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Pressure-Induced Cis to Trans Isomerization of Poly(*o*-methoxyphenylacetylene) Polymerized by Rh Complex Catalyst. A Raman, X-ray, and ESR Study

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We have reported the highly stereoregular polymerizations of phenylacetylene (PA),[1] its homologues,[2] and alkyl propiolate[3] catalyzed by a Rh complex, i.e., [Rh(norbornadiene)Cl]$_2$, [Rh(NBD)Cl]$_2$, where an unusual organic base such as triethylamine (TEA) was used as the polymerization solvent, and cis–transoid polymers with a helical structure were formed selectively in high yields. Further, we revealed that the Rh catalysts quantitatively gave rise to an ultra-high-molecular-weight poly(phenylacetylene) (UHMW PPA), M_w *ca.* 4.30 × 10^6, which could be considered as a new polymer materials.[2] The effect of the organic bases was considered to function as the dissociator of the binuclear complex [Rh(NBD)Cl]$_2$ into the monomeric species which may be an important initiation species for this polymerization[2,4] as shown in Scheme 1. In addition, we found that the Rh complex initiated the living polymerization of *m*-chlorophenylacetylene where the molecular weight could be controlled precisely and a block polymer of AAABBB type with a cis–transoid form was also synthesized.[1]

Intrigued by these results, we performed the polymerization of *o*-methoxyphenylacetylene (OMPA) monomer[5] with a bulky ortho substituent using the active and stereospecific catalyst in such a strong amine. In the course of measurement of the resonance Raman (RR) spectra[6] of POMPA we noticed by chance that the POMPA polymer with a yellow color was changed to a dark red material when the polymer was compressed using the manufacturing machine for making a KBr disk of solid polymer. Finally we concluded that this change corresponded to the isomerization of POMPA bearing cis–transoid form to trans form. Therefore, we report in this paper the pressure–induced isomerization of *cis*-POMPA to *trans*-POMPA together with the detailed characterization of POMPA using RR, wide-angle X-ray scattering (WAXS), and ESR methods.

After the treatment of 7.0 × 10^{-1} mol of OMPA with 7.0 × 10^{-3} mol of [Rh(NBD)Cl]$_2$ in dried TEA (3 mL) at 30 °C for 24 h, POMPA was obtained in a fairly high yield, 70%, as a fine yellow powder which was relatively soluble in chloroform and tetrahydrofuran (THF) and insoluble in methanol.

No report on the polymerization of OMPA monomer including the pressure-induced cis–trans isomerization of poly(phenylacetylene) and its homologues has been published to data to the best of our knowledge, irrespective of the potentially important materials from the point of view not only of scientific but also of possible industrial interests, e.g., a model compound of a ferromagnetic polymer,[7] oxygen permeability,[8] and nonlinear optical properties.[9]

Gel permeation chromatography of the polymers using the solvent, THF, as eluent showed a molecular weight of 9.08 × 10^5.

The 400-MHz ^{1}H NMR spectra of the polymers observed in a CDCl$_3$ solution showed a singlet at 3.41 ppm for the CH$_3$ group, a singlet at 5.50 ppm for C=CH, and a multiplet at 6.15–6.90 ppm for the four phenyl protons. The intensity ratio of the C=CH and four phenyl protons was estimated to be 4:1. This indicates that the resulting polymer has no cyclohexadienyl moiety arising from an intramolecular cyclization which is included in the polymer of phenylacetylene catalyzed with WCl$_6$ catalyst.[10]

Scheme 1

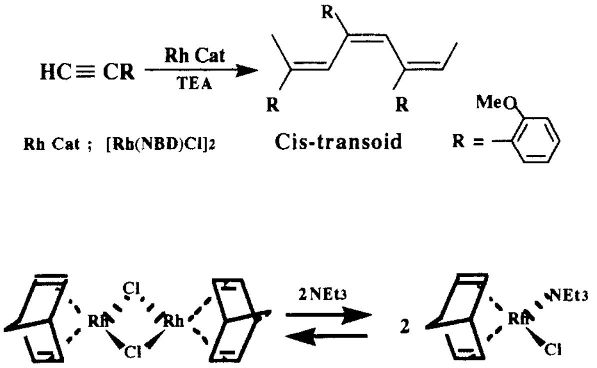

Figure 1 shows the resonance Raman (RR) spectra of POMPA observed in the light of an Ar$^+$ laser with magnitudes of the pressure imposed on the POMPA polymers. The peak at 1520 cm^{-1} observed before the compression is assigned to the stretching C=C band in the *cis*-polyacetylene although the peak is overlapped with that of the phenyl ring.[11] Interestingly, the compression increased the intensity of the peaks at 1485 and 1210 cm^{-1} and inversely decreased the intensity of the peak at 980 cm^{-1} which is assigned to the C–H deformation of the cis form. The peak at 1485 cm^{-1} with a shoulder at 1475 cm^{-1}

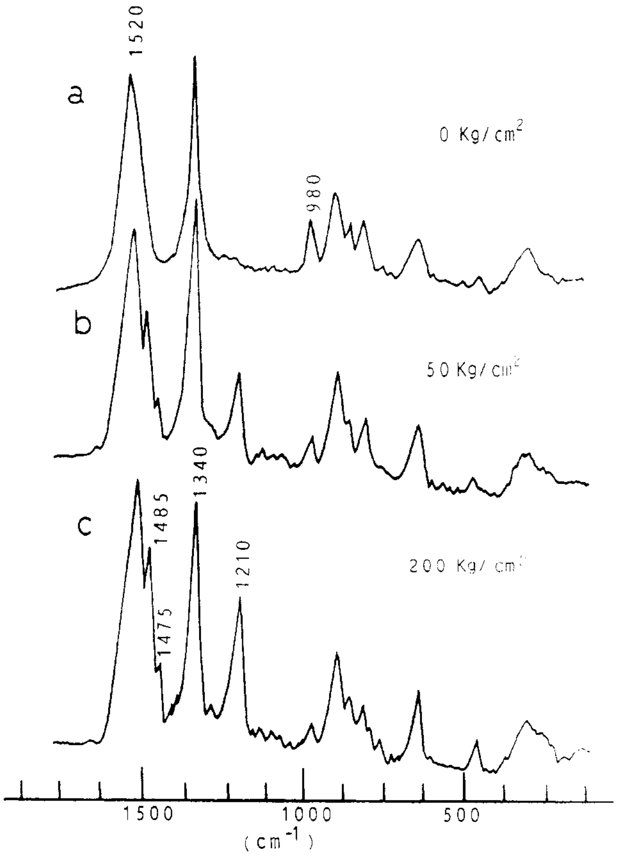

Figure 1. Resonance Raman spectra of POMPA polymers observed at room temperature: (a) before compression; (b) after compression at 50 kg/cm^2; (c) upon compression at 200 kg/cm^2.

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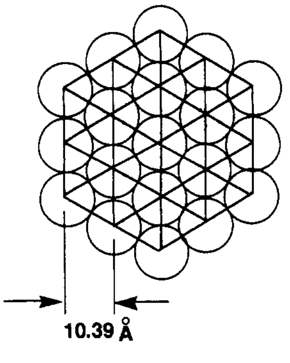
is attributed to that of the trans C=C bond with a fairly long conjugated length.[11,12] The peak at 1210 cm^{-1} is attributed to the vibrational band of the C–C bond in the trans chain, coupled with that of the C–H bond in the C=CH group. This peak was observed in poly(phenylacetylene) derivatives bearing a fairly long trans sequence which was obtained by γ-ray irradiation of a phenylacetylene derivative in the solid state.[12]

Thus the peaks of the RR spectra observed after the compression are characteristic of those of the *trans*-polyacetylenes synthesized by Shirakawa et al.,[13] supporting that the compression of POMPA may result in a conformational change from the cis to the trans form which may be incorporated in the original cis sequence. It should be stressed here that the increase in the intensity of the clear peaks observed at 1485 and 1210 cm^{-1} and the decrease in the intensity of the peak at 980 cm^{-1} were found to stop at a pressure of around 200 kg/cm^2 although a much higher pressure, i.e., 10 000 kg/cm^2, was imposed on the sample. Further support for the assignments derives from the fact that poly[*o*-(trimethylsilyl)phenylacetylene] (PTMSPA)[8,14] polymerized with WCl_6 which has a dark violet color and known as an oxygen-permeable material showed a RR spectrum quite similar to that of the POMPA compressed polymer (see Figure 1c) and the compression did not induce the RR spectral change appreciably even at 10 000 kg/cm^2. These facts support that PTMSPA polymerized with the so-called metathesis catalysts, WCl_6 or $MoCl_5$,[8,10,14] has been composed of a trans conjugated sequence as has been believed. This indicates that the polymer with the trans sequence form does not change to the cis form on compression due to thermodynamic preference.

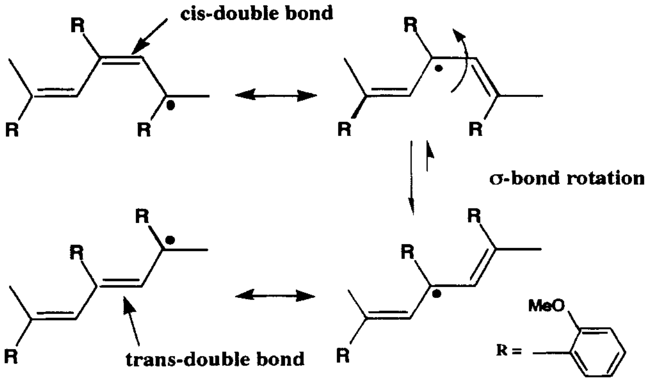
It seems that to the best of our knowledge mono- or disubstituted polyacetylenes with the complete trans conjugated chain has never been reported including the unequivocal characterization method. Therefore, the compression of polyacetylenes with substitutent groups may be quite important because one can prepare the trans conjugate polyacetylene at room temperature without heat treatment of the cis polymer at higher temperature.[10]

The wide-angle X-ray scattering (WAXS) of the pristine polymer exhibited a single crystalline peak at $2\theta = 8.5°$ ($d = 10.39$ Å) and a duffuse amorphous peak at 19.0° ($d = 4.67$ Å). The former peak was interpreted in terms of the (10$\bar{1}$0) reflection of a pseudohexagonal lattice with a rigid hexagonally packed chain. The crystal may have a hexagonal structure similar to cis–transoid with *ca.* a 3/1 screw as proposed by modified molecular mechanics calculations.[3] The appearance of the two peaks at 8.5° and at 19.0° shows that the POMPA polymer has a helical chain with an interchain distance of 10.39 Å, whose structure is shown below.



It has been reported to data that the poly(alkyl propiolate) polymerized by the same Rh complex catalyst[3] and poly(vinylcarbazole)[15] polymers have such hexagonal packing structures.

Scheme 2



It is interesting to note here that the compression of the yellow polymer at 200 kg/cm^2 induced a shift in the peaks at $2\theta = 8.5°$ ($d = 10.39$ Å) to a higher side angle, $2\theta = 9.0°$ ($d = 9.82$ Å), together with an increment in the line width. These changes observed in the WAXS spectra demonstrate that on compression the interchain distance in the polymer with the pseudohexagonal structure was shortened from 10.39 to 9.82 Å in such helical polymers. The increase in the line width observed may be related to the increase in the disorder in the amorphous POMPA polymer, reflecting the incorporation of the trans sequence into the original long cis sequence as mentioned above.

The ESR spectra[16] of POMPA before and after compression were examined in detail using JEOL FE 1XG (100-kHz field modulation). We found, interestingly, that compression of POMPA at room temperature resulted in an increase in the radical concentration, around 32 times, i.e., from 9.55×10^{17} to 2.86×10^{19} spins/g. Further, we found that the signals before and after compression can be well simulated as Lorentzian line shapes with line widths $\Delta H_{msl} = 10.5$ G ($g = 2.0028_0$) and 9.5 G ($g = 2.0023_5$), respectively, indicating that before compression the magnetic interaction between radical spins stabilized in the cis chain and oxygen with a large spin orbit coupling constant in the MeO group exists[17] and after compression the spin delocalizes in the formed trans sequence as has been demonstrated in the *trans*-polyacetylene.[18]

The radicals which are stabilized in the pristine polymer are considered to be created by the isomerization of the cis polymer to the trans polymer and/or the intracyclization during the polymerization and/or on standing in solution.[10,19]

The pressure-induced cis–trans isomerization can be explained by a radical mechanism because the radicals were detected before and after compression. Obviously, the compression enhanced the isomerization to the more stable trans form as shown in Scheme 2. The polyacetylene with high cis content may function as the origin of the radical spins necessary for forming an organo magnetic material because two radicals per one cis double bond may in principle be produced as a biradical when a π-bond in the cis C=C bond is scissioned as predicted in our previous report.[4]

In conclusion, we have succeeded in the stereoregular synthesis of a POMPA polymer with a helical chain in the presence of a new stereoregular polymerization catalyst, $[Rh(NBD)Cl]_2$, and have characterized the compressed POMPA where the conformational change, i.e., isomerization from cis to trans, was induced together with the generation of a number of radical spins.

We are currently studying the magnetic properties of the compressed polymer using a SQUID magnetometer and whether aromatic polyacetylenes other than the POMPA polymer also occur on pressure-induced isomerization to generate potential useful radical spins.

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