^2[\mathrm{M_2}]^2)^{1/2}} \qquad (12)$$

Assuming that the cross-termination rate is approximately the mean of the homotermination rates. We get

$$R_\mathrm{p} = \frac{R_\mathrm{i}^{1/2}(k_{11}[\mathrm{M_1}] + 2k_{12}[\mathrm{M_2}])}{k_{\mathrm{t}11}^{1/2} + k_{\mathrm{t}22}^{1/2}\dfrac{k_{12}}{k_{21}}\dfrac{[\mathrm{M_2}]}{[\mathrm{M_1}]}} \qquad (13)$$

If the second term in the denominator is larger than the first, $(k_{\mathrm{t}22})^{1/2}k_{12}/k_{21} > 10(k_{\mathrm{t}11})^{1/2}$, eq 13 will be reduced to eq 14.

$$R_\mathrm{p} = \frac{R_\mathrm{i}^{1/2}}{(k_{\mathrm{t}22})^{1/2}}k_{21}\left(2 + \frac{k_{11}[\mathrm{M_1}]}{k_{12}[\mathrm{M_2}]}\right)[\mathrm{M_1}] \qquad (14)$$

Equation 14 provides the copolymerization rates which fit the experimental data of the present copolymerization rates satisfactorily as shown in Figure 2, by applying the method of least squares. (In doing this, the value of 0.25 is used for k_{11}/k_{12}, which is obtained from Fineman–Ross plot in Figure 5.)

Thus, the present copolymerizations are explained in terms of the termination processes in which the contribution of the homotermination of VCZ radical species is negligibly small when compared with that of DEM or DMM radical species or with the cross-termination process, despite the fact that the Q values of these electron-accepting monomers are smaller than that of VCZ, that is, the growing chain radicals of these electron-accepting monomers appear to be less stable than VCZ radical species.

Acknowledgment. The authors are grateful to Professor M. Litt of Case Western Reserve University for his suggestion to use eq 13 which enabled them to include all three termination steps in the discussion.

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Polymerization of Phenylacetylenes. III. Structure and Properties of Poly(phenylacetylene)s Obtained by WCl_6 or $MoCl_5$

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ABSTRACT: Structure and properties of poly(phenylacetylene)s were investigated. The poly(phenylacetylene)s were obtained in the polymerization at 30° by WCl_6 or $MoCl_5$ in several solvents (C_6H_6, CCl_4, $CHCl_3$, and CH_2Cl_2). Molecular weights of the polymers were 5500–12000. The polymers produced by WCl_6 in polar solvents showed high softening points (~226°), a small absorption at 870 cm^{-1} in ir spectrum, and an emission at 430 nm by excitation at 250 nm; these were correlated with high content of trans structure. On the other hand, the polymers formed by $MoCl_5$ in nonpolar solvents showed low softening points (~215°), a large absorption at 870 cm^{-1}, and an emission at 360 nm, which were attributed to high content of cis structure. The numbers of unpaired spin of the polymers were in a range of 10^{16}–10^{17} spin g^{-1}, and the electric conductivities were 10^{-18}–10^{-15} ohm^{-1} cm^{-1}.

In a previous paper[1] we reported that phenylacetylene was polymerized by WCl_6 or $MoCl_5$ to produce poly(phenylacetylene)s with molecular weights of ca. 10000. The polymer produced was completely soluble in benzene. Little amount of methanol-soluble oligomer was formed. The effects of solvent and ring substituent on the polymerization of phenylacetylene were different from those observed in the cationic polymerization of styrene by WCl_6.[1,2]

Phenylacetylene has been reported to polymerize by coordination,[3-7] radical[8-10] or cationic[11,12] mechanism. Only oligomers with molecular weights of ca. 1000, however, are formed by radical or cationic mechanism. In coordination polymerizations, not only polymers with a molecular weight of several thousand but also benzene-insoluble polymers and methanol-soluble oligomers (including a cyclic trimer) are usually formed. Very recently, Woon and Farona[7] reported that phenylacetylene was polymerized by molybdenum complexes to yield high polymers.

The structure and properties of poly(phenylacetylene) have been investigated mainly with the samples produced by either Ziegler-Natta catalysts or thermal initiation. For example, Kern[4] synthesized cis- and trans-rich polymers, and examined their structure mainly by means of ir spectroscopy. Simionescu et al.[13] investigated the structure of poly(α-naphthylacetylene) in a similar manner. These studies were generally performed with fractional samples in coordination polymerization product, that is, with benzene-soluble and methanol-insoluble fractions. On the other hand, the polymerization of phenylacetylene by WCl_6 or $MoCl_5$ provides almost selectively benzene-soluble and

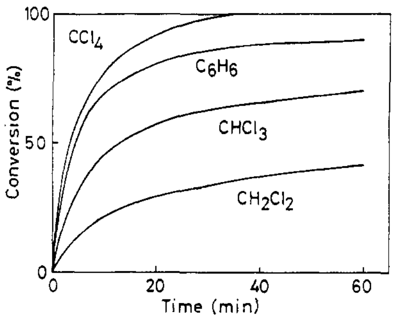


Figure 1. Solvent effect in the polymerization of phenylacetylene by WCl_6 at 30°: $[M]_0 = 1.0\ M$, $[WCl_6 \cdot \frac{1}{2}H_2O]_0 = 1.0 \times 10^{-2}\ M$.

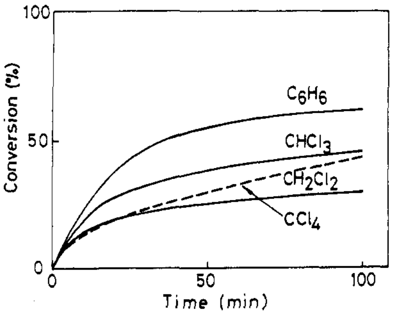


Figure 2. Solvent effect in the polymerization of phenylacetylene by $MoCl_5$ at 30°: $[M]_0 = 1.0\ M$, $[MoCl_5 \cdot \frac{1}{2}H_2O]_0 = 1.5 \times 10^{-2}\ M$.

methanol-insoluble high polymer. Therefore, it seems very interesting to investigate the polymer structure using poly(phenylacetylene)s obtained by WCl_6 or $MoCl_5$.

In the present study the structure of poly(phenylacetylene)s obtained by WCl_6 or $MoCl_5$ was investigated by ir, uv, and emission spectroscopies, and further their magnetic and electric properties were investigated. It was found by the spectroscopic studies that cis-rich or trans-rich polymer can be formed by a suitable choice of polymerization conditions.

Experimental Section

Phenylacetylene was synthesized by the bromination of styrene and the subsequent dehydrobromination.[14] Catalysts and solvents used for the polymerization were purified as described previously.[1] Solvents used for the spectroscopic studies were commercially obtained (spectroscopic grade reagents).

Polymerization was carried out at 30°, under a dry nitrogen atmosphere, the initial monomer concentration being 1.0 M. Water, half as much as the amount of catalyst, was added to the catalyst solution as a cocatalyst. The conversion of monomer was followed by dilatometry. The polymers produced were purified by reprecipitation from benzene solution.

The number-average molecular weight of polymers was determined by vapor pressure osmometry (VPO) using a Hitachi 117 osmometer. Molecular weight distribution (MWD) was observed by gel permeation chromatography (GPC) by use of a Toyo Soda HLC 802 chromatograph. Based on the GPC curve number- and weight-average molecular weights were tentatively calculated using a calibration curve for polystyrene. Ir spectra were measured in KBr disk using a Shimadzu IR 27 G grating spectrophotometer. Uv and visible spectra were measured in ethylene dichloride solution ($2.0 \times 10^{-4}\ M$) using a Shimadzu UV 210 spectrophotometer. Emission spectra were measured in ethylene chloride solution ($2.0 \times 10^{-4}\ M$) using a Shimadzu RF501 spectrofluorophotometer. It was rather difficult to obtain very reproducible emission spectra, probably because the instability of the polymer solution toward measuring light and air. ESR spectra were recorded with a Varian E6 spectrometer in a degassed 10% benzene solution; g value and spin density were determined using 1,1-diphenyl-2-picrylhydrazyl and di-*tert*-butyl nitroxide as references. Electric conductivity was measured by the DC steady-state method with a Takeda Riken TR8651 electrometer; a disk sample, both surfaces of which were painted with silver paste (Du Pont), was used.

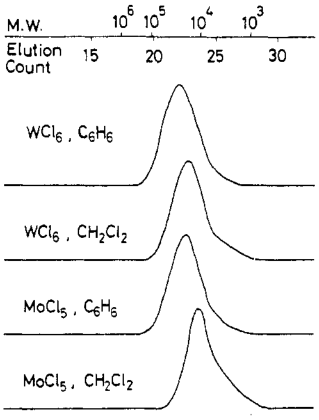


Figure 3. Gel permeation chromatograms of poly(phenylacetylene)s. See Table I as to polymerization conditions; the mol wt shown pertains to polystyrene.

Results and Discussion

Polymerizations under Several Conditions. Figures 1 and 2 show the time-conversion curves for the polymerizations of phenylacetylene in several solvents catalyzed by WCl_6 and $MoCl_5$, respectively. The time-conversion curve for the polymerization catalyzed by $MoCl_5$ in carbon tetrachloride is shown by a dotted line, because the catalyst was not completely soluble in carbon tetrachloride. As is seen from these figures, the polymerization rate decreased with the increase of the solvent dielectric constant. As mentioned in a previous paper,[1] this solvent effect is just opposite to that observed in the cationic polymerization of styrene catalyzed by WCl_6. The poly(phenylacetylene)s obtained in the polymerizations of Figures 1 and 2 were subjected to the structural analyses as described below.

Molecular Weight and Properties of Poly(phenylacetylene). More than 90% of the product was a methanol-insoluble polymer. The polymer was powdery and easily soluble in organic solvents such as benzene, carbon tetrachloride, and methylene chloride. The rest of the product (several percent) was a methanol-soluble yellow oligomer. WCl_6 polymers (this means the polymers obtained by WCl_6, and so forth) were dark red or brownish red and $MoCl_5$ polymers were orange or yellow.

The elementary analyses were agreed fairly well with the calculated value (e.g., WCl_6–C_6H_6 polymer (this means the polymer obtained by WCl_6 in benzene, and so forth). Calcd for C_8H_6: C, 94.08; H, 5.92. Found: C, 92.95; H, 6.15.). As shown in Table I, number-average molecular weight of the poly(phenylacetylene)s obtained was in a range of 5500–12000; it reaches ca. 15000 under appropriate conditions.[1] These values belong to the largest among those of poly(phenylacetylene)s so far reported.[6] Figure 3 shows the MWD of poly(phenylacetylene)s. These distributions are similar to those of polystyrenes formed by WCl_6 or $SnCl_4$.[15] The M_n's tentatively determined by GPC with a calibration curve for polystyrene were one to two times as large as those determined by VPO (Table I). The ratio M_w/M_n was ca. 2 irrespective of polymerization conditions. This value indicates that the reaction proceeds homogeneously through a single propagating species.

The softening point of the WCl_6–CH_2Cl_2 polymer was the highest (226°), and that of the $MoCl_5$–C_6H_6 polymer was the lowest (214°). In general, the softening point of polymer was higher when a polymerization was carried out in a more polar solvent by WCl_6. The softening points ob-

Table I
Molecular Weight and Several Properties of Poly(phenylacetylene)s[a]

Run	Cat.	Solv	M_n (VPO)	M_n (GPC)	M_w (GPC)	M_w/M_n (GPC)	Softening point, °C	D_{870}/D_{910}	No. of unpaired spin, g^{-1}	σ_{20}, ohm^{-1} cm^{-1}
1	WCl_6	C_6H_6	11800	15000	30800	2.06	221–222	0.746	7.9×10^{16}	3.8×10^{-15}
2	WCl_6	CCl_4	7800				223–224		6.4×10^{16}	
3	WCl_6	$CHCl_3$	7500				225–226		7.0×10^{16}	
4	WCl_6	CH_2Cl_2	6100	9320	20500	2.20	226–227	0.568	8.5×10^{16}	0.68×10^{-15}
5	$MoCl_5$	C_6H_6	5900	12000	24600	2.05	214–215	1.27	5.1×10^{17}	1.2×10^{-18}
6	$MoCl_5$	CCl_4	6200				216–217		2.7×10^{17}	
7	$MoCl_5$	$CHCl_3$	5900				220–221		3.1×10^{17}	
8	$MoCl_5$	CH_2Cl_2	5600	5150	11600	2.26	220–221	0.909	1.9×10^{17}	2.0×10^{-18}

[a] Polymerized at 30°, $[M]_0 = 1.0\ M$; either $[WCl_6 \cdot \frac{1}{2}H_2O]_0 = 1.0 \times 10^{-2}\ M$, 60 min, or $[MoCl_5 \cdot \frac{1}{2}H_2O]_0 = 1.5 \times 10^{-2}\ M$, 100 min.

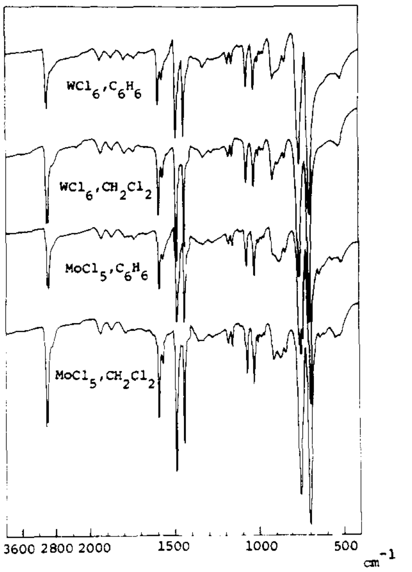


Figure 4. Ir spectra of poly(phenylacetylene)s. See Table I as to polymerization conditions.

served are higher than those so far reported for soluble poly(phenylacetylene)s (152–219,[4] 90–128,[5] 175–190,[8] 100–205,[9] 160–210°[10]).

Spectrophotometric Analyses. Figure 4 shows the ir spectra of poly(phenylacetylene)s. In all the polymers, absorptions due to stretching vibration of a polyconjugated double bond are seen at 1550–1600 cm^{-1}, and those due to C–H out-of-plane deformation of monosubstituted benzene at 755 and 693 cm^{-1}. Therefore, the polymerization product is considered to be a linear polymer with a polyene structure. Further, the polymers possessed three absorptions at 910, 870, and 840 cm^{-1}. In the WCl_6–CH_2Cl_2 polymer the absorption at 910 cm^{-1} was the largest of the three, and the absorption at 870 cm^{-1} the largest in the $MoCl_5$–C_6H_6 polymer. The absorption at 870 cm^{-1} is characteristic of cis structure in poly(phenylacetylene),[4,6] and a ratio D_{870}/D_{910} can be used as a measure of cis-structure content (Table I).

The uv and visible spectra are given in Figure 5. Every polymer possessed a maximum absorption at 225 nm (ϵ 5–6 $\times 10^3$). At longer wavelengths, a few shoulders were observed and absorptions existed as far as ca. 500 nm. The absorption near 500 nm was larger in WCl_6 polymers than in $MoCl_5$ polymers.

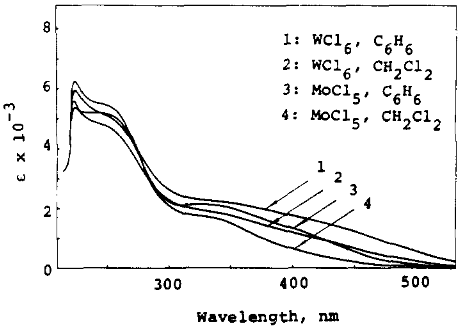


Figure 5. Uv and visible spectra of poly(phenylacetylene)s. See Table I as to polymerization conditions.

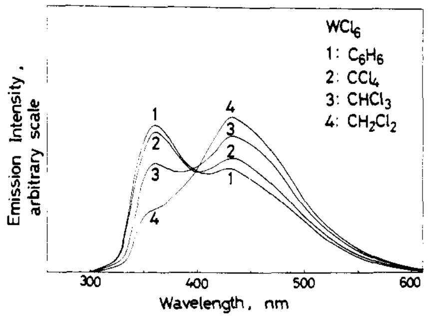


Figure 6. Emission spectra of poly(phenylacetylene)s obtained by WCl_6. See Table I as to polymerization conditions.

To know more about microstructure of the polymers, emission spectra were examined. The results are given in Figures 6 and 7. The WCl_6–C_6H_6 polymer showed two emissions at 360 and 430 nm, when it was excited at 250 nm (Figure 6). The maxima in the excitation spectra of both emissions were located at 250 nm. On the other hand, only an emission at 430 nm was observed with the WCl_6–CH_2Cl_2 polymer. Just contrary to this, the $MoCl_5$–C_6H_6 polymer exhibited only an emission at 360 nm. Thus, the effects of catalyst and solvent were proved to be surprisingly large. Generally, a polymer produced by WCl_6 rather than by $MoCl_5$ and in a less polar solvent showed a stronger emission at 360 nm. The effects of catalyst and solvent seem to closely relate to polymer microstructure (see below). The correlation between polymer structure and emission spectrum is anticipated but it has scarcely been investigated.[16] The great variation of emission spectrum found in this study seems to present an important example on the structure–emission relationship.

Magnetic and Electric Properties. The presence of unpaired electrons and the electric conductivity have been pointed out as properties of polyacetylenes. ESR spectra of poly(phenylacetylene)s obtained in the present investigation are shown in Figure 8. The g values were all 2.0027 ± 0.0001. At ambient temperature, the spectra consisted of

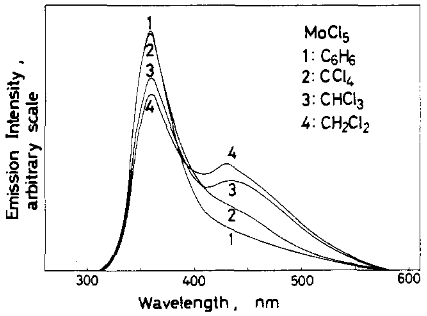


Figure 7. Emission spectra of poly(phenylacetylene)s obtained by $MoCl_5$. See Table I as to polymerization conditions.

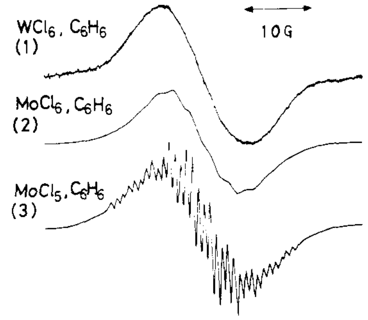


Figure 8. ESR spectra of poly(phenylacetylene)s. See Table I as to polymerization conditions: (1, 2) measured at ambient temperature without aging; (3) measured at 150° after aging at 150° for 2 hr. Sensitivity ratio of (1):(2):(3) = 25:2.5:1.

Table II
Spin Density of the Poly(phenylacetylene) Obtained by $MoCl_5$ in Benzene

Measuring temp, °C	Aging temp, °C	Aging time, min	No. of unpaired spin, g^{-1}	Hfs[a]
16	16	10	0.51×10^{18}	+
60	60	10	0.61×10^{18}	+
100	100	10	2.5×10^{18}	++
150	150	10	5.2×10^{18}	++
150	150	60	2.2×10^{18}	++
150	150	120	2.5×10^{18}	++
150	150	180	1.9×10^{18}	++
16	60	20	0.70×10^{18}	+
16	100	20	2.6×10^{18}	+
16	150	20	3.7×10^{18}	+
16	150	20	0.38×10^{18} [b]	—

[a] ++, a hyperfine structure (hfs) observed; +, a weak hfs; —, no hfs. [b] Aerated when measured.

Table III
Stability of Poly(phenylacetylene)

		Standing period, month			
		0	2	4	6
M_n	−20°, in the dark	7100	7100	7300	7100
	Room temp, in light	7100	4500	4100	4100
D_{870}/D_{910}	−20°, in the dark	0.602		0.602	0.592
	Room temp, in light	0.602		0.549	0.565

an almost structureless single line with a peak-to-peak width of 10–13 G (Figure 8). With increasing temperature (to 100° or 150°), highly split spectra were observed. Unpaired spin densities of WCl_6 polymers were $\sim 10^{16}$ g^{-1} and those of $MoCl_5$ polymers were $\sim 10^{17}$ g^{-1} (Table I), which are comparable to those reported in the literature ($\sim 10^{17-18}$ g^{-1},[6] $\sim 10^{17-19}$ g^{-1},[8] $\sim 10^{16}$ g^{-1} [17]). ESR spectrum of the $MoCl_5$–C_6H_6 polymer was measured under various conditions (Table II). The Curie law did not hold; unpaired spin density increased as the aging temperature was raised. The density depended mainly on the aging temperature and was slightly affected by the measuring temperature and the aging time. The increase of the unpaired spin density might be ascribed to the formation of biradicals by the kink of double bonds and by the subsequent irreversible degradation of the polymer.[18]

The data for electric conductivity are given in Table I. Specific conductivities of WCl_6 polymers were $\sim 10^{-15}$ ohm^{-1} cm^{-1}, and that of $MoCl_5$ polymers $\sim 10^{-18}$ ohm^{-1} cm^{-1}, which are similar to those reported before ($\sim 10^{-17-18}$ ohm^{-1} cm^{-1},[6] $\sim 10^{-16}$ ohm^{-1} cm^{-1},[9] $\sim 10^{-11}$ ohm^{-1} cm^{-1} [19]).

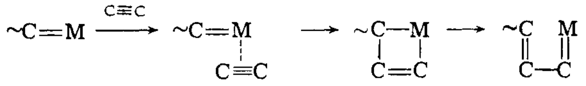
Stability of Poly(phenylacetylene). Stability of poly(phenylacetylene) was examined with a sample prepared in benzene by WCl_6 at a monomer concentration of 5.0 *M* (Table III). When the sample was stored at −20° in the dark for 6 months, no changes in molecular weight and in the ratio D_{870}/D_{910} in ir spectrum were observed. When the polymer was left standing at room temperature in light for 6 months, the molecular weight decreased to about half as much as the original sample, while no remarkable change was observed with the ratio D_{870}/D_{910}.

Polymerization Conditions and Polymer Microstructure. In the present study, polymers were synthesized under several conditions. Among these, the WCl_6–CH_2Cl_2 polymer possessed the highest softening point, showed a small absorption at 870 cm^{-1} in ir spectrum, and emitted only at 430 nm by excitation at 250 nm. On the other hand, the $MoCl_5$–C_6H_6 polymer possessed the lowest softening point, showed a large absorption at 870 cm^{-1} in ir spectrum, and emitted only at 360 nm by excitation at 250 nm. Further, the $MoCl_5$–C_6H_6 polymer showed an absorption at 738 cm^{-1} in the ir spectrum (see Figure 4). This absorption has been assigned to C–H out-of-plane deformation for cis structure.[4,6] It has been demonstrated both experimentally and theoretically that also in polyacetylene only cis isomer shows an absorption at 740 cm^{-1}.[20,21] Therefore, the $MoCl_5$–C_6H_6 polymer in this study must be rich in cis structure or composed exclusively of cis structure. On the other hand, the WCl_6–CH_2Cl_2 polymer should be rich in trans structure or composed entirely of trans structure. In general, a poly(phenylacetylene) with more trans structure is formed in a more polar solvent and by WCl_6 than by $MoCl_5$. It has been reported that in metathesis polymerizations the catalysts involving WCl_6 provide a polyalkenamer with more trans structure than those involving $MoCl_5$.[22] These are in good correspondence, though the reason is not clear.

Further Problems on Polymer Structure. In the present study, it was not determined whether the poly(phenylacetylene) obtained consists of regular head-to-tail structure or includes head-to-head structure. A head-to-head structure, however, will be least probable, because internal acetylenes such as phenylpropyne are much less reactive in this polymerization.[23]

Another problem on polymer structure is whether one single bond of the triple bond in phenylacetylene opens or two single bonds do in the polymerization. It should be noted in this connection that four-membered rings containing W or Mo have been proposed as active species in the metathesis of olefins and in the metathesis polymerization of cycloolefins.[24,25] It will be probable that the active species in the present polymerization is also a four-membered metallocycle, because the metathesis polymerization and the present polymerization exhibit many common features (for example, organotin compounds act as a good cocatalyst in both polymerizations[26,27]). If the active species in the present polymerization is a four-membered metallocycle, as shown in Scheme I, the polymer structure should be expressed in a more accurate form, $\{\!\text{CH—C(Ph)}\!\}_n$. This is a problem to be proved in a future investigation.

Scheme I



(M = W or Mo)

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Characterization of Sequence Distributions in Methyl Acrylate–Styrene Copolymers to High Conversion by Pyrolysis Gas Chromatography

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ABSTRACT: The sequence distributions in methyl acrylate–styrene copolymers over a wide range of composition and conversion were investigated by means of pyrolysis gas chromatography. Copolymer samples ranging from 0.2 to 0.5 mg were pyrolyzed under a flow of nitrogen at 510°C in a furnace type pyrolyzer directly attached to a gas chromatograph. Each cluster of dimer and trimer peaks appearing on the pyrogram was identified by means of mass spectrometry and was interpreted in terms of dyad and triad concentrations in the copolymer chain. Experimental results for the sequence distributions were fairly compatible with those predicted by the usual theories of copolymerization for low and high conversion.

Characterization of sequence distributions in copolymer chains has mostly been carried out by NMR and/or ir. Although these methods are most powerful for some types of copolymers, their effectiveness is sometimes limited because of inadequate resolution and intensity of the spectra and because of difficulty in finding suitable solvents for the copolymers. The sequence distributions in styrene (St) and methyl acrylate (MA) copolymers have been studied by NMR[1] and ir,[2] but such spectra do not afford quantitative information about sequence distributions.

On the other hand, pyrolysis gas chromatography (PGC) has recently been recognized as an effective tool in the field of polymer characterization. In our earlier work,[3] PGC was employed for the first time to determine triad distributions in vinylidene chloride–vinyl chloride copolymers, where specific degradation products such as benzene and chlorinated benzenes, formed through dehydrochlorination and subsequent cyclization reactions, were used. Basically, the same degradation mechanisms mentioned above were applied to elucidate the microstructures of chlorinated polyethylenes,[4] chlorinated poly(vinyl chlorides),[5,6] polypropylenes,[7] and ethylene–propylene copolymers.[8]

In previous PGC work, the dyad distributions in some vinyl-type copolymers of low conversion such as acryloni-