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Polymerization of *o*-Trifluoromethyl(phenylacetylene) Initiated by $[Rh(norbornadiene)Cl]_2$ and $MoOCl_4$−*n*-Bu_4Sn−EtOH Catalysts. Formation of Order and Disorder Trans Sequences

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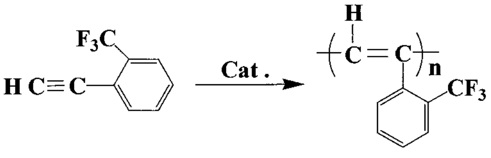
ABSTRACT: *o*-Trifluoromethyl(phenylacetylene) (*o*TFMPA) was successfully polymerized by a Rh complex, $[Rh(norbornadiene)Cl]_2$ catalyst, in the presence of triethylamine as the polymerization solvent under mild conditions. Structural differences between the Rh polymer and the Mo polymer prepared with a metathesis initiator, $MoOCl_4$−*n*-Bu_4Sn−EtOH, using the same monomer were compared using laser Raman, ^1H and ^{19}F NMR, solution and diffuse reflective UV, and electron spin resonance (ESR) methods. The Rh complex produces the aromatic polyacetylene bearing regular head-to-tail, ordered trans sequences where more mobile unpaired electrons generated through the rotational scission of the cis C═C bonds are stabilized, although the Rh catalyst is known to selectively generate the cis−transoid isomer. The Mo-based initiators produce also complete trans−transoid polyacetylene involving irregular head-to-head and/or tail-to-tail units of ca. 32% disordered trans sequences, where less mobile unpaired electrons are stabilized in the irregular trans sequences, although the Mo initiators are known to produce cis-rich polyacetylenes.

Introduction

We previously reported that *o*-methoxy- and *o*-ethoxyphenylacetylenes can be stereospecifically polymerized with a Rh complex, $[Rh(norbornadiene)Cl]_2$, in the presence of an alcohol or triethylamine to selectively produce the corresponding cis−transoid polyacetylenes.[1−4] *o*-Trifluoromethyl(phenylacetylene) (*o*TFMPA) has been successfully polymerized using metathesis initiators, e.g., WCl_6, $MoCl_5$, and $MoOCl_4$, to quantitatively produce poly(*o*-trifluoromethyl(phenylacetylene)) (P*o*TFMPA).[5,6] The resulting P*o*TFMPA has a fairly high molecular weight and narrow polydispersity; the WCl_6- and $MoCl_5$-based initiators have been considered to be those that generate the corresponding trans- and cis-rich polyacetylenes, respectively.[7]

Polymers produced with Mo metathesis initiators are promising not only for nonlinear optical (NLO) materials[8,9] but also as an oxygen permeable film.[10] However, to the best of our knowledge, the polymers lack detailed structural characterizations of their geometrical isomers and/or solid structures. There also is no preparation method for the complete trans regular polyacetylene, although the Mo-produced polymer is conjectured to have trans π-conjugation lengths, which contribute to the third harmonic generation (THG) coefficient, $\chi^{(3)}$.[8,9] We recently found that the *o*TFMPA even with its bulky *o*-trifluoromethyl substituent can be polymerized by the Rh complex, $[Rh(norbornadiene)Cl]_2$, to generate a regular or ordered trans sequence polymer when triethylamine was adopted as a cocatalyst. We have shown that the Rh initiator produces selectively the cis−transoid polymer.[1−4,11] This paper reports that detailed characterization of the structural differences between the resulting Rh- and Mo-produced polymers using laser Raman, solution and diffuse reflective UV, ^1H and ^{19}F NMR, and electron spin resonance (ESR) methods. Unequivocal assignment of the resulting geometric isomers is needed to develop new and promising advanced materials.

Scheme 1



Initiator : $MoOCl_4$/*n*-Bu_4Sn / Ethanol
or $[Rh(NBD)Cl]_2$ / Triethylamine

Experimental Section

Materials. The monomer *o*TFMPA was prepared according to the method described in the literature[6] and used after distillation under reduced pressure from CaH_2 (purity >99.5% by gas chromatography). $[Rh(norbornadiene)Cl]_2$, $[Rh(NBD)Cl]_2$ (Aldrich), and $MoOCl_4$ (Strem) were used without further purification. *n*-Bu_4Sn (Tokyo Kasei) was used after distillation under reduced pressure from CaH_2 (purity >99% by gas chromatography) and stored as a 200 mmol/L toluene solution. Ethanol (EtOH) was distilled twice from $Mg(OEt)_2$ and stored as 200 mmol/L toluene solution. Triethylamine (TEA) used in this experiment was dried using sodium benzophenone ketyl. Toluene was distillated from CaH_2.

Polymerization. Polymerization of the *o*TFMPA monomer induced by the Mo-based initiator was performed at the monomer of 0.85 g, 5 mmol, $MoOCl_4$, 101.6 mg, 0.4 mmol, toluene solutions (200 mmol/L) of *n*-Bu_4Sn, 2.0 mL, and toluene solutions (200 mmol/L) of EtOH, 2.0 mL, and toluene, 16 mL, at 30 °C for 24 h. Polymerization induced by the Rh complex was also carried out at a monomer concentration of 0.51 g, 3

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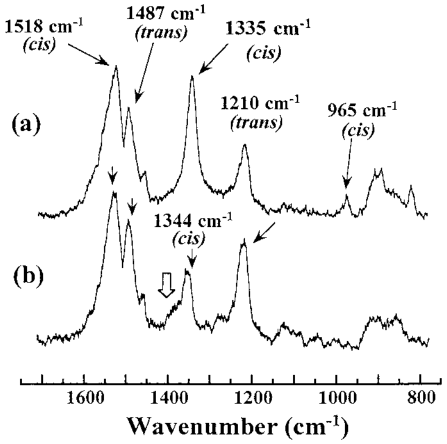


Figure 1. Laser Raman spectra of P*o*TFMPA polymers observed at room temperature: (a) $[Rh(NBD)Cl]_2$ initiator; (b) $MoOCl_4$−*n*-Bu_4Sn−EtOH initiator.

mmol, and $[Rh(NBD)Cl]_2$, 27.6 mg, 60 μmol, in the triethylamine, 3.0 mL as the cocatalyst at 30 °C for 48 h. The resulting polymers were poured into excess methanol or water to stop the polymerization, filtrated by a glass filter, and dried, ca. 10^{-3} Torr, at 30 °C for 24 h.

Characterization. Molecular weights of the resulting polymers were estimated by gel permeation chromatography (GPC) calibrated with polystyrene standards using tetrahydrofuran (THF) as an eluent. Laser Raman spectra of KBr pellets were recorded on a JEOL JRS 400T, equipped with triple monochromators using Ar^+ laser light at 514.5 nm. ^1H NMR and ^{19}F NMR spectra were recorded on a JEOL GX 270 MHz and a Hitachi FT-NMR R-1900 at 25 °C using tetrahydrofuran as solvent, respectively. However, a small amount of $CDCl_3$, 99.8 atom %, which contains 1% v/v TMS was added to the THF solution to observe internal standard signals, i.e., $CHCl_3$ and TMS. Solution and diffuse reflective UV (DRUV) spectra of the polymers were recorded on a JASCO V550 equipped with ISV-469. Electron spin resonance (ESR) spectra were observed on a JEOL FE1XG with 100 kHz field modulation at room temperature and 77 K. The third harmonic generation coefficient, $\chi^{(3)}$ (esu), was measured using a fundamental wavelength of 1.907 μm and fused silica as a standard material at room temperature under nitrogen.

Results and Discussion

Polymerization. *o*TFMPA was successfully polymerized with $[Rh(NBD)Cl]_2$ to produce poly(*o*TFMPA), in a yield of 48.0%, and the molecular weight and its polydispersity were $M_n = 34\,300$ and $M_w/M_n = 1.93$, respectively. The polymerization induced by $MoOCl_4$−*n*-Bu_4Sn−EtOH in toluene was also performed at 30 °C for 24 h to quantitatively produce polymer with $M_n = 34\,000$ and $M_w/M_n = 1.35$, respectively. Both polymers were dark-brown powders, and the Mo-produced polymer was soluble in ordinary solvents like chloroform, tetrahydrofuran (THF), and toluene. The Rh-produced produced polymer was partly insoluble in chloroform and toluene but soluble in THF.

Raman Spectra. Figure 1 shows the laser Raman spectra of the Rh- and Mo-produced polymers using Ar^+ laser at 514.5 nm. The peak at 1518 cm^{-1} in the Rh-produced polymer was assigned to the stretching vibration of the C=C bond in the cis isomer, although the peak is overlapped with that of the phenyl ring.[4c,d] The peak at 1487 cm^{-1} was observed for both the Rh- and Mo-produced polymers. This indicates formation of fairly long trans conjugation lengths in both polymers; this peak was observed in the aromatic polyacetylenes, e.g., poly(*o*-methoxy- and *o*-ethoxy(phenylacetylene))s with fairly long trans conjugation lengths, which were created by compression of the initially formed by polymers having cis−transoid sequences.[1−3] This assignment is supported by the fact that such peaks are never observed in the cis−transoid of *o*- and *p*-methoxy(phenylacetylene)s initiated by $[Rh(NBD)Cl]_2$ in triethylamine (TEA) solvent.[1−2,4] The peak at 1210 cm^{-1} was ascribed to the stretching vibration of the C−C bond in the polyacetylene,[2] coupled with that of C−H in the C=C−H group of the Rh-produced and Mo-produced polymers, because the same peak was also reported in both nonsubstituted *trans*-polyacetylene[12] and compressed poly(*o*-methoxy(phenylacetylene)).[1] The peak at 965 cm^{-1} in the Rh-produced polymer can also be assigned to the stretching vibration of the C−H bond in the cis−transoid sequences as we previously reported.[1−2,4]

The trans conjugation sequence length is approximately $n = 22$ based on the 1487 cm^{-1} peak and Shirakawa chart.[12] Thus, all the peaks in the Raman spectra of the Rh-produced polymer, except those at 1518 and 1344 cm^{-1} corresponding to the cis isomer overlapped with phenyl rings, are similar to those of the nonsubstituted *trans*-polyacetylenes synthesized by Shirakawa et al.[12] This clearly indicates that the Rh polymerization of the *o*TFMPA monomer results in a conformational change from the cis to the trans form without compression and/or heat treatment at higher temperatures. Of course, the resulting trans sequences may be incorporated in the original cis−transoid sequences during the polymerization and/or on standing of the solution. The remaining cis sequences in the Rh-produced polymer detected by the peak at 965 cm^{-1} due to the cis C−H bond.

The Raman spectrum of the Mo-produced polymer has four clear peaks at 1518, 1487, 1344, and 1210 cm^{-1}; there is no peak at 965 cm^{-1}. This indicates that the Mo-produced polymer also has trans conjugated sequences; i.e., the Mo complex also functions as a catalyst for isomerization from the cis to the trans form during the polymerization in toluene and/or on standing of the solution as previously reported by Masuda et al.[13] However, the intensity of the peak at 1210 cm^{-1} for the Rh-produced polymer is fairly small compared to that of the Mo-produced polymer, indicating that its trans content is lower. There is a fairly broad shoulder at ca. 1360−1400 cm^{-1} in the Mo-produced polymer. The peak at ca. 1340 cm^{-1} can be assigned to the stretching vibration of the cis main-chain C−C bonds coupled to the =C−C bond in the phenyl rings.[14] A broad peak at ca. 1340 cm^{-1} was not observed when poly(α-naphthylacetylene) was stereoregularly prepared using the Rh initiator but could be observed when prepared with $MoCl_5$.[15] This may be due to irregular disordered, head-to-head and/or tail-to-tail sequences incorporated in the main chain of the Mo-produced polymer.[16] Incorporation of such disordered trans sequences in the main chain may strongly change physicochemical properties; e.g., as mentioned in the Experimental Section, the Mo-produced polymer is much more soluble than the Rh-produced polymer in THF or $CHCl_3$.

Solution UV Spectra. UV spectra of the Rh-produced and Mo-produced polymers in chloroform solutions are shown in Figure 2. The cis isomer and trans isomer are assumed to have the same absorption coefficient in order to semiquantitatively compare their absorption intensities. The peaks at ca. 450 nm in both polymers are ascribed to π−π* transition bands of the

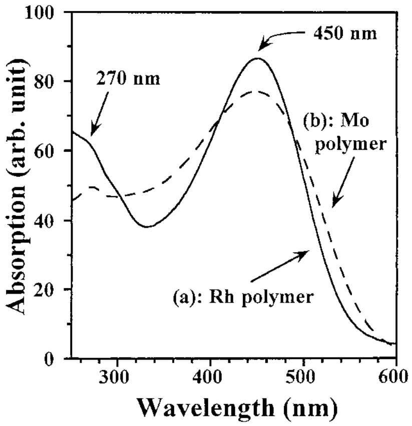


Figure 2. UV spectra of PoTFMPA polymers observed in $CHCl_3$ solution at room temperature: (a) $[Rh(NBD)Cl]_2$ initiator; (b) $MoOCl_4-n\text{-}Bu_4Sn-EtOH$ initiator.

trans sequences,[2,4] although the half-width of the absorption bands in the Rh-produced polymer is narrower than that of the Mo-produced polymer. This suggests that the Rh-produced polymer has less irregular trans structure, and inversely, the Mo-produced polymer may involve irregular trans sequences to some extent in the main chain. An absorption at a lower wavelength region at ca. 270 nm in the Rh-produced polymer is assigned to a part of the chromophore of the (*o*-trifluoromethyl)phenyl moiety of the polymer as previously reported for the poly(*o*-methoxy(phenylacetylene)).[1] However, the peak intensity in the Rh-produced polymer is larger than in the Mo-produced polymer. This also suggests that the (*o*-trifluoromethyl)phenyl moiety works as an independent chromophore from the main-chain chromophores in the Rh-produced polymer. In other words, the (*o*-trifluoromethyl)phenyl group of the Rh-produced polymer is twisted out of the planar trans conjugated sequences. The side chain chromophore in the Mo-produced polymer can be cooperated with the main-chain trans conjugation sequences where disorder trans sequences are already formed to relax the steric hindrance between the neighboring phenyl groups. Spectra similar to the UV spectrum observed in the Rh-produced polymer were also observed for the poly(*o*- and *p*-methoxy(phenylacetylene))s[1-4] and poly(*o*-ethoxy(phenylacetylene)) polymer[2] when they were compressed.

Diffuse Reflective UV Spectra. Diffuse reflective UV (DRUV) spectra of these polymers were also measured in order to determine the trans conjugation lengths of the Rh-produced and Mo-produced polymers in the solid state as shown in Figure 3. The absorption maximum in the Mo polymer is observed at ca. 450 nm and that of the Rh-produced polymer at ca. 480 nm. This is explained by the formation of a more regular trans planar sequence called ordered trans in the Rh-produced polymer and, inversely, formation of irregular trans units, e.g., head-to-head and/or tail-to-tail, disordered trans in the Mo-produced polymer, suggesting that the latter irregular sequence disturbs the trans π-conjugation in the main chain because of an effectively shorter conjugation length; i.e., the longer the trans conjugation length, the larger the absorption maximum shifts to a longer wavelength.

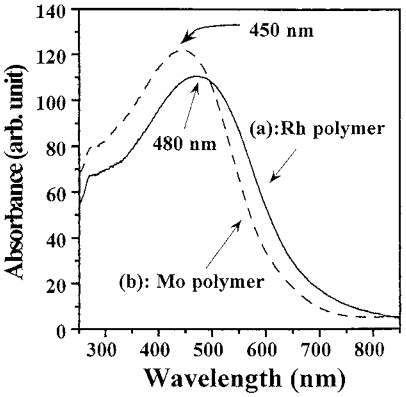


Figure 3. Diffuse reflective UV spectra of PoTFMPA polymers observed at room temperature: (a) $[Rh(NBD)Cl]_2$ initiator; (b) $MoOCl_4-n\text{-}Bu_4Sn-EtOH$ initiator.

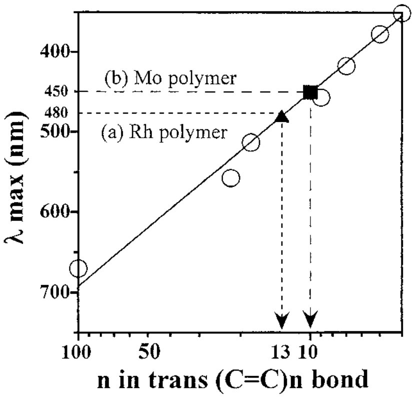


Figure 4. Shirakawa's relationship with respect to the sequence length number of trans C=C bonds for UV absorption maximum in the trans polyenes: (a) $[Rh(NBD)Cl]_2$ initiator; (b) $MoOCl_4-n\text{-}Bu_4Sn-EtOH$ initiator.

It is noteworthy, however, that the longer wave shift of ca. 30 nm in the solid state means formation of more regular and extended π-conjugation sequences called *ordered trans structures* unlike *relaxed (or distorted) trans structures* in solution. The trans conjugation length of the solid state is estimated as ca. $n = 10$ and 13 for Mo-produced and Rh-produced polymers, respectively, using the so-called Shirakawa relationship between the length, *n*, in trans polyenes, $(C{=}C)_n$, and UV absorption maxima.[12] It is necessary to explain why the trans sequences lengths of both polymers estimated by the above Raman data and this DRUV data are not the same. In our resonance Raman method the Ar^+ laser wavelength, 514.5 nm, was used to estimate the resulting trans sequence length. However, this value does not rule out the existence of various trans sequence distributions because the observed trans sequence lengths are appearantly compatible. It is possible to exact evaluatation of the trans sequences with $n = 10-13$ if a dye laser having 450 or 480 nm wavelength is used.

THG Coefficient. Previously, the third harmonic generation (THG) coefficients, $\chi^{(3)}$, of polyphenyacetylene (PPA)s prepared with the Rh and WCl_6 initiators were reported as ca. $(0.38 \pm 0.5) \times 10^{-12}$ and $(0.54 \pm 0.5) \times 10^{-12}$ esu, respectively,[9] using a fundamental wavelength, 1.907 μm, and $\chi^{(3)}$, 1.4×10^{-14} esu, of fused silica as the standard material. The third harmonic generation (THG) coefficients, $\chi^{(3)}$, of the Rh-produced and Mo-produced polymer films were also measured using fused silica as the reference material, ca. $1.7 \times 10^{-12} \pm 0.5$ and $3.0 \times 10^{-12} \pm 0.5$ esu, respectively, at a fundamental wavelength, 1.907 μm. The THG coefficient is considered to depend on the length of trans conjugation of the relevant polymer. The THG coefficients observed are almost equivalent to each other within experimental error, although the trans content in the Rh-produced

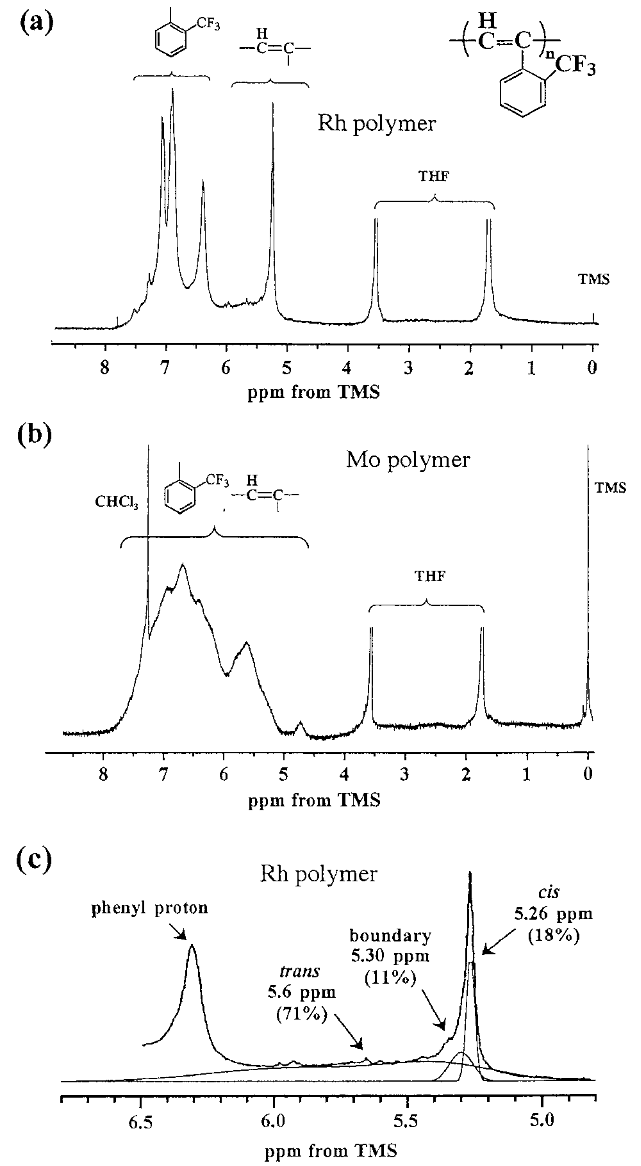


Figure 5. ^{1}H NMR spectra of P*o*TFMPA polymers observed in THF solutions which contain a small amount of chloroform-*d*, 99.8 atom %, with 1% v/v TMS at room temperature: (a) [Rh(NBD)Cl]$_2$ initiator; (b) MoOCl$_4$–n-Bu$_4$Sn–EtOH initiator; (c) expanded spectrum for [Rh(NBD)Cl]$_2$ initiator.

polymer is notably lower than in the Mo-produced polymer.

^{1}H NMR Spectra. Figure 5 shows the ^{1}H NMR spectra of the Rh- and Mo-produced polymers observed in THF-d_8 solution including CDCl$_3$ and TMS as the internal standards at 30 °C. The ^{1}H NMR spectrum (a) of the Rh-produced polymer features sharp line widths compared with that (b) of the Mo-produced polymer. In Figure 5a the peak at 5.26 ppm was assigned to that of =CH protons in the cis main chains; however, the sharp cis proton peak is superposed with an extremely broad proton peak ranging from 5.0 to 6.7 ppm. Such a broad peak has been ascribed to that of trans =C–H protons.[15a,16] The ratio of the relevant cis and trans isomers was determined by deconvoluting the range of the chemical shift in ca. 4.9–6.7 ppm using a Machintosh computer, i.e., the Kaleida Graph as shown in Figure 5c. The broad peak was interpreted by three components, i.e., cis ratio $\approx$18% centered at 5.26 ppm, trans ratio $\approx$71% centered at ca. 5.0–6.7 ppm, and a minor component $\approx$11% centered at ca. 5.30 ppm. The minor component may be attributed to the proton peak in the boundary regions connecting the cis and trans main chain sequences. Three sharp peaks observed between ca. 6.2 and 7.8 ppm were ascribed to those of the cis and/or trans aromatic protons in the Rh-produced polymer. It should be noted that in the Rh-produced polymer the =C–H proton peak observed at 5.26 ppm is a fairly higher magnetic field compared with around 5.4–5.6 ppm of ordinary poly(phenylacetylene)s, which value is similar to that of the PoMeOPA polymer.[1] This indicates that the (*o*-trifluoromethyl)phenyl moiety is fairly twisted out of the cis main chain plane, i.e., θ degree as depicted in Figure 7a. The plane of the (*o*-trifluoromethyl)phenyl moiety is fairly perpendicular to the cis C=C bond plane. Therefore, the cis =C–H protons are located spatially above the phenyl ring planes and are shielded by the phenyl ring current as depicted in Figure 7a. This explains why the cis =C–H protons are observed at higher magnetic field,[1] although the longer cis sequences are composed of helical structures as previously reported by us.[17]

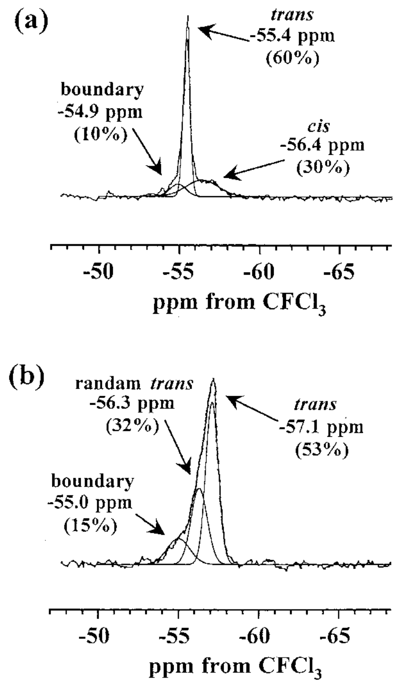


Figure 6. ^{19}F NMR spectra of PoTFMPA polymers observed in THF-d_8 including a small amount of C$_6$F$_6$ as the internal standards at room temperature: (a) [Rh(NBD)Cl]$_2$ initiator; (b) MoOCl$_4$–n-Bu$_4$Sn–EtOH initiator.

In the ^{1}H NMR spectra the cis peak of ordinary monosubstituted polyacetylenes involving trans isomers usually is an unsymmetrical line shape, indicating existence of boundary components to some extent. Therefore, the cis ratio has been precisely determined and might be overestimated by as much around 10–20%.

In the case of the Mo-produced polymer, such spectral assignment is extremely difficult due to the broad and complex spectra, ranging in ca. 4.5–8 ppm as shown in Figure 5b. The broad peak has been ascribed to that of trans =C–H protons.[15a,16] Because such a broad spectrum as shown in Figure 5c can be observed in the ^{1}H NMR spectrum of poly(phenylacetylene)s (PPAs) involving the trans form which was prepared with the Rh initiator.[4b] This also means that the Rh complex is the only preferred initiator to determine not only the precise chemical shifts but also the conformation of both

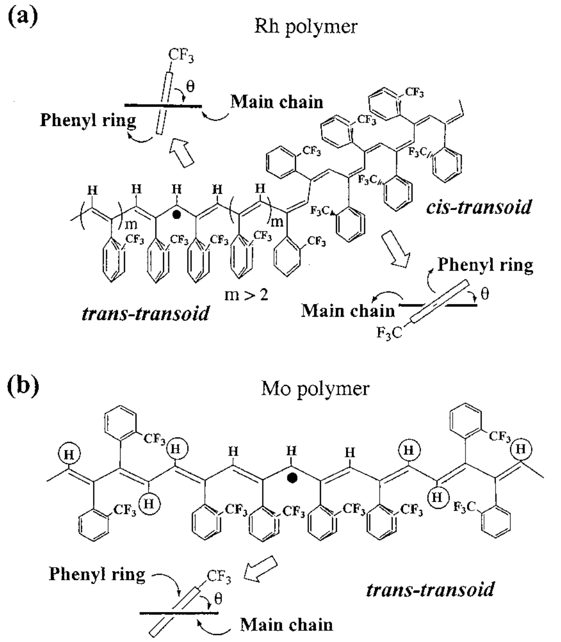


Figure 7. Proposed conformations of P*o*TFMPA polymers prepared with (a) $[Rh(NBD)Cl]_2$ initiator and (b) $MoOCl_4$−*n*-Bu_4Sn−EtOH initiator.

isomers; to the best of our knowledge, however, such detailed spectral assignments have not been reported to date.

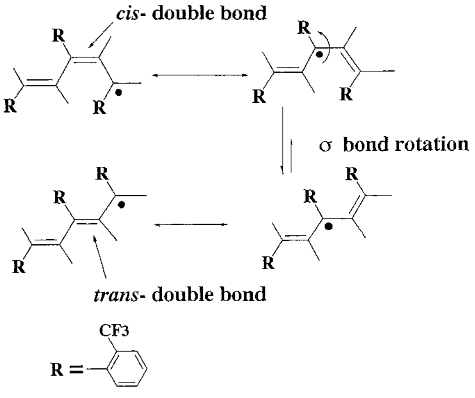
^{19}F NMR. Figure 6 shows the ^{19}F NMR spectra of the Rh-produced and Mo-produced polymers observed in THF-d_8 solutions at 30 °C using a hexafluorobenzene, C_6F_6, as an internal standard signal. A signal with a clear shoulder at the side of higher magnetic field at ca. −55.4 ppm was ascribed to the ^{19}F signal of the *o*-trifluoromethyl moiety in the phenyl ring of the Rh-produced polymer. Peak deconvolution was also performed to determine the ratios of the cis and trans isomers as shown in Figure 6a. The peaks at −56.4, −55.4, and −54.9 ppm are ascribable to those of the cis, trans, and boundary component, respectively, of which were estimated as ca. 30%, 60%, and 10%, respectively. In the trans sequences of the Rh-produced polymer, the trifluoropheny moieties are nearly perpendicular to the trans zigzag conjugated plane, i.e., $\theta \approx 90°$ because large steric hindrance is generated between the neighboring phenyl rings bearing the CF_3 groups as shown in Figure 7a. The CF_3 moieties are located spatially above the π electron clouds of the trans planar sequences which induces a fairly higher magnetic field shift of the CF_3 peak than that of a trifluoromethylbenzene as the reference compound.

In the cis sequences the CF_3 group is located spatially above the neighboring phenyl rings because of large steric hindrance as shown in Figure 7a. This specific conformation in the cis sequences may also induce notably higher magnetic field shift due to shielding effects of the phenyl rings compared with the trans sequences. The minor component estimated as $\approx$10% at −54.9 ppm may be assigned reasonably to the boundary fluorine peaks connecting the cis and trans sequences. The relaxed structure means that there is no large steric hindrances in the boundary region (see Figure 7a,b).

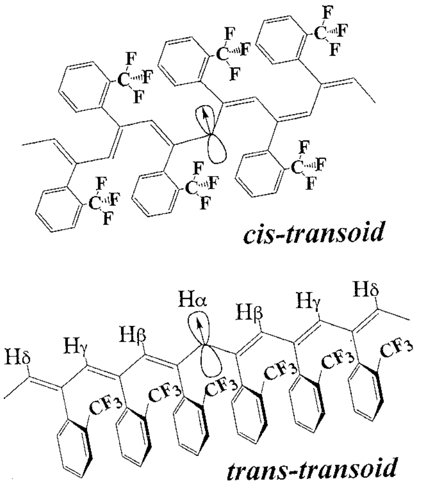
In the case of the Mo-produced polymer, a broader signal at ca. −57.1 ppm due to the CF_3 groups was also deconvoluted into three components; i.e., the peaks at −57.1, −56.3, and −55.0 ppm were ascribable to the sequences of trans, random trans, and boundary trans, respectively, whose ratios were estimated as 53%, 32%, and 15%, respectively, because the Mo-produced polymer was considered to have no cis isomers but disordered trans sequences as deduced by the Raman spectrum (see Figure 1b). It should be noted that the trans peak at −57.1 ppm in the Mo-produced polymer is a fairly higher magnetic field at ca. −1.7 ppm compared with −55.4 ppm of the Rh-produced polymer. The higher magnetic field shift may be induced by distortion of the main chain where the trifluoromethyl approaches the neighboring phenyl ring planes. The main chain distortion of the Mo-produced polymer may be evidenced by the fact that the absorption maximum of the UV spectrum of the Mo-produced polymer in solution is observed at rather shorter wavelength compared with that of the Rh-produced polymer, i.e., $\lambda_{max} = 480$ nm in the Rh-produced polymer and $\lambda_{max} = 450$ nm in the Mo-produced polymer. This distortion may be also proven by temperature dependence of the ESR line width. The peak at −56.3 ppm may be assigned to that of random trans sequences by which not only the π-conjugation but also the delocalization of the unpaired electrons, called π-radical or solitons, is disturbed to some extent. In the random trans and boundary trans sequences of the Mo-produced polymer there is no severe steric hindrance between the neighboring trifluorphenyl rings, because in the relaxed or disordered structures the trifluoromethylphenyl groups are placed in the plane of the trans C=C bonds as shown in Figure 7a,b. Therefore, the random trans and boundary trans peaks may be observed at lower magnetic regions, ca. −56.3 and −55.0 ppm, respectively, although the boundary peaks in both polymers were observed at nearly the same chemical shifts, suggesting the formation of similar boundary structures. Thus, the Mo-produced polymer is composed of *disordered trans sequences* called trans, random trans, and boundary trans which should induce wide distribution of the chemical shifts compared with regular trans of the Rh-produced polymer as suggested above. This explains why the ^{1}H and ^{19}F NMR spectra show much wider line width and complex chemical shifts as shown in Figures 5b and 6b, respectively. Thus, ^{1}H and ^{19}F NMR data clearly agreed with the Raman, solution, and solid UV data.

Conformation. In our previous paper[16] it was disclosed by a reliable spectroscopic method, a laser Raman spectrometer, that an aliphatic polyacetylene, poly(pentynoate), which was prepared with the Rh complex under mild conditions, does not have cis−cisoid (c−c) or trans−cisoid (t−c) forms but a cis−transoid form. In the cis−transoid (c−t) form the conjugation between the main chain and $-CH_2CH_2-COOR$ (R = alkyl) moiety as the side chain is completely decoupled with the ethylene moiety. Therefore, the conjugation length was correctly evaluated as n = ca. 2.5 in $(C{=}C)_n$ even in the cis form using the so-called Shirakawa relation.[12] This conjugation length clearly indicates the formation of the cis−transoid sequences. In the case of the trans−cisoid form two double bonds both take cis configuration so that conjugation between their bonds does not explain the observed Raman data even if the t−c form is thermodynamically favored.[16] Thus, the possibility for forming trans−cisoid (t−c) sequences is ruled out. It should be noted that not only the aliphatic cis−transoid polymer but also aromatic polyacetylenes prepared with

Scheme 2



Scheme 3



the Rh complex under mild conditions features an extremely sharp line width ^{1}H NMR spectrum in solution despite the very high molecular weight polymer together with very low concentration on the radical spins as immobile unpaired electrons.[1−6]

Table 1. ESR Parameters Observed in the Poly(*o*-trifluoro(phenylacetylene))s Prepared with the [Rh(NBD)Cl]$_2$ and MoOCl$_4$−*n*-Bu$_4$Sn−EtOH Initiators[a]

polymer	solvent	*g* value	ΔH_{msl}/G[b] rt	77 K	spins/g ($\times 10^{18}$)
Mo polymer	toluene	2.0027_7	10.7	12.0	2.04
Rh polymer	TEA	2.0028_2	9.2	11.8	2.25

[a] Polymers were prepared with the Rh complex in the presence of triethylamine at 30 °C for 48 h and Mo-based initiator in toluene at 30 °C for 24 h. [b] ΔH_{msl}: line width in gauss.

ESR. It should be noted that the trans−cisoid form may be generated in the cis−transoid sequences when the cis−transoid form isomerizes to trans−transoid form, i.e., rotational scission of the cis double bonds to give two radicals as biradicals (see Scheme 2).[1,11] The t−c sequences will be partly incorporated in the cis−transoid sequences as shown in Scheme 3. The resulting trans−cisoid form may isomerize to the trans−transoid sequences, i.e., the ordered trans sequences because of the thermodynamically less stable form as shown in Scheme 3.[18] Therefore, the trans−transoid form can stabilize the resulting unpaired electrons produced by the isomerization (see Schemes 2 and 3). It has also been demonstrated that in aromatic polyacetylenes the more mobile unpaired electrons can move along the trans−transoid conjugated sequences, showing motional narrowing in the line width of the ESR spectrum;[1−6] however, in less ordered trans sequences as well as the cis form such a large motional narrowing effect is not expected in the ESR line width. Thus, the ESR method can be used to determine whether the resulting trans sequences are regular or not at the molecular level. The ESR spectra of the Rh-produced and Mo-produced polymers were also measured carefully at room temperature and 77 K in order to deduce their geometrical structures. The observed ESR parameters are shown in Table 1. Interestingly, the Rh- and Mo-produced polymers have almost the same amount of radical spin concentration, i.e., (2.04−2.25) × 10^{18} spins/g. The radicals observed in the pristine polymers have been proven to be created when isomerization from the cis isomer to the trans isomer was induced by the rotational scissions of the cis C=C bonds during the polymerization and/or on standing of the solution even at room temperature.[1,3] It should be noted, however, that the spin concentrations of the Rh- and Mo-produced polymers are nearly the same as that of a nonsubstituted trans polyacetylene prepared with the so-called Ziegler−Natta catalyst[19] at higher temperatures. The spin concentration of the PoMeOPA polymer containing trans sequences obtained after compression also agreed with those of both polymers.[1,2] It is also noted that the ESR spectrum observed after the compression of the PoMeOPA polymer could be well simulated using the Lorentzian line shape, indicating motional narrowing of the resulting unpaired electrons in the regular trans zigzag conjugation sequences.[2,8] If the unpaired electrons called trans spins stabilized in the Rh-produced polymer move around along ca. 13 carbons, $m = 2$ in the regular and planar trans (see Scheme 3 and Figure 7a), they are the mobile unpaired electrons, called solitons, as depicted in Figure 7a,[1−4c,20−22] and the ESR spectral line widths clearly should show fairly large temperature dependency (see Table 1), even if the resulting Rh-produced polymer involves cis−transoid structures, ca. 30%. However, in the case of the Mo-produced polymer the temperature dependence is not large compared with that of the Rh-produced polymer, i.e., the temperature dependency in the line widths, ΔH_{msl}, was ca. 2.6 and 1.3 G in the Rh-produced and Mo-produced polymers, respectively. Such a difference in temperature dependency in the line widths clearly indicates that in the Mo-produced polymer the resulting trans planar sequences have neither regular structures nor more ordered structures compared with the Rh-produced polymer. Therefore, these ESR data allow us to conclude that the Rh-produced polymer has more *ordered trans sequences* which can stabilize the mobile unpaired electrons (solitons). Inversely in the Mo-produced polymer, the temperature dependences can be explained by the formation of the *disordered trans* sequences. Thus, these ESR data agreed clearly with other spectral data, e.g., laser Raman, ^{1}H and ^{16}F NMR, and DRUV as shown above.

Conclusion

Phenylacetylene bearing a bulky substituent, i.e., a trifluoromethyl group in the ortho position, *o*TFMPA monomer, was successfully polymerized using both a [Rh(NBD)Cl]$_2$ initiator in the presence of triethylamine at 30 °C to yield the trans−transoid and the so-called metathesis initiator, MoOCl$_4$−*n*-Bu$_4$Sn−EtOH, in the presence of toluene. The resulting Rh-produced and Mo-produced polymers were in detail characterized using laser Raman, solution and diffuse reflective UV, ^{1}H and ^{19}FNMR, and ESR methods. The Rh-produced polymer prepared with the Rh complex catalyst, which is known to give the corresponding cis−transoid polyacetylenes, bears regular trans−transoid sequences as the major structures with cis sequence to some extent when triethylamine is used as the polymerization solvent. The resulting Rh-produced polymer was proven to have regular head-to-head trans structures called *ordered trans sequences* in comparison with the Mo polymer in which head-to-head and/or tail-to-tail units as the irregular trans structure called *disordered trans sequences* are incorporated as the main chain sequences. On the basis of ESR, DRUV and solution UV, and Raman data, we concluded that the Rh-produced polymer produces conjugated trans chain lengths, $n = 13$ in the trans $(C{=}C)_n$ sequences, which can stabilize the mobile unpaired electrons. The resulting Rh-produced polymers are promising NLO materials which give similar $\chi^{(3)}$ value to that of the Mo-produced polymer bearing irregular trans−transoid conjugation sequences, although the cis sequence still remained, ca. 30%, in the Rh-produced polymer. These new findings with respect to the resulting trans sequences contribute to development of nonlinear optical (NLO), electrical conductive, and electroluminesence (EL) materials whose important physical properties are always correlated with the degree of π-conjugation length and its regularity involved in the polymers.

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