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Geometrical structures of poly(haloalkyl propiolate)s prepared with a [Rh(norbornadiene)Cl]$_2$ catalyst

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Abstract

The polymerization of ω-haloalkyl propiolates initiated by [Rh(norbornadiene)Cl]$_2$ in methanol has been investigated in detail together with the geometrical forms of the resulting polymers. The polymer yield and molecular weight of poly(2-haloethyl propiolate)s (P(2XEPA)s) were markedly reduced in the order of X = Cl, Br, and I. ^{1}H NMR, electron spin resonance, and diffuse reflective UV–vis spectroscopic studies of P(2XEPA)s revealed that the content of *cis* form regarding the C═C was markedly decreased from 60% for P(2ClEPA) to 15% for P(2IEPA). The decrease in the *cis* content also resulted in notable reduction of the crystallinity of the polymer from 30% for P(2ClEPA) to less than 10% for P(2IEPA). Compression of P(2XEPA)s at room temperature induced the so-called *cis*-to-*trans* isomerization accompanied with decomposition of the polymers.

Keywords: Conjugated polymers; Isomerization; Substituted acetylenes

1. Introduction

A large number of substituted acetylenes such as phenylacetylene derivatives and alkyl propiolates are known to stereoregularly polymerize in the presence of [Rh(nbd)Cl]$_2$ (nbd = norbornadiene) catalyst under rather mild conditions in alcohols and alkylamines, which could coordinate to the Rh catalyst [1–9]. Substituted poly(acetylene)s prepared in their poor solvents, such as alcohols and alkyl amines, mainly have a *cis–transoid* structure except for a few cases, such as *o*-trifluoromethylphenylacetylene and *p*-nitrophenylacetylene [10,11]. These findings strongly suggest that the Rh catalyst is crucial for the stereoregular polymerization. Previously we found that the *cis*-to-*trans* isomerization of the substituted poly(acetylene) was induced by the application of pressure, heat treatment, γ-ray irradiation, electron beam irradiation, and photo-illumination to the pristine polymers [11–15]. Detailed studies of the geometrical structure of poly(phenylacetylene) derivatives such as *p*-nitrophenyl [11], alkoxyphenyl [16,17], *o*-trifluoromethylphenyl [10], and *p*-methylthiophenyl [9] acetylenes have been carried out. Apparently, the polymers of the substituted acetylenes exhibit unique characteristics which are expected to be closely related to their *cis–transoid* and pseudo-hexagonal structures generated [2,16]. However, in the case of poly(propiolate)s, no detailed geometrical structures have been investigated except for simple poly(*n*-alkyl propiolate)s [2,16]. In this report, the Rh-catalyzed polymerization of ω-haloalkyl propiolates (Scheme 1) was studied to determine the effect of the ω-haloalkyl ester group on the

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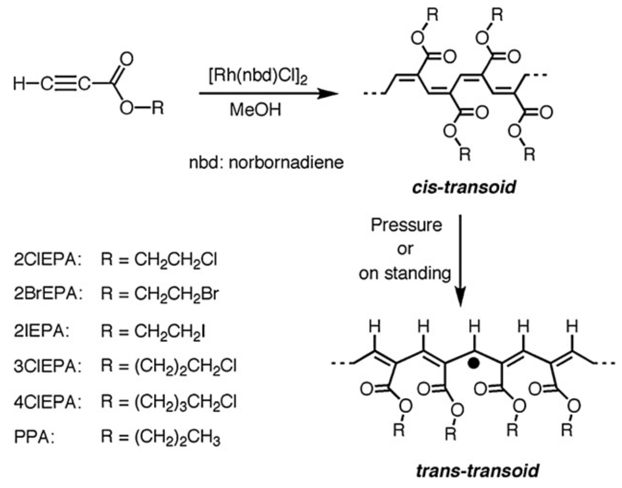


Scheme 1.

polymerizability and the geometrical structure of the resulting polymers.

2. Experimental

2.1. Materials

Propiolates were prepared by dehydration of the corresponding alcohols and propiolic acid in the presence of dried *p*-toluenesulfonic acid followed by distillation under reduced pressure as the same procedure for *n*-propyl propiolate (PPA) and 4-chlorobutyl propiolate (4ClBPA) [2,6]. Commercial $[Rh(nbd)Cl]_2$ (Aldrich) was used without further purification. Solvents were purified by conventional methods.

2-Chloroethyl propiolate (2ClEPA). ^{1}H NMR ($CDCl_3$): $\delta = 2.96$ (s, 1H, C$H\equiv$), 3.73 (t, 2H, CH_2), 4.45 (t, 2H, CH_2). ^{13}C NMR ($CDCl_3$): $\delta = 40.72$ (CH_2Cl), 65.40 (OCH_2), 73.99 ($\equiv CCO$), 75.75 ($CH\equiv$), 152.11 ($C{=}O$). Anal. Calcd for $C_5H_5ClO_2$: C, 45.31; H, 3.80; Cl, 26.75. Found: C, 45.06; H, 3.81; Cl, 26.75%. Bp = 105 °C/77 mmHg.

2-Bromoethyl propiolate (2BrEPA). ^{1}H NMR ($CDCl_3$): $\delta = 2.96$ (s, 1H, C$H\equiv$), 3.54 (t, 2H, CH_2), 4.50 (t, 2H, CH_2). ^{13}C NMR ($CDCl_3$): $\delta = 27.44$ (CH_2Br), 65.17 (OCH_2), 74.02 ($\equiv CCO$), 75.77 ($CH\equiv$), 152.03 ($C{=}O$). Anal. Calcd for $C_5H_5BrO_2$: C, 33.93; H, 2.85; Br, 45.14. Found: C, 33.84; H, 2.94; Br, 45.05%. Bp = 122 °C/85 mmHg.

2-Iodoethyl propiolate (2IEPA). ^{1}H NMR ($CDCl_3$): $\delta = 2.95$ (s, 1H, C$H\equiv$), 3.32 (t, 2H, CH_2), 4.46 (t, 2H, CH_2). ^{13}C NMR ($CDCl_3$): $\delta = -1.46$ (CH_2I), 66.05 (OCH_2), 74.18 ($\equiv CCO$), 75.66 ($CH\equiv$), 151.94 ($C{=}O$). Anal. Calcd for $C_5H_5IO_2$: C, 26.81; H, 2.25; I, 56.65. Found: C, 26.81; H, 2.25; I, 56.65%. Bp = 125 °C/77 mmHg.

3-Chloropropyl propiolate (3ClPPA). ^{1}H NMR ($CDCl_3$): $\delta = 2.16$ (m, 2H, CH_2), 2.95 (s, 1H, C$H\equiv$), 3.65 (t, 2H, CH_2Cl), 4.36 (t, 2H, OCH_2). ^{13}C NMR ($CDCl_3$): $\delta = 31.07$ (CH_2), 40.75 (CH_2Cl), 62.80 (OCH_2), 74.33 ($\equiv CCO$), 75.05 ($CH\equiv$), 152.43 ($C{=}O$). Anal. Calcd for $C_6H_7ClO_2$: C, 49.17; H, 4.81; Cl, 24.19. Found: C, 48.99; H, 4.71; Cl, 24.49%. Bp = 121 °C/56 mmHg.

2.2. Polymerization

All polymerizations were carried out using the specially designed U-type glass ampoules under the following conditions: $[\text{monomer}] = 0.5\ \text{mol L}^{-1}$ and $[Rh(nbd)Cl]_2 = 0.01\ \text{mol L}^{-1}$ in methanol, at 40 °C for 4 h, under reduced pressure [2]. The reaction was stopped by pouring into a large amount of methanol. Insoluble parts in methanol were filtered, washed with methanol, and dried under vacuum (ca. 10^{-2} mmHg) for 24 h at room temperature. Compression of polymers was carried out using an oil press for manufacturing pellets under dynamic vacuum at 10^{-2} mmHg at room temperature.

2.3. Measurements

Number average molecular weights (M_ns) and molecular weight distributions (MWDs) were measured using a JASCO GPC 900-1 equipped with two Shodex K-806L columns and RI detector. Chloroform was used as an eluent at 40 °C and poly(styrene) standards ($M_n = 800{-}1{,}090{,}000$) were employed for calibration. ^{1}H NMR spectra were measured on a JEOL JNM-A400II using deuteriochloroform and tetramethylsilane as solvent and internal standard, respectively, at room temperature. Diffuse reflective UV–vis (DRUV–vis) spectra were recorded on a JASCO V570 equipped with ISN-470; polymer (3 mg) and α alumina (200 mg) were mixed using a mortar and a spatula, and then DRUV–vis spectra from the alumina were first measured followed by the measurement of the mixed sample in order to obtain the spectrum of the polymer by subtraction of the alumina's spectrum as a background spectrum from the mixed sample's spectrum. Electron spin resonance (ESR) spectra were recorded on a JEOL FE1XG with 100 kHz field modulation at room temperature. X-ray diffraction (XRD) patterns were recorded on a JEOL JDX-3500 with a bent optical crystal monochromator and using Cu Kα as a radiation source. Laser Raman spectra were observed on a Jasco TRS-401 equipped with triple monochromators with Ar^+ laser at 514.5 nm.

3. Results and discussion

3.1. Polymerization

Polymerizations of ω-haloalkyl propiolates were carried out in the presence of $[Rh(nbd)Cl]_2$ catalyst. The results of the polymerizations are summarized in Table 1 together with that of PPA as a comparison. In the polymerization of 2-haloethyl propiolates (2ClEPA, 2BrEPA, and 2IEPA), the polymer yields and M_n values were smaller than those of PPA and were markedly decreased in the order of halogen atoms, $Cl > Br > I$. As shown in Fig. 1, MWDs of the polymers were bimodal and the ratio of the higher molecular weight product to the lower was significantly decreased in the same order. In the case of PPA, which does not contain any halogen atom, the polymer yield was close to the cases of 2ClEPA, however, no shoulder at lower molecular weight side was observed in the MWD. Comparing the polymerization of

Table 1
Results of the polymerization of ω-haloalkyl propiolates at 40 °C[a]

Monomer	Yield (%)	$M_n \times 10^{-3}$		Color	
		Pristine[b]	Compressed[c]	Pristine[b]	Compressed[c]
PPA	54.2	45	n.d.[d]	Pale yellow	n.d.[d]
2ClEPA	52.4	27[e]	5.5[e]	Yellowish-pink	Dark-yellow
2BrEPA	42.1	20[e]	5.1[e]	Dark yellowish-pink	Dark-orange
2IEPA	32.4	11[e]	1.2[e]	Brown	Dark-brown
3ClPPA	53.9	32[e]	n.d.[d]	Yellowish-pink	n.d.[d]
4ClBPA	44.1	22[e]	n.d.[d]	Yellowish-pink	n.d.[d]

[a] [Monomer] = 0.5 mol L^{-1} and [Rh(nbd)Cl]$_2$ = 0.01 mol L^{-1} in methanol for 4 h.
[b] The polymer obtained by precipitation in methanol.
[c] The polymer obtained by compression of the pristine polymer under 200 kg cm^{-2}.
[d] Not determined.
[e] Approximately estimated for the higher molecular weight fraction.

2ClEPA, 3ClPPA, and 4ClBPA, which have chloroalkyl ester groups with different number of carbon, 4ClBPA resulted in slightly lower polymer yield than the others (Table 1) and no marked trend was observed in M_n and MWD (Fig. 2). These results suggest that the ω-haloalkyl ester groups reduce the polymerizability (polymer yield and molecular weight of the polymer) and the extent of the reduction increases in the order of Cl, Br, and I. The order of the polymerizability in the monomer having Cl, Br, and I may be simply explained in terms of degree of bulkiness, i.e., steric hindrance of the halogenated ester moiety whose effects may work when the 2-haloethyl propiolates were coordinated to the Rh complex to produce a propagation species of this polymerization. Polymerization of 2IEPA was also carried out in the dark and the results were similar to those obtained in the white light. This rules out the possibility of light-induced dehalogenation from the monomer and/or polymer. The purity of the polymers (P(2XEPA)s) was examined by elemental analyses as follows: P(2ClEPA) (C, 44.78; H, 3.83; Cl, 26.33%), P(2BrEPA) (C, 33.79; H, 2.92; Cl, 44.74%), P(2IEPA) (C, 27.03; H, 2.32; Cl, 55.60%), P(3ClPPA) (C, 48.79; H, 4.76; Cl, 23.87%), and P(4ClBPA) (C, 51.75; H, 5.54; Cl, 21.88%). These values well agree with the theoretical values calculated from their monomers (C, 52.35; H, 5.65; Cl, 22.08% for 4ClBPA and see Section 2 for the others). The fact proves that the polymers did not undergo dehalogenation and other side reactions, which insert and/or expel substituents.

Color of the resulting P(2XEPA)s drastically varied depending on the ω-haloalkyl ester groups (Table 1). Such marked changes, which are induced by simple difference in the ester group of the monomer, have not been reported. Difference in the number of carbon in the ester alkyl group of the monomer, i.e., 2ClEPA, 3ClPPA, and 4ClBPA, did not cause any notable color change in the polymers (Table 1).

All polymers readily dissolved in dichloromethane. However, solubility of P(2XEPA)s in chloroform decreased in the order of P(2ClEPA) > P(2BrEPA) > P(2IEPA) in spite of decreasing the molecular weight of the polymers in this order. Therefore, dependence of the solubility on X could not be explained solely by polymer chain–solvent interaction. Remarkable changes in MWDs were not detected even when a chloroform solution of P(2XEPA)s was left for 48 h at room temperature. This shows that P(2XEPA)s are stable in solution, though poly(phenylacetylene) derivatives were reported to readily undergo main-chain scission in the same solvent via autoxidative degradation [18,19].

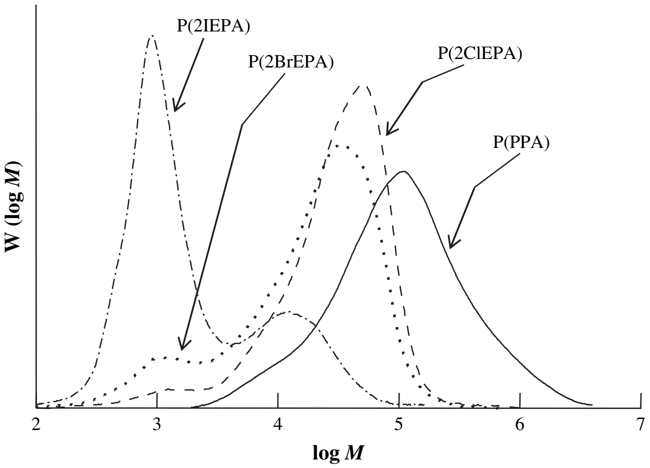


Fig. 1. GPC elution curves of P(PPA) (—), P(2ClEPA) (---), P(2BrEPA) (……), and P(2IEPA) (—·—).

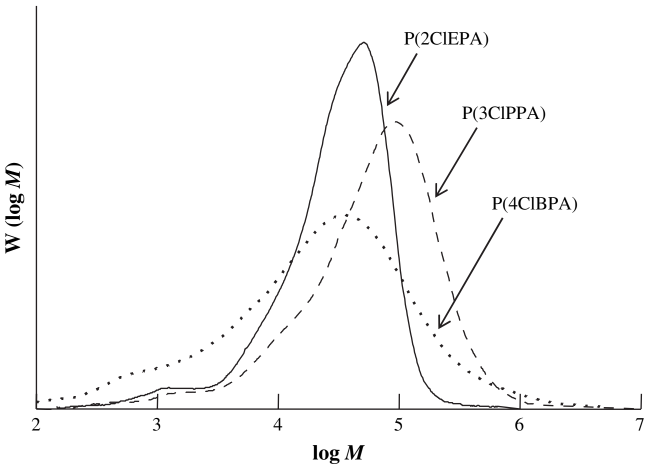


Fig. 2. GPC elution curves of P(2ClEPA) (—), P(3ClPPA) (- - -), and P(4ClBPA) (……).

3.2. ^1H NMR

Fig. 3(a) shows the ^{1}H NMR spectrum of P(2ClEPA). Characteristic resonances due to P(2ClEPA), i.e., the *cis*-vinyl proton of the main chain (a), the methyleneoxy protons (b), and the methylene protons (c) were observed. In the case of P(2BrEPA) and P(2IEPA), additional resonance peaks due to tris(2-haloethyl) 1,3,5-benzenetricarboxylate called cyclotrimer (d–f in Fig. 3(b)), which would be formed by cyclotrimerization [20], were also detected. Currently the mechanism in detail for the cyclotrimerization is not clear, however, it is deduced that the cyclotrimerization may be related to the formation of low molecular weight products as seem in GPC trace. We believe that the source of benzenetricarboxylate as the so-called cyclotrimer is the helical *cis*–*transoid*. Because benzenetricarboxylate may be easily eliminated from the helical *cis*–*transoid* conformers in order to release the tortional energy from the distorted conformation of the polymer in the solution. In another word, such helical conformations may be energetically and spatially favorable for the cyclotrimarization, although such elimination reaction mechanism is still unknown [19].

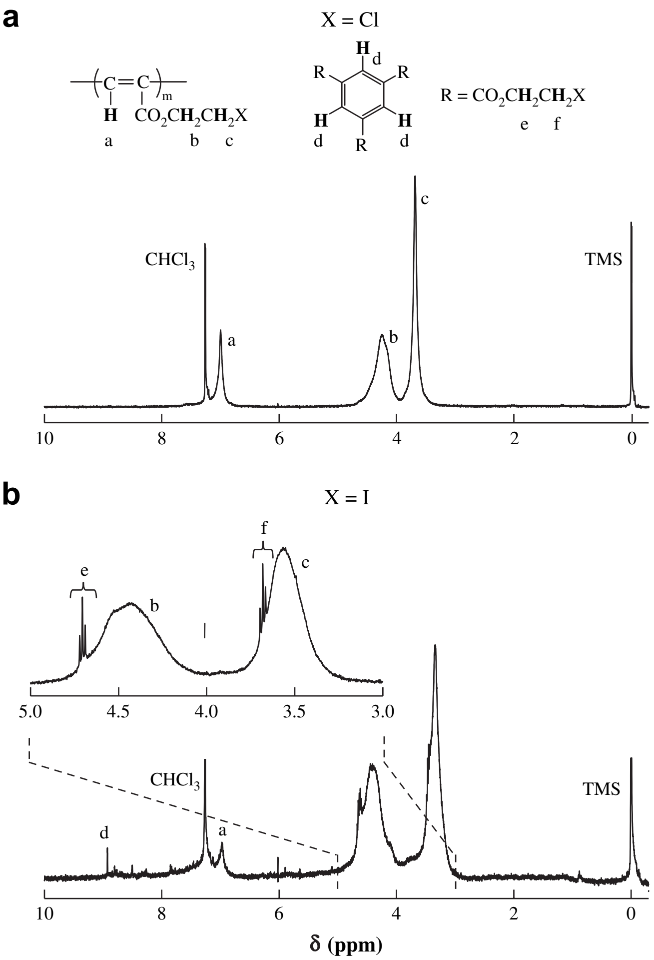
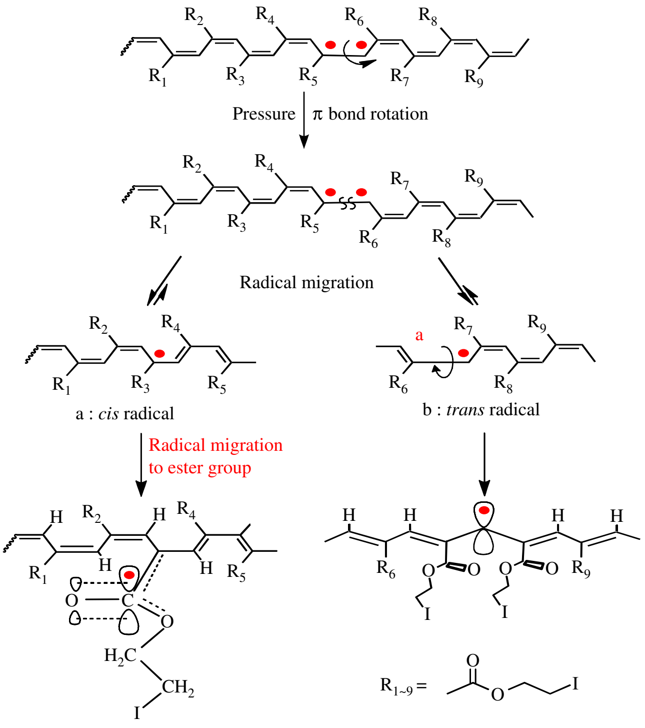


Fig. 3. ^{1}H NMR spectra of P(2ClEPA) (a) and P(2IEPA) (b) observed at room temperature.

The GPC chromatogram intensity measured with the refractive index (RI) detector exactly shows the amount of solute in the solution so that the intensity is reliable. However, the intensity of the solution ^{1}H NMR spectra is not always reliable when a stable organic radical, e.g., TEMPO radical (2,2,6,6-tetramethylpiperidine 1-oxyl) or π-conjugated radical, i.e., *trans* forms (see Scheme 1) incorporated in the pristine *cis*–*transoid* polymer sequences is involved in the solution. In this case not only the spectral intensity but also the line width and even the chemical shift in the ^{1}H NMR spectrum lose the reliability [9,17,23,25]. For example, the line width (see Fig. 3(b)) is extremely broadened by the so-called magnetic dipole–dipole (D–D) interaction between the polymer protons and the radical spins stabilized in the polymer of the solution even at room temperature. Therefore, it is not unreasonable to assume that the spectral intensity of the cyclotrimer observed in the ^{1}H NMR spectrum is not so strong, though the intensity in the GPC chromatogram is fairy large.

Previously we have reported that the *trans* vinyl proton peak due to *trans* –C=C–H is not observed as a sharp peak but as a notably broad one unlike the case of the *cis* –C=C–H [9,17,23]. In the *trans* sequence forms, two magnetic spins as unpaired electrons generated by rotational scission of the *cis* –C=C double bonds. They are stabilized to create two unpaired electrons as π radicals which can migrate along the resulting *trans* planar conjugated sequences to be stabilized as no only *trans* π-conjugated radicals called the so-called soliton, i.e., a mobile unpaired electron but also *cis* radicals as relatively immobile unpaired electrons when the pristine *cis*–*transoid* polymer was subjected to pressure or the polymer solution was on standing at room temperature (see Scheme



Scheme 2. Possible *cis*-to-*trans* isomerization mechanism through the *cis* double bond rotation.

2). The magnetic spins as the so-called π-conjugated radicals are delocalized in the resulting fairly planar *trans* sequence region, especially in the vicinity of the *trans* vinyl radical protons, i.e., H_α, H_β, H_γ, and H_δ, and $H_{\alpha''}$, $H_{\beta'}$, $H_{\gamma'}$, and $H_{\delta'}$, called the seven *trans* −C=C−H protons together with the *cis* radical protons, i.e., H_β, and H_γ, and $H_{\beta'}$, $H_{\gamma'}$ as shown in Scheme 2. It is clear, therefore, that the so-called fairly large magnetic dipole−dipole interaction is induced between the *trans* and *cis* radical protons and the magnetic spins in order to significantly broaden not only the line width of the *trans* sequence protons but also other protons in the polymer solution together with such markedly distortion of the baseline as shown in the case of Figs. 3(b) and 8 where no longer the line width does reflect the rate of rotational motion of molecules dissolved in the solution. We can observe such a typical example, i.e., a ^{1}H NMR spectrum of chloroform solution including a TEMPO radical where the reliability regarding the intensity, the line width, and the chemical shift has been no longer hold [25]. In another word, the *trans* −C=C−H sequence protons are not easily observed as a sharp peak but as a notably broad or completely smeared peak, i.e., just as we have observed such cases shown in Figs. 3(b) and 8, respectively. On the other hand, the non-magnetic *cis* −C=C−H sequence protons which are fairly far from the magnetic center is not significantly affected by the D−D interaction. Therefore, the *cis* protons can be observed at around 6.9 ppm as a fairly sharp peak where the peak intensity keeps the reliability, though the line width was relatively increased when the molecular weight is large. Based on these facts, we can estimate the *cis* % if the integral peak area due to the *cis* peak at around 6.9 ppm is compared with the peak area at ca. 3.7 ppm due to CH_2 in the OCH$_2$$CH_2$X whose protons are fairly far from the main chain and ascribed to the total protons from the *cis* and *trans* forms. Thus, the important *trans* content can be reasonably estimated with enough accuracy. It seems, unfortunately, that the past and recent papers regarding substituted polyacetylenes do not care such caution when the *cis* % is calculated.

In the case of P(2IEPA), line width broadening of the ^{1}H NMR peaks due to the *trans* form, which may be produced by rotational cleavage of the *cis* C=C bond accompanied with production of magnetic spins, was also observed [9,10]. The *cis* contents of the polymers were estimated based on the peak intensities and are listed in Table 2. The *cis* contents of P(PPA), P(2ClEPA), P(2BrEPA), and P(2IEPA) were markedly decreased in this order, which is the same order as the polymerizability decrease. It is noteworthy that the *cis* content drastically changes depending on the substituents of the propiolate monomer when the polymerization was initiated by [Rh(nbd)Cl]$_2$.

3.3. ESR

Previously we have shown that the substituted polyacetylenes having the *cis−transoid* form synthesized using the Rh complex catalyst have a helical structure and is isomerized to the *trans−transoid* form when the pristine *cis* polymer was subjected to compression or photo-illumination at room temperature [9,11,14]. It is said, therefore, that the origin of the *trans* form is the pristine *cis−transoid* form. Because the *trans* form is generated when the *cis* C=C double bonds, i.e., π-bonds were rotationally scissioned by compression in order to create two unpaired electrons as π radicals which can migrate along the resulting planar conjugated sequences to be stabilized as no only *trans* π-conjugated radicals called the so-called soliton, i.e., a mobile unpaired electron but also *cis* radicals as relatively immobile unpaired electron as mentioned above (see Scheme 2). In the case of the *trans* radical the main-chain protons take a planar structure in order to effectively stabilize the mobile unpaired electrons and the plane of the side chains is approximately perpendicular to the main chain due to sterically large crowding. On the other hand, in the *cis* radical the plane of the ester side chain is on the decline to some extent to the main-chain plain to migrate the unpaired electron even to the side ester moiety.

The ESR spectra of P(2XEPA)s in solid state were measured at the microwave power of 0.01 mW and the spin concentrations are listed in Table 2. The spin concentrations increased in the order of P(PPA) < P(2ClEPA) < P(2BrEPA) and the order agrees with the order of the decrease in the *cis* content determined by ^{1}H NMR. Although, the spin concentration of P(2IEPA) is lower than that of P(2BrEPA), the *cis* content of P(2IEPA) is much lower than that of P(2BrEPA). The apparent inconsistency may be related to the amount of

Table 2
Geometric properties of P(2XEPA)s

Polymer	*cis* Content[a] (%)		*g* Value[b]	Spins × 10^{-18} (mol^{-1})		Crystallinity (%)	
	Pristine[c]	Compressed[d]	Pristine[c]	Pristine[c]	Compressed[d]	Pristine[c]	Compressed[d]
P(PPA)	82	n.d.[e]	2.0045	2.7	n.d.[e]	60	n.d.[e]
P(2ClEPA)	64	47	2.0040	5.9	8.4	30	<10
P(2BrEPA)	50	45[f]	2.0044	13.0	18.0	<20	≈0
P(2IEPA)	15	n.d.[g]	2.0047	9.9	16.0	<10	≈0

[a] Estimated by ^{1}H NMR: the *cis* content (%) = [*cis* −C=C−*H*]/[OCH_2CH_2X] × 100.

[b] Measured under irradiation of 0.01 mW of microwave power.

[c] The polymer obtained by precipitation in methanol.

[d] The polymer obtained by compression of the pristine polymer under 200 kg cm^{-2}.

[e] Not determined.

[f] The value may be erroneous because of broadened resonances of the vinyl proton.

[g] The value could not be determined because of too weak resonances of the vinyl proton.

oligomeric products including cyclotrimerized products otherwise a lower *cis* content of P(2IPE) than P(2BrEP) would bring about a higher spin concentration of P(2IEP) than P(2BrEP).

The ESR spectra of P(2ClEPA) observed at the microwave power of 0.01 mW and 10 mW are shown in Fig. 4(a) and (b), respectively. Saturation of the spectrum was observed at 0.40 mW. The line width and the g value increased from $\Delta H_{\mathrm{msl}} = 12.5$ G and $g = 2.0040$ at 0.01 mW to $\Delta H_{\mathrm{msl}} = 19.0$ G and $g = 2.0045$ at 10 mW, respectively, associated with a clear change of the line shape. This shows that P(2ClEPA) contains at least two spectral components, such as *cis* and *trans* radicals, which have different ΔH_{msl}s and g values and show different saturation effect [11]. The saturation effect and the changes in ΔH_{msl}s and g values were also observed in the case of P(2BrEPA) and P(2IEPA). The g values of P(2ClEPA), P(2BrEPA), and P(2IEPA) increased in that order (Table 2). This suggests that the radical spin is fairly delocalized even to the π-haloalkyl ester groups. The spin–orbit coupling constant (ζ) of the halogen atoms increases in the order of $\zeta_{\mathrm{Cl}} = 586\ \mathrm{cm}^{-1}$, $\zeta_{\mathrm{Br}} = 2460\ \mathrm{cm}^{-1}$, and $\zeta_{\mathrm{I}} = 5060\ \mathrm{cm}^{-1}$. The fact would result in increasing g value when the radical spin delocalizes to the ω-haloalkyl ester group [21]. Although the g value of P(PPA) is larger than that of P(2ClEPA) and P(2BrEPA), the ζ value of the carbon atom ($\zeta = 29\ \mathrm{cm}^{-1}$) is much smaller than that of Cl and Br. Possible rationalization is that steric hindrance by the ester groups, i.e., *n*-propyl and ω-haloethyl ester groups, would cause a different extent of spin delocalization to the ester groups accompanied with such apparent deviation in g values.

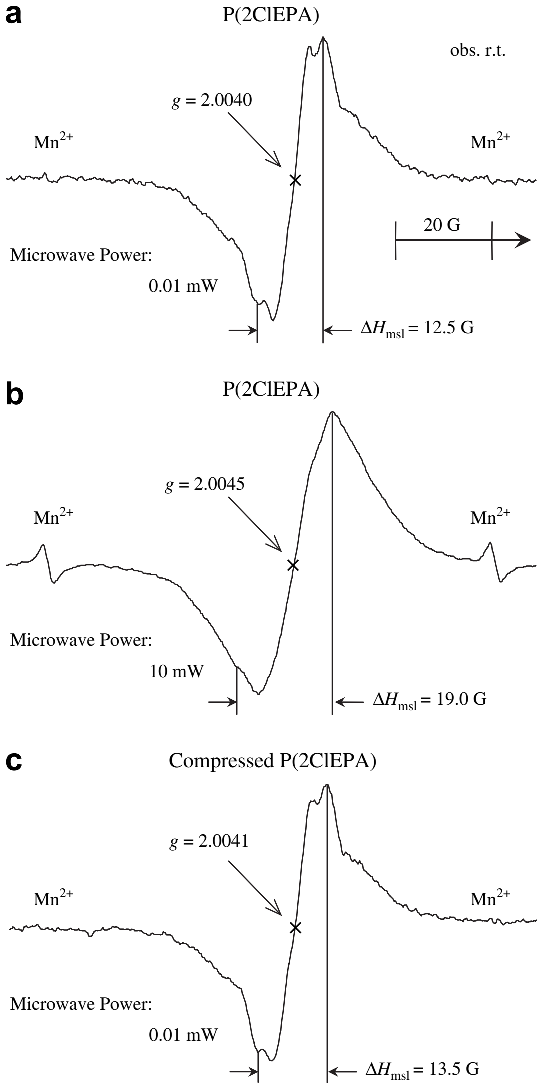


Fig. 4. ESR spectra of P(2ClEPA) recorded at room temperature under irradiation of 0.01 mW (a) and 10 mW (b) of microwave power, and P(2ClEPA) after compression under 200 kg cm^{-2} recorded at room temperature under irradiation of 0.01 mW of microwave power (c).

3.4. DRUV–vis

The DRUV–vis spectra of P(2XEPA)s are shown in Fig. 5 together with that of P(PPA). P(2ClEPA) and P(2BrEPA) showed shorter $\lambda_{\max}$ (375 nm) than in the case of P(PPA) ($\lambda_{\max} = 395$ nm), where these absorptions can be assigned to the π-conjugated *cis* forms. This result indicates that the *cis* forms of P(2ClEPA) and P(2BrEPA) have less π-conjugation length than P(PPA) due to a steric and/or dipole repulsion between ω-haloalkyl ester groups. In the case of P(2IEPA), it is difficult to determine the $\lambda_{\max}$ value because of the very broad spectrum. Not only P(2IEPA) but also P(2BrEPA) shows relatively broad spectrum, where the origin of the broad spectra can be attributed to the π-conjugated *trans* form having much longer π-conjugation length than the *cis* form. The relative spectral intensity of the peaks due to *trans* to *cis* forms can qualitatively reflect the *cis* and *trans* contents, and the relative intensity increases as follows: P(PPA) ≈ P(2ClEPA) < P(BrEPA) < P(2IEPA). The order agrees with the results from ^{1}H NMR and ESR measurements mentioned above. Based on these results, it is shown that the *trans* content was increased with increasing steric and/or dipole repulsions among ω-haloalkyl ester groups. The DRUV–vis spectra can explain the drastic change in the color of P(2XEPA)s. The peaks of P(2BrEPA) and P(2IEPA) gradually last to longer

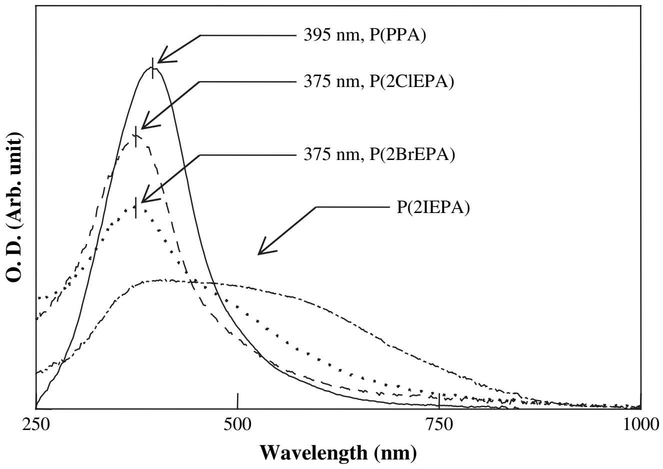


Fig. 5. DRUV–vis spectra of P(PPA) (—), P(2ClEPA) (---), P(2BrEPA) (······), and P(2IEPA) (– · –).

wavelength and cause darken color, such as yellowish-pink and brown for P(2BrEPA) and P(2IEPA), respectively.

3.5. XRD

Previously we have reported that *n*-alkylpropiolate polymers prepared with the Rh complex catalyst in the presence of methanol as the polymerization solvent gave typical XRD patterns ascribing to pseudo-hexagonal crystal (= columnar) patterns in the solid state [2,4,22]. In the XRD pattern of P(ClEPA) (see Fig. 6) the sharp peak observed at 11.2 Å at a lower angle side can be similarly assigned to the (100) reflection of the so-called columnar structure. This assignment is also strongly supported by the molecular mechanics calculation with MMFF94 force field (Wavefunction, Inc., Spartan ′04 Windows version 1.03) [26] where a helical structure having the column diameter around 13.2 ± 0.5 Å is more energetically stable. Thus, the observed diameter obtained by the XRD measurement clearly coincides with that of the calculated one.

The crystallinity was determined by comparing the total area in the reflection pattern of XRD with the sharp peak due to the columnar at the lower angle side. However, the XRD patterns of P(2BrEPA) and P(2IEPA) did not show any sharp diffraction peak because of low crystallinity. In fact, crystallinity of P(2XEPA)s decreased from 30% for P(2ClEPA) to less than 10% for P(2IEPA) (Table 2). It seems, thus, that the crystallinity decreases with decreasing the *cis* content, i.e., with increasing *trans* content.

3.6. Compressed polymers

P(2XEPA)s were compressed under 200 kg cm^{-2}. The compression darkened the polymer color in comparison with the original polymers due to changes in the geometrical structure and π-conjugation length as described later (Table 1). The MWD of compressed P(2ClEPA) was found to shift to a lower molecular weight region suggesting decreasing hydrodynamic radius and/or decomposition of the polymer (Fig. 7(a)). Apparent M_n for the higher molecular weight peak was estimated to be about one-fifth of that of the original P(2ClEPA) (Table 1). Similar shift of the MWD was observed in the case of P(2BrEPA), and compression of P(2IEPA) resulted in a much more pronounced decrease in M_n of the main peak (Fig. 7(b) and Table 1).

In the ^{1}H NMR spectrum of P(2ClEPA) after compression, the peak due to the vinyl proton (a) was markedly broadened probably due to the isomerization from the *cis* to the *trans* forms as mentioned above.

Furthermore, new peaks assignable to tris(2-chloroethyl) 1,3,5-benzenetricarboxylate (d–f) as the cyclotrimer were observed (Fig. 8). In the case of compressed P(2BrEPA) and P(2IEPA), similar line broadening phenomena were observed and the intensities of the peaks due to tris(2-haloethyl) 1,3,5-benzenetricarboxylates became to be larger than that of the original polymer. The ^{1}H NMR and GPC observations indicate that cyclotrimerization results in a decrease in molecular weight, i.e., decomposition of the polymer, though the decomposition mechanism is not clear at present.

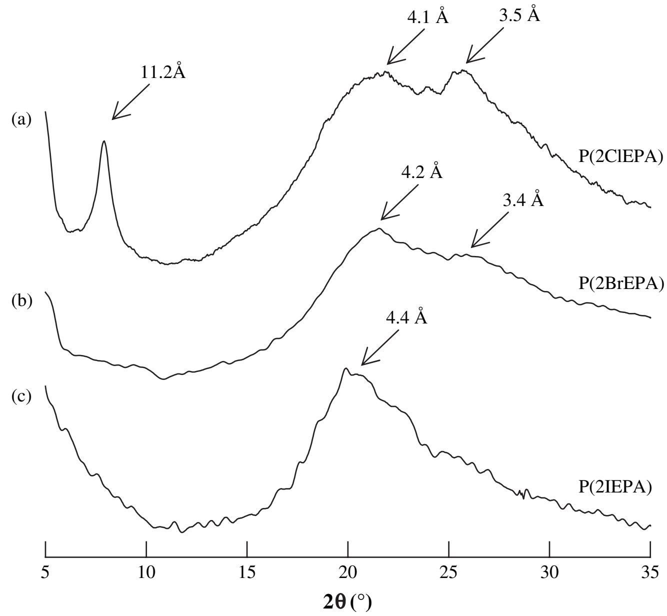


Fig. 6. XRD patterns of P(2ClEPA) (a), P(2BrEPA) (b), and P(2IEPA) (c) observed at room temperature.

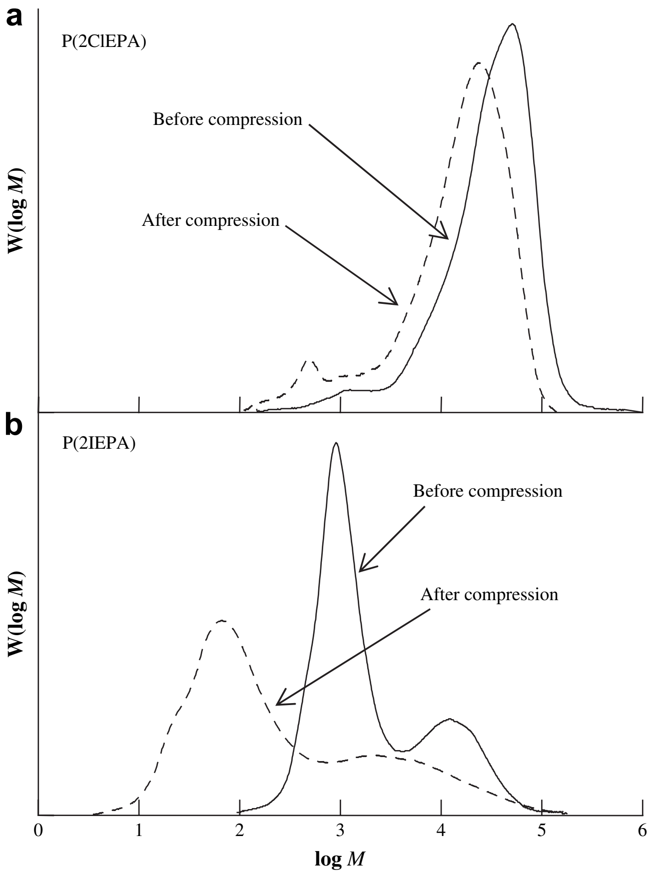


Fig. 7. GPC elution curves of P(2ClEPA) (a) and P(2IEPA) (b) before (—) and after compression under 200 kg cm^{-2} (---).

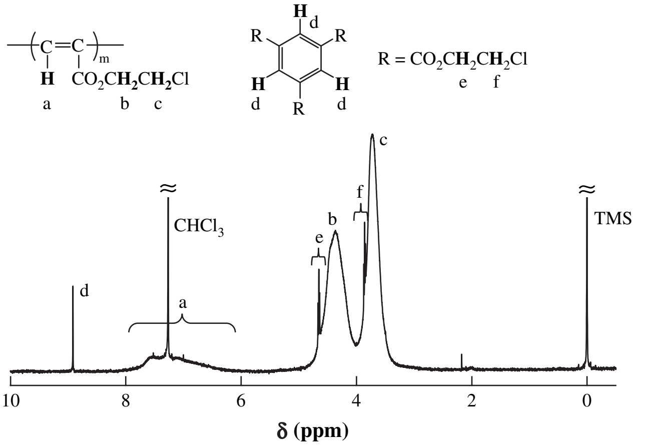


Fig. 8. ^{1}H NMR spectrum of compressed P(2ClEPA) under 200 kg cm^{-2} and recorded at room temperature.

The spin concentrations were increased after the compression of P(2XEPA)s as previously observed (Table 2) [23]. However, the shape of the ESR spectra and *g* values were hardly affected (Fig. 4(c)). The sharp diffraction peak seen in the XRD pattern of the original P(2ClEPA) disappeared after the compression and the crystallinities decreased in all cases (Table 2). The laser Raman spectra of P(2ClEPA), P(2BrEPA), and P(2IEPA) were also observed before and after compression. Raman spectra of P(2ClEPA) before and after compression are shown in Fig. 9. The peaks at 1630 cm^{-1} and 1525 cm^{-1} can be attributed to the *cis* and *trans* C=C stretching vibrations, respectively [24]. After compression, peak intensity of the *cis* C=C stretching was decreased on the contrary to an increase of the *trans* C=C stretching. All these facts clearly show the *cis*-to-*trans* isomerization induced by compression. The Raman spectra of P(2IEPA) were different from others and were extremely broadened even before compression. This may be explained by the formation of *trans* π-conjugated sequences bearing unpaired electrons, i.e., polymer radicals together with the low content of the columnar component [17]. Because generally such radical compounds have been considered as a fluorescence source in order to disturb the observation of the Raman spectra. Further the broadened spectra may be related with a fairly low amount of crystallinity as the columnar to some extent as evidenced by the XRD data shown in Fig. 6(c) and Table 2.

The DRUV–vis spectrum of compressed P(2ClEPA) showed a clear red shift of λ_{max} from 370 nm to 395 nm (Fig. 10(a)). Similar red shift and broad absorption were also observed in the spectrum of P(2BrEPA). In Fig. 10 the fairly sharp absorption at around 370 nm was assigned to that of *cis* forms and an extremely broad ranging from ca. 450 nm to ca. 1000 nm was also ascribed to that of the resulting *trans* planar π-conjugated sequences which may be incorporated in the pristine *cis* sequences. The activation energy for the pressure-induced *cis*-to-*trans* isomerization may be deduced as less than around 615 kJ mol^{-1} from the binding energy of an ordinal C=C double bond, though the C=C bond is not a π-conjugated double bond. Therefore, the spectral change is due to the *cis*-to-*trans* isomerization and elongated π-conjugation, and the wide absorption band can explain the deep color of the compressed polymers. In contrast, compressed P(2IEPA) showed a blue shift of the λ_{max} to 365 nm, suggesting compression shortened π-conjugation arising from a significant decrease in M_n (see Table 1). However, broad absorption was still observed.

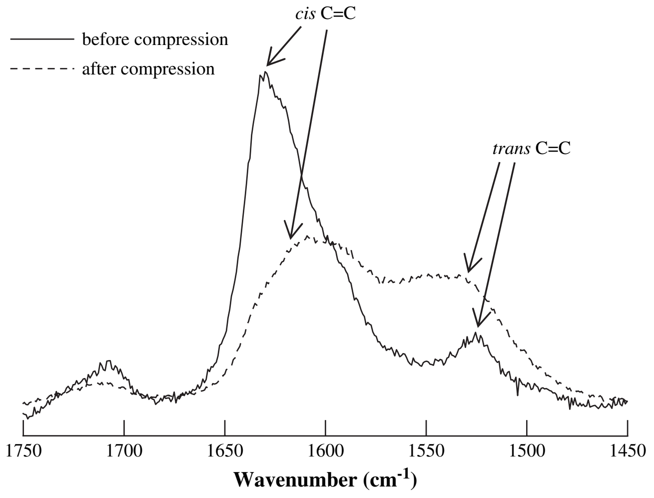


Fig. 9. Raman spectra of P(2ClEPA) before (—) and after (---) compression under 200 kg cm^{-2}.

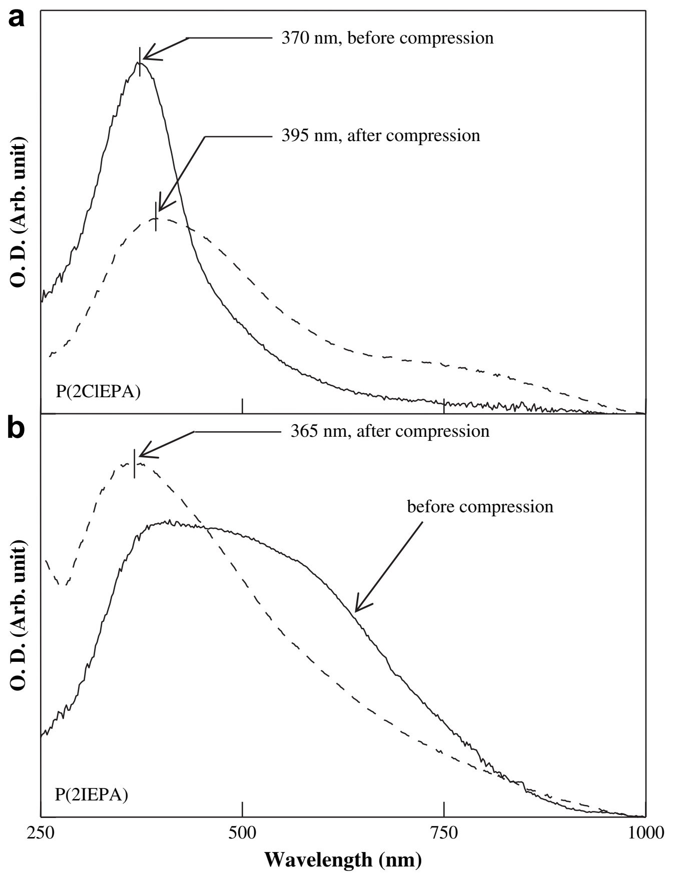


Fig. 10. DRUV–vis spectra of P(2ClEPA) (a) and P(2IEPA) (b) before (—) and after (---) compression under 200 kg cm^{-2}.

4. Conclusion

Polymerizations of ω-haloalkyl propiolates (*n*XRPAs; $n = 2-4$, X = Cl, Br, and I) were initiated by $[Rh(nbd)Cl]_2$ catalyst in methanol at 40 °C. The polymerizability (polymer yield and molecular weight of the polymer) of 2ClEPA, 2BrEPA, and 2IEPA was markedly reduced in that order. In the case of 2ClEPA, 3ClPPA, and 4ClBPA, polymer yield of 4ClBPA was slightly reduced and no significant effect on molecular weight was observed. Polymerizations of 2IEPA and 2BrEPA resulted in the formation of tris(2-haloethyl) 1,3,5-benzenetricarboxylate together with the polymers. ^{1}H NMR, ESR, and DRUV–vis spectra showed that the *cis* content of P(2ClEPA), P(2BrEPA), and P(2IEPA) decreased in that order and the *trans* content increased in the reverse order. The increase in the *trans* content resulted in significant decrease in the crystallinity of P(2XEPA)s. The polymerizability of 2XEPAs and geometrical structure of the resulting polymers are strongly affected by the ω-haloalkyl ester groups. Based on the microwave saturation effect of ESR, two radical components, so-called *cis* and *trans* radicals, were proven to be generated. Compression of P(2XEPA)s induced *cis*-to-*trans* isomerization accompanied with decrease in crystallinity and molecular weight reduction by a scission of the main chain expelling the tris(2-haloethyl) 1,3,5-benzenetricarboxylate moieties. The π-conjugation lengths of the compressed polymers were elongated and thus the polymer color changed to dark except for P(2IEPA). Further studies including copolymerizations of ω-haloalkyl propiolates are currently progressing in our laboratory.

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