NOTES

Synthesis of Ultra-High-Molecular-Weight Aromatic Polyacetylenes with [Rh(norbornadiene)Cl]$_2$-Triethylamine and Solvent-Induced Crystallization of the Obtained Amorphous Polyacetylenes

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The recent interest in the conducting,[1] magnetic,[2] and nonlinear optical properties[3] of polyacetylene promoted us to develop a new catalyst for the preparation of a highly stereoregular polyphenylacetylene (PPA) and its homologues, which have not only an extremely high-molecular-weight (HMW) but also a rather narrow molecular weight distribution (MWD). So far the polymerization of the phenylacetylene (PA) monomer has been carried out by $(Bu_3P)_2NiCl_2$–$NaBH_4$,[4] $RhCl_2$–$LiBH_4$,[5] $Fe(acac)_3$–$AlH(i$-$Bu)_2$[6] and group VI (Mo, W) transition metal catalysts.[7]

Recently, it was also presented[8] that the modified rhodium catalyst, [Rh(cyclooctadiene)bipyridine]PF$_6$ served as a catalyst for the polymerization of the PA monomer in the presence of an inorganic base, NaOH as cocatalyst. However, we found[9a,b] that [Rh(norbornadiene)Cl]$_2$, [Rh(NBD)Cl]$_2$ also polymerizes efficiently the PA monomer to produce a PPA with rather high molecular weight, $M_w = 3 \times 10^5$ when triethylamine was used as solvent. In this communication we will report the first polymerization of PA and *p*-methylphenylacetylene (*p*-MePA) initiated with [Rh(NBD)Cl]$_2$-triethylamine catalyst, by which PPA having an extremely HMW, *i.e.*, the so called ultra-high-molecular-weight

(UHMW) PPA is formed, together with the solvent-induced crystallization of the obtained amorphous polymers with *cis*-transoidal structure.

EXPERIMENTAL

Materials

Phenylacetylene (Aldrich) was distilled prior to use and *p*-MePA was prepared according to the literature.[10] The catalyst, [Rh(NBD)Cl]$_2$ was employed as purchased and triethylamine (TEA) was dried with Na prior to use. Weight-average-molecular-weight, M_w of the polymer was determined by gel permeation chromatography on the base of a polystyrene calibration.

RESULTS AND DISCUSSION

The solvent effect other than ethanol, such as TEA and toluene was carefully examined in order to synthesize higher molecular weight aromatic polyacetylene in the presence of [Rh(NBD)Cl]$_2$ catalyst. Table I shows the solvent effect toward the molecular weights of the PPA and P(*p*-MePA) polymerized with the Rh complex catalyst. Among the three solvents triethylamine produced a PPA polymer in the

Table I. Polymerization of phenylacetylene and *p*-methylphenylacetylene initiated with [Rh(NBD)Cl]$_2$-triethylamine

Monomer	Solvent	Cat. conc.	Yield	Polymer: M_w
		mM	%	$M_w/10^4$
PA	Ethanol[b]	5.00	83.3	4.00
	Benzene[b]	5.00	78.9	2.50
	TEA[a]	5.00	100	102.2
	TEA[a]	1.00	100	139.0
	TEA[a]	0.50	100	164.7
	TEA[a]	0.05	27.0	286.6[c]
	TEA[a]	0.01	9.4	442.8[c]
p-MePA	Ethanol[b]	5.00	67.3	3.80[c]

[a] Polymerized at 30°C for 1 h.
[b] Polymerized at 30°C for 20 h.
[c] THF soluble part.
Monomer = 0.65 M, catalyst, [Rh(NBD)Cl]$_2$.

highest yield and molecular weight, M_w *ca.* 102.2×10^4, when the concentration of catalyst was 5 mM. Interestingly the M_w of the polymer obtained was found to progressively increase inversely proportional to the catalyst concentration, and reached the highest molecular weight, $M_w = 442.8 \times 10^4$, at the lowest concentration of catalyst, which was called Ultra-high-molecular-weight (UHMW) PPA. Here it should be noted that the molecular weight listed in Table I is that of a THF soluble part of PPA or P(*p*-MePA) polymer. Therefore the insoluble part of PPAs into THF may be composed of too high molecule weight polymer or cross-linked polymer. The formation of such a UHMW PPA indicates that triethylamine used serves as the useful cocatalyst to activate the Rh complex. This cocatalyst effect by triethylamine was confirmed by ¹H NMR data at the initiation stage in the polymerization,[11] where the amine acts as a promoter to dissociate the dimer catalyst, [Rh(NBD)Cl]$_2$ into the monomeric form as active initiation species shown below.

Dimer ⇌ 2 Monomeric form (TEA)
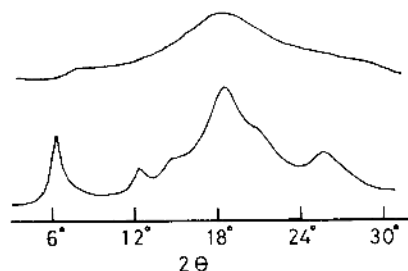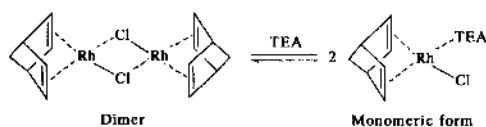
Figure 1. X-Ray diffractograms of poly(*p*-methylphenylacetylene) observed: a, pristine; b, after solvent treatment with toluene.

It is worthy to mention that the UHMW PPA has a fairly narrow MWD, $M_w/M_n = 3.42$—5.30, in spite of such a huge molecular weight. This may suggest that the polymerization initiated with [Rh(NBD)Cl$_2$]-triethylamine is living-like where the propagation species formed from the monomeric catalyst with the living property is formed as reported in our preceding paper.[9a]

To our best knowledge there is no report on the preparation of polyphenylacetylenes which have such a high molecular weights as shown in Table I up to date.

The pristine PPA and P(*p*-MePA) polymers, which were synthesized using triethylamine or ethanol under the condition shown in Table I, were composed of a very fine powder with bright yellow color. The average diameter of the polymer particles were measured as *ca.* 300—2000 Å by scanning electron microscope. It was found, interestingly, that the colour of the yellow powder was changed to red by the treatment with solvents such as toluene or chloroform.

Figure 1 shows X-ray diffractograms of the P(*p*-MePA) polymer observed before and after the solvent treatment. The yellow powder showed a halo with a peak centred at $2\theta = 19°$ as can be seen in Figure 1, indicating typical amorphous material. On the other hand, the red polymer which was insoluble into common solvents was a crystalline material because some of the peaks appeared at $2\theta = 6.6°$, $12.5°$,

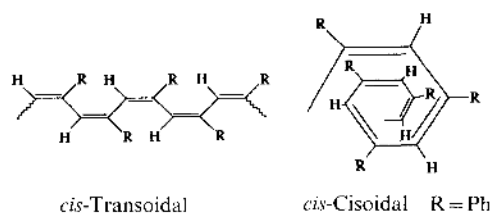*cis*-Transoidal   *cis*-Cisoidal   R = Ph

Figure 2. Structure of *cis*-transoidal and *cis*-cisoidal conformers of PPA.

19.0°, and 25.3°. The crystallinity of the red polymer was estimated as 75—80%. Based on this fact we concluded that the solvent treatment of the amorphous yellow polymer generated the crystalline polymer with red colour. We were also able to successfully observe the similar solvent induced crystallization in our PPA, although the crystallization was limited in the case of a polymer with the molecular weight of more than, $M_w = 1 \times 10^5$. In this case the crystallinity was more than 75%. A similar solvent-induced crystallization also was found in the cases of poly(*p*-chlorophenylacetylene) and poly(3,5-dimethyl-phenylacetylene).[12]

Simionescu, *et al.*[5] and Kern[6] showed that the *cis*-transoidal and *cis*-cisoidal PPA polymers polymerized by $RhCl_3$–$LiBH_4$ or Fe-$(acac)_3$–$AlH(i$-$Bu)_2$ catalyst can be characterized by IR method. In the IR spectrum of our yellow PPA two peaks at $740 \, cm^{-1}$ and $760 \, cm^{-1}$ with a shoulder at $770 \, cm^{-1}$ were observed. According to the literature the two peaks, $740 \, cm^{-1}$ and $760 \, cm^{-1}$ have been assigned to those of *cis*-transoidal polymer although the shoulder peaks at $770 \, cm^{-1}$ was not cited by them. We found that the $770 \, cm^{-1}$ signal disappeared when the yellow polymer was treated by the solvent like toluene or chloroform and then the peak intensity at $760 \, cm^{-1}$ did not changed. Inversely, the solvent treatment of the yellow polymer resulted in an increase of the peak intensity at $740 \, cm^{-1}$. These experimental facts show that the yellow pristine polymer synthesized by the Rh complex catalyst has *cis*-transoidal struc-

ture and the peak at $770 \, cm^{-1}$ can be assigned to that of the *cis*-transoidal structure and moreover the red polymer induced by the solvent treatment has the peak at $740 \, cm^{-1}$. Here it should be cited, however, that the peak observed at $760 \, cm^{-1}$ can not be ascribed to the peak of the *cis*-transoidal structure unlike the assignment of the literature.[5] We have carried out a deuteration of the vinyl proton in PPA in order to know whether or not our spectal assignment is reasonable. Consequently we found that there is no shift of the peak at $760 \, cm^{-1}$, indicating that the peak can not be assigned to that of the vinyl proton but to that of the phenyl ring in PPA.[13]

Simionescu *et al.*[6] also reported that the *cis*-cisoidal polymer of PPA is a crystalline one insoluble into common solvents with crystallinity of 50—60%. There properties seems to agree with those observed in our experiment as stated above. If the *cis*-cisoidal conformer in PPA has a helical and lod-like structure with a rather narrow intramolecular pitch distance in the polymer chain the helical polymer may be not solvated sufficiently by coordination of solvent molecules like toluene or chloroform as shown in our experiment. Therefore, it seems reasonable to conclude that our red crystalline polymer has the *cis*-cisoidal structure with such helical structure though a detailed X-analysis is needed to unequivocally prove that the red polymer has the *cis*-cisoidal structure.

Here, it seems worthwhile to mention that the PPA polymer with more than one million molecular weight only crystallized in hard mass with red color by the solvent treatment.

CONCLUSION

It was examined whether or not ultra-high-molecular-weight (UHMW) polyphenylacety-lene (PPA) was produced with rhodium based catalyst, $[Rh(NBD)Cl]_2$. We found that triethylamine (TEA) among solvents used worked as the quite useful cocatalyst of the rhodium complex to synthesize such UHMW

PPA in a fairy good yield except for the case of low concentration of the Rh catalyst where *cis*-transoidal PPA polymer selectivity is produced as a major product. Therefore, the $[Rh(NBD)Cl]_2$-TEA can be called a stereospecific polymerization catalyst of aromatic acetylene monomers like phenylacetylene. The *cis*-transoidal PPA synthesized by the Rh catalyst was amorphous powder with yellow color. The amorphous PPA was found to change into crystalline polymer with *cis*-cisoidal structure when the PPA polymer was poured into toluene or chloroform.

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