

Optically Active Poly(phenylacetylene) Film: Simultaneous Change of Color and Helical Structure

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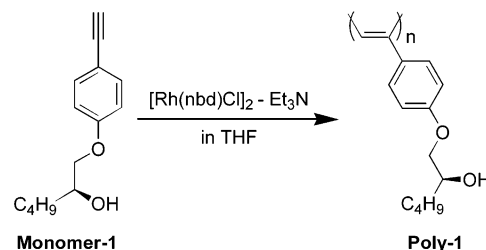
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Many conjugated polymers have been synthesized, and some optical properties both in solution and in the solid state have been studied, aiming for the application to the next-generation optical devices, sensing devices, nonlinear optical materials (NLO), electroluminescent (EL) materials, and so on. Poly(phenylacetylene) derivatives (PPAs) having all-*cis* main-chain structure were prepared with a Rh complex catalyst¹ and have attracted much attention for those helical structures. One-handed helical structural PPAs were obtained from the monomers with a chiral substituent² or from the achiral monomers with a Rh catalyst–chiral cocatalyst system.³ Helical conformation of *cis*-PPAs in solution can be changed by external conditions including temperature,⁴ pH,⁵ solvent polarity,⁶ and the addition of a chiral molecule⁷ because of their flexible main-chain structure in solution. As regards the solid *cis*-PPAs, colors of powdery poly(*p*-alkoxyphenylacetylene)s were reported to change by the external stimulation such as compression⁸ and contacting with organic solvents.⁹ For example, a yellow powder of *cis*-poly(phenylacetylene) having a 2-hydroxyethoxy group at the *para* position could be changed to red or black by contacting with organic solvent vapor.¹⁰ We recently reported about the color-changeable films of PPAs.¹¹ These color-changeable PPAs have a relatively long linear alkyl or alkoxy group and/or polar group such as OH group at the *para* position.

There have been some examples of helical conformational change of polymers in the solid state by thermodynamical phase transition. For instance, helical inversion occurred reversibly for optically active polypeptide¹² and polysilane.¹³ Helical conformational change in the solid state is expected to be applicable to practical use like a micromachine, a molecular motor, and optical devices, though the study of helical structural *cis*-PPAs in the solid state has scarcely been conducted. It is expected that helical structure of PPAs is changed by the molecular motion during the color change described above. We designed a novel optically active and color-changeable PPA (poly-1 in Scheme 1) having a chiral OH group which should form a hydrogen bond to affect the helical structure. The helical conformational change of this polymer in the film state was studied by circular dichroism (CD) spectroscopy.

The monomer-1 was prepared according to the literature.¹⁴ Polymerization was conducted with [Rh(norbornadiene)Cl]₂–Et₃N catalyst system to afford a red polymer in good yield. The polymer was only soluble in DMSO, DMF, and Et₂NH. The number-average molecular weight (*M*_n) of poly-1 was estimated to be 5.7×10^4 . The specific optical rotation ($[\alpha]_D$) of the polymer (*c* = 0.10 g/dL) at room temperature was +167.7 (DMF) and +612.0 (Et₂NH), while $[\alpha]_D$ of monomer was –10.2

Scheme 1. Chemical Structure of Color-Changeable Poly(phenylacetylene)



(*c* = 1.01 g/dL, DMF). In laser Raman spectroscopy, poly-1 showed peaks of the *cis* isomer at 1340 and 960 cm^{–1} due to C–C and C–H bond vibrations, respectively, while the characteristic peak of the *trans* isomer¹⁵ at 1200 cm^{–1} was not observed. These results indicated that poly-1 possesses a highly *cis*–*transoidal* structure.

It was reported that color and helical conformation of some PPAs in solution are dependent on its solvent.^{6,17} However, no significant change of color and absorption was observed for yellow poly-1 solution in DMF, DMSO, and Et₂NH (Figure 1). The first, second, and third Cotton effects in poly-1 solution were 441, 373, and 330 nm (negative, positive, and negative), respectively. These split-type spectral patterns were typical for helical PPAs.^{6,17,18} The monomer showed no CD band longer than 300 nm, suggesting that the polymer main chain should take helical conformation with an excess of one-handedness. CD and absorption patterns of the yellow film prepared from Et₂NH solution were similar to those in solution, though the

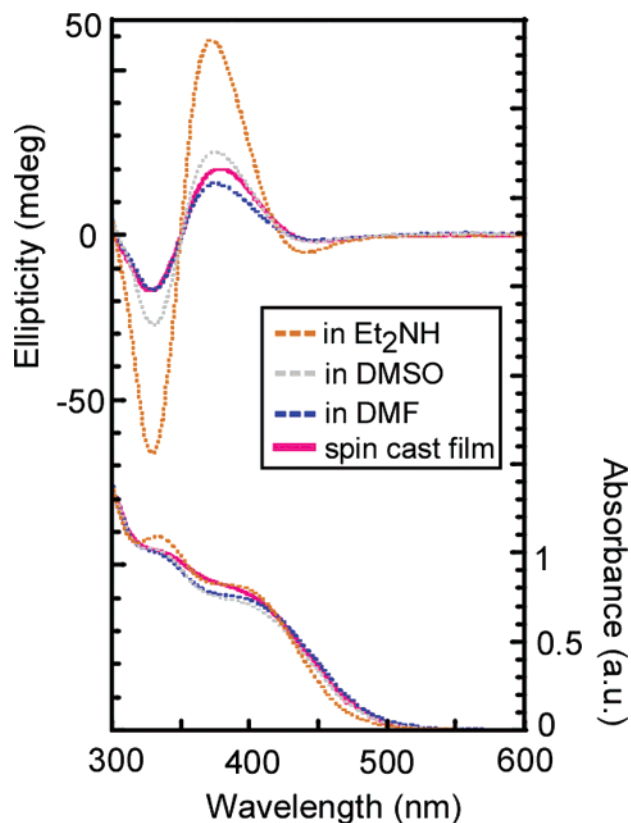


Figure 1. CD (top) and absorption (bottom) spectra of poly-1 in (a) Et₂NH, (b) DMF, (c) DMSO (*c* = 0.25 mM), and (d) a spin-cast film from Et₂NH solution.

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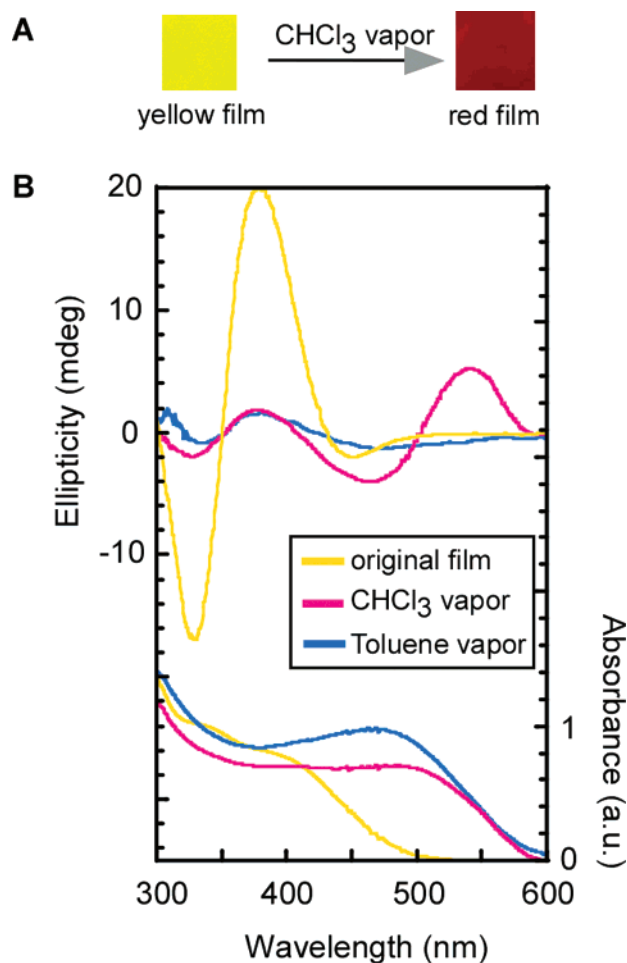


Figure 2. (A) Color change and (B) CD (top) and absorption (bottom) spectra of poly-1 spin-cast film before (yellow line) and after contacting with CHCl_3 (red line) and toluene (blue line) vapor at room temperature for 0.5 h.

intensity of CD was lower. Helical structure of poly-1 in the film was basically the same as in solution.

When the yellow poly-1 film was exposed to solvent vapor such as toluene, acetone, methanol, THF, and CHCl_3 at ordinary temperature and pressure, the film turned to red, and a novel absorption around 500 nm appeared. When *n*-hexane was used, this color change was not observed. The wavelength of the newly appeared absorption depended on the kind of solvent; namely, λ_{max} by polar (acetone, methanol, THF, and CHCl_3) and nonpolar (toluene) solvents was 490 and 469 nm, respectively. The ϵ_{max} increased with increasing exposure time, though the λ_{max} was not shifted. No color change was observed even after these films were dried under reduced pressure for several hours. It was confirmed by weight balance that solvent vapor was not absorbed into the film. Hence, this color change must be induced by change of higher order structure.

When this film was exposed to toluene vapor, the CD pattern was dramatically changed. The Cotton effects with a positive sign at 381 nm and a negative sign at 328 nm were remarkably reduced. Interestingly, when polar solvent vapor including acetone, methanol, and THF was used, not only the reduction of the original Cotton effect but also the appearance of a novel positive Cotton effect at 550 nm was observed. During these changes, no shift of the original Cotton effect was observed. Such a change of CD pattern was not observed by solvent vapor such as *n*-hexane, which induced no color change. These results indicate that the helical conformational change greatly depends

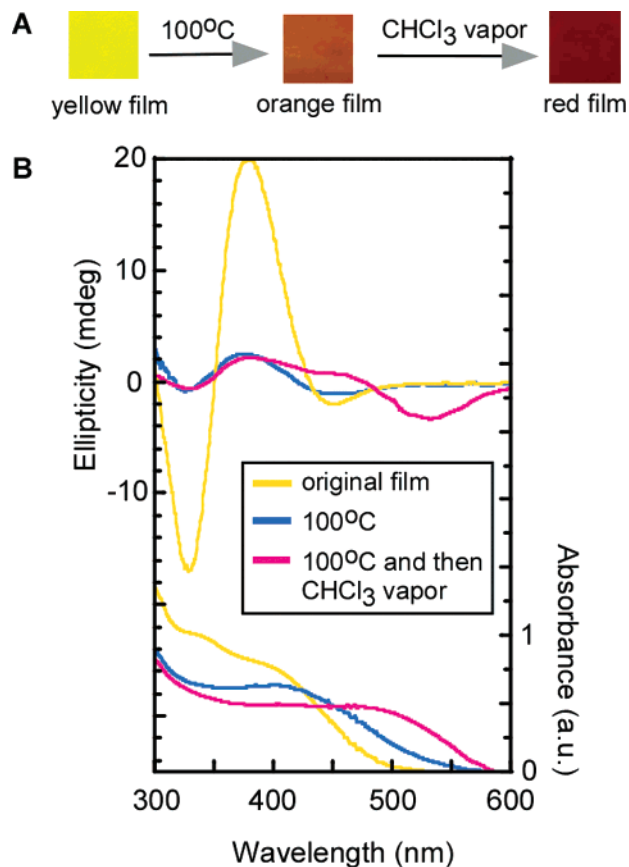


Figure 3. (A) Color change and (B) CD (top) and absorption (bottom) spectra of poly-1 spin-cast film before (yellow line) and after heating at 100 °C for 3 min (red line), followed by contacting with CHCl_3 vapor at room temperature for 0.5 h (blue line).

on the kind of solvent. The novel CD signal in the longer wavelength region does not appear in color-changeable helical PPAs in solution.^{4b,6} As far as we know, this type of color and helical conformational change induced by solvent vapor has not been reported.

In some PPAs, color and helical structure in solution are reversibly changed by temperature,^{4,6} though the change in the film state has never been reported. As a result of CD and absorption measurement of poly-1 in Et_2NH , a reversible change was observed according to the temperature. When the yellow poly-1 film was heated at 100 °C for 3 min, the color of the film turned to orange and novel absorption appeared around 450 nm (Figure 3). This change in the film state was not reversible upon cooling to room temperature.

The wavelength of the newly appeared absorption was shorter than that by solvent vapor. The intensity of the CD signal around 450 nm decreased exceedingly by heating, though the CD signal around 500–600 nm which appeared by solvent vapor was not observed. These results indicate that the conjugation and helical structure could be changed even in the film state by thermal treatment. When the film of poly-1 was heated at 100 °C for 3 min and then exposed to polar organic solvent vapor like acetone, methanol, THF, and CHCl_3 at room temperature for 0.5 h, the preheated orange film turned to red. In the CD spectrum of this film, a novel Cotton effect around 550 nm appeared. Interestingly, this Cotton effect was negative and opposite to that of the film exposed to solvent vapor without thermal pretreatment. When nonpolar toluene vapor was used, however, no Cotton effect around 550 nm was observed. Thus, this novel helical structure was only formed by polar solvent vapor. The original Cotton effect around 450 nm was not

changed by the exposure and was similar to that induced by solvent vapor without thermal pretreatment, though the screw sense of the novel Cotton effect was opposite. This indicates that the novel helical structure should be formed separately from the original helical structure probably by self-organization. These changes of color and helical conformation of poly-1 film were not due to *cis-trans* isomerization because the polymer backbone remained *all-cis* structure even after solvent and/or thermal treatment, which was confirmed by laser Raman spectroscopy. In addition, when poly-1 films after solvent and/or thermal treatment were dissolved in Et₂NH, color and helical conformation of the polymer returned to the original. This result also suggested that these changes of color and helical conformation should not be due to *cis-trans* isomerization. The reason why the Cotton effect is inverted by thermal preheating is not clear at present, but it can be considered that some phase transition at 71–76 °C observed in DSC may concern this phenomenon. A detailed study about the mechanisms of these changes is now in progress.

As described above, the color of the yellow poly-1 film was changed to red or orange by contacting with organic solvent vapor or by heating. Poly-1 film had one-handed helical structure which was almost collapsed by contacting with organic solvent vapor while novel helical structure was formed to cause the Cotton effect in the longer wavelength region. Moreover, screw sense of the novel helix was inverted by preheating before contacting with solvent vapor, though the screw sense of the original helix remained. Thus, color and helical structure of poly-1 were simultaneously changed in the film state by simple solvent and/or thermal treatment.

Supporting Information Available: Experimental procedures for synthesis and analytical data of polymer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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