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Thermal isomerization of *cis*-poly(phenylacetylene). Scission of polymer main-chain and formation of 1,3,5-triphenylbenzene as a pyrolysis product

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After *cis*-poly(phenylacetylene)s (*cis*-PPAs) were heated at 180°C for 1 h, the M_ns decreased from 5000–53 000 to 2000–2600, 1,3,5-TPB corresponding to the cyclic trimer of phenylacetylene was formed, and the yields of the annealed PPA and 1,3,5-triphenylbenzene (1,3,5-TPB) did not significantly vary. A peak at 280 nm due to the phenyl ring and broad band up to 600 nm due to the π–π* transition of the main-chain were observed in the u.v./vis. spectrum of *cis*-PPA. On the other hand, the absorption due to the conjugated main-chain disappeared for annealed PPA, though the phenyl group absorption was detected. The disappearance of the main-chain absorption can be explained by deflection of the main-chain. Copyright © 1996 Elsevier Science Ltd.

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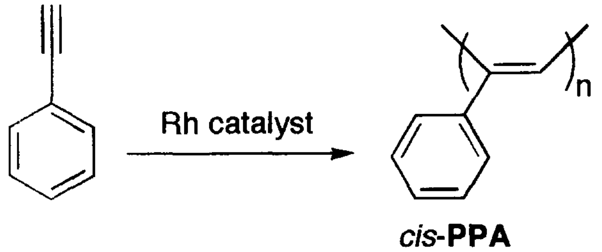
The thermal property of substituted polyacetylene, especially the *cis–trans* isomerization of the main-chain, is interesting in that the geometric structure is expected to affect the conductivity and other properties, for instance, the second harmonic generation and magnetic property[1–4]. Among the substituted polyacetylenes, poly(phenylacetylene) (PPA) has been studied in terms of its synthesis, characterization, electric property, and application[5,6]. Percec *et al.* reported that the cycloaromatization and scission of the polymer chain were observed during the thermal treatment of PPA prepared using metathesis catalysts, even with insufficient characterization of the polymers before and after heating[7,8]. Since Furlani *et al.* found that the Rh complex is an excellent catalyst for the polymerization of substituted acetylene[9], various acetylene monomers have been designed and polymerized for synthesizing polyacetylenes with specific properties[10–12]. Recently, Noyori *et al.* reported that a novel Rh complex, $Rh(C{\equiv}C{-}C_6H_5)(nbd)[(Ph_3)_3P]_2$ (nbd = 2,5-norbornadiene), performed as a catalyst for the living polymerization of phenylacetylene to produce the highly steroregular PPA, i.e., *cis*-PPA[13,14]. Therefore, using *cis*-PPA, the thermal *cis–trans* isomerization mechanism of substituted polyacetylene is expected to be clarified.

Here we report the characterization of PPA prepared using the Rh catalyst before and after thermal treatment and additionally the formation of the cyclic trimer of phenylacetylene as a pyrolysis product. Moreover, we estimated the main-chain structure of the annealed PPA based on the u.v. spectrum and semi-empirical molecular orbital calculations (CNDO/S)[15].



For the d.s.c. and t.g.a. measurements, the exothermic peaks at 170 and 212°C were observed and no weight loss appeared up to ca. 260°C, therefore, PPA sealed in a glass tube under N_2 gas was heated at 180°C. The colour change from orange to glassy dark-red was observed. After 1 h, the polymer sample was dissolved in chloroform and then poured into *n*-hexane to yield a yellow polymer (annealed PPA). The filtrate was evaporated and the residue was purified by column chromatography on alumina. After recrystallization from methanol, the obtained white needle crystals had a *mz* of 306 corresponding to three times the value of phenylacetylene. The ^1H and ^{13}C n.m.r. spectra and melting point of the isolated compound were identical with those of 1,3,5-triphenylbenzene (1,3,5-TPB), i.e., the cyclic trimer of phenylacetylene.

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Table 1 Thermal treatment of *cis*-PPA at 180°C under N_2 gas for 1 h

cis-PPA	Annealed PPA[b]		1,3,5-TPB[c]
M_n (M_w/M_n)[a]	Yield (%)	M_n (M_w/M_n)[a]	yield (%)
5000 (1.62)	47.1	2000 (1.35)	21.1
19 000 (2.56)	38.7	2300 (1.32)	23.2
25 000 (1.76)	42.3	2500 (1.43)	24.5
53 000 (4.11)	46.0	2600 (1.38)	20.9

[a] Determined by g.p.c. in $CHCl_3$ using polystyrene as standard
[b] *n*-Hexane-insoluble polymer
[c] 1,3,5-Triphenylbenzene, *n*-hexane-soluble part purified by column chromatography on alumina in toluene

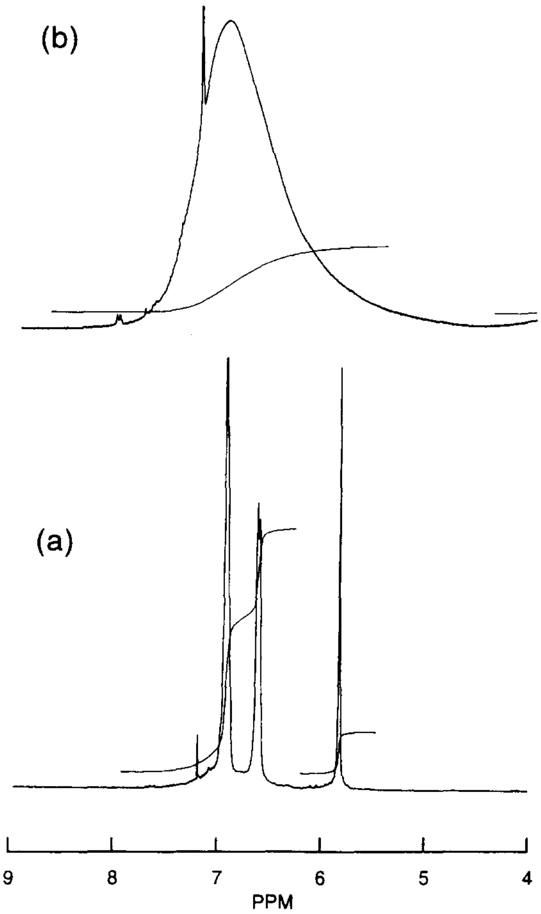

Figure 1 ^1H n.m.r. spectra of *cis*-PPA (a) and annealed PPA (b) in $CDCl_3$

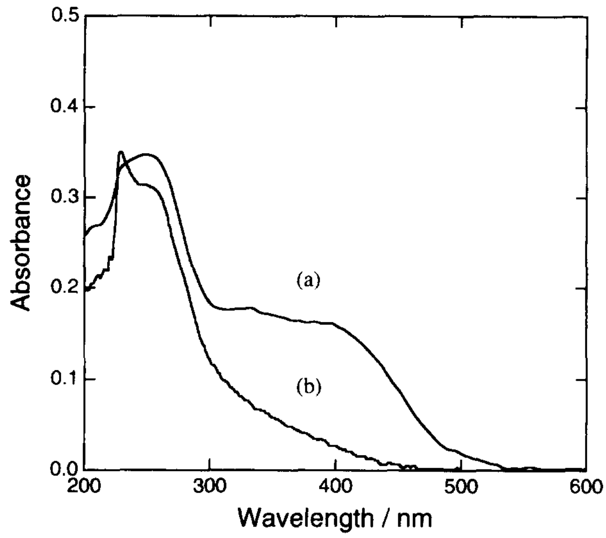

Figure 2 U.v./vis. spectra of *cis*-PPA (a) and annealed PPA (b) in $CHCl_3$

Table 1 lists the results of the thermal treatment of *cis*-PPA synthesized using $Rh(C{\equiv}C{-}C_6H_5)(nbd)[(PH_3)_3P]_2$[13]. Even though *cis*-PPAs with various number-average molecular weights (M_n) were used, the yields for annealed PPA and 1,3,5-TPB did not significantly vary, i.e., from 38.7 to 47.1% for PPA and from 20.9 to 24.5% for 1,3,5-TPB. In addition, the M_ns decreased from 5000–53 000 to 2000–2600, and the molecular weight distribution (M_w/M_n; M_w, weight-average molecular weight) of the annealed PPAs were narrowed to 1.32–1.43, independent of the *cis*–PPA used. Although the weight loss of PPA was observed over ca. 260°C in the t.g.a. spectrum, the decrease in M_n due to the scission of the polymer main-chain occurred below ca. 260, i.e., at 180°C. Moreover, 1,3,5-TPB was only formed and the other cyclic trimers, 1,2,3-TPB and 1,2,4-TPB, were not observed, which indicates that the polymer backbone polymerized using the Rh catalyst consisted of head-to-tail bonding. For the *n*-hexane soluble part, the other compounds except for 1,3,5-TPB could not be characterized, because they were absorbed on alumina. This will be dealt with in a further study.

The sharp signal at 5.84 ppm due to the main-chain protons was observed, as shown in *Figure 1*, which were previously found in the PPAs prepared using various Rh complex catalysts. However, the extremely broad absorption at 4.6–8.2 ppm, which is expected to appear instead of the *cis*-proton after thermal isomerization, was observed. This was similar to the result of the ^{13}C n.m.r. spectra of PPA before and after thermal treatment. Therefore, the structural information for annealed PPA was insufficient. As shown in *Figure 2*, a peak at 280 nm due to the phenyl ring and broad band up to 600 nm due to the π–π^* transition of the main-chain were observed for the u.v./vis. spectrum of *cis*-PPA in $CHCl_3$. On the other hand, the absorption due to the conjugated main-chain disappeared for the annealed PPA, though the phenyl group absorption was detected. The disappearance of absorption due to the conjugated main-chain can be explained by the deflection of the main-chain, i.e. the internal rotation of the main chain around the single bonds[16,17]. The theoretical u.v./vis. spectrum might be estimated on the basis of a semi-empirical molecular orbital calculation using the CNDO/S hamiltonian. Assuming that the dihedral angle between two neighbouring double bonds is 10° and 70–110° for the *cis*- and *trans*-PPAs, respectively, the calculated spectra agreed with the observed ones. Thus, the disappearance of absorption due to the conjugated main-chain of the annealed PPA should be caused by the deflection of the main-chain, i.e., annealed PPA lost its coplanar nature of the conjugated double bonds.

In summary, after *cis*-PPA was heated at 180°C, the M_n decreased from 5000–53 000 to 2000–2600, 1,3,5-TPB corresponding to the cyclic trimer of phenylacetylene being formed, and the yields for annealed PPA and 1,3,5-TPB did not significantly vary. The remarkable decrease in the M_n before and after annealing together with the formation of the cyclic trimer means that pyrolysis randomly occurred at the polymer backbone.

Moreover, 1,3,5-TPB was only formed and the other cyclic trimers, i.e., 1,2,3-TPB and 1,2,4-TPB, were not observed, which indicates that the polymer backbone was polymerized using the Rh catalyst consisting of head-to-tail bonding. Further studies are underway to investigate the main-chain configuration of PPA before and after thermal treatment using a semi-empirical molecular orbital calculation method.

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