Highly Stereoregular Polymerization of Aromatic Acetylenes by [Rh(norbornadiene)Cl]₂ Catalyst

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(Communicated by Seizo OKAMURA, M. J. A., Sept. 12, 1995)

Abstract : The highly stereoregular polymerization of phenylacetylene and its homologues has been achieved by a Rh complex, [Rh(norbornadiene)Cl]₂ where an unusual organic base such as triethylamine was used as the polymerization solvent, and cis-transoid polymers were selectively obtained in very high yields. Further, the organic base was considered to work as the dissociator of the dimeric catalyst, [Rh(norbornadiene)Cl]₂ into the monomeric species responsible to the initiation species in this polymerization. The resulting poly(*o*-methoxyphenylacetylene) was found to be isomerized from cis to trans form when the polymer was compressed with pressure of 200 Kg/cm². The π -radical spins were found to be created by the ruptures of the C=C bonds in the cis form by the compression. We found that the broad signals in the ESR spectrum of the PPA polymer are created by storage at 77K. The appearance of the broad signals was interpreted in terms of an aggregation of the radical spins produced during and/or after the polymerization of PPA where internal fields with different energy levels between the spins are generated. The broad signals of the PPA polymer induced by cooling at 77 K is responsible to the magnetic spin ordering which was called "Time Induced Magnetic Spin Order (TIMSO)" phenomenon.

Key words : Polyacetylene; Rh complex; stereoregular polymerization; Cis-transoid; Cis-trans isomerization; radical; spin aggregation.

Introduction. In recent years, precise syntheses of polymers are under intensive research in various polymerization systems.¹⁾⁻⁵⁾ Although stereospecific polymerization provides the polymers having controlled steric structures, only a few examples of them are known up to date.³⁾ Especially the stereospecific living polymerization of polyphenylacetylene (PPA) derivatives are important.⁴⁾ Because they are considered as model compounds of ferromagnetic polymers,⁶⁾ non linear optical (NLO) materials,⁷⁾ and oxygen permeable materials⁸⁾ where the geometrical structure of main chain and molecular weight dispersity (MWD) have to be controlled in order to draw useful properties from them.

Intrigued by these studies we performed the polymerization of phenylacetylene and its homologues using the Rh complex catalyst, i.e. [Rh(norbornadiene)

Cl]₂, [Rh(NBD)Cl]₂ using various solvents. Consequently, we found that phenylacetylene and its homologues can be stereoregularly polymerized by the Rh complex in the presence of organic base such as triethylamine (TEA) or alcohol in very high yields even at room temperature where the polymers having cis-transoid structures are formed selectively.⁹⁾ Therefore, we report here that the highly stereoregular polymerizations of acetylene monomers with various phenyl groups are induced by the Rh complex catalyst together with detailed characterizations of the resulting polymers using ¹H NMR, laser Raman, electron spin resonance (ESR), and superconductive quantum interference device (SQUID) methods.

Experimental. Rhodium complex; [Rh(NBD)Cl]₂, [Rh(cyclooctadiene)Cl]₂, [Rh(COD)Cl]₂ and [Rh bis (cyclooctadiene)Cl]₂ (Aldrich) were used as received. Phenylacetylene (PA) (Aldrich) was distilled under reduced pressure, and *p*-methoxyphenylacetylene (*p*-MeOPA),¹⁰⁾ and *m*-chlorophenylacetylene were synthesized according to the literature¹⁰⁾ and purified by reduced pressure before use. The polymerization

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Scheme 1

solvent: triethylamine (TEA), tetrahydrofuran (THF), benzene, ethanol (EtOH), and 1,8-Diazabicyclo[5,4,0]undec-7-en, (DBU) (Aldrich) were purified and dried by standard methods.

Polymerizations were carried out under dry nitrogen at a monomer concentration of 0.65 M, a catalyst concentration of 0.005 M, and a temperature of 30°C for 24 hr. When triethylamine or ethanol was used as solvent, polymers precipitated as a yellow or orange fine powder during polymerization. The resulting polymer powder was filtered off, washed with hot methanol, and dried under reduced pressure at 10^{-3} Torr for 24 hr. For PA, *p*-Me-OPA and *m*-ClPA monomers except for *o*-MeOPA monomer the polymerizations proceed homogeneously in solvents such as benzene or THF. The polymerization was terminated by addition of methanol or acetic acid to the reaction solution. The product was purified by precipitation using THF and methanol, and dried under vacuum at 10^{-3} Torr for 24 hr.

^1H NMR spectra were recorded on Hitachi R-90 H (90 MHz) spectrometer in CDCl_3 solutions with TMS as internal standard. Laser Raman spectra were recorded on a JEOL 400 T triple laser Raman

spectrometer. The molecular weights were determined by gel permeation chromatography (GPC) calibrated with polystyrene standard and equipped with two TSK columns (G 2000H8 and G 5000H6, THF solvent) from TOSOH Ltd. ESR spectra were recorded on a JEOL FE1XG with 100 kHz field modulation at 77 K. Magnetic moments were measured on a Quantum Design MPMS-5S SQUID from 300 K to 10 K.

Results and discussion. Para-substituted phenylacetylenes were polymerized with $[\text{Rh}(\text{NBD})\text{Cl}]_2$ and $[\text{Rh}(\text{COD})\text{Cl}]_2$ catalysts in several solvents to know how the ligand in the Rh based catalyst affects the polymerization. Table I shows the polymerization results. It is clear that the reactivity of the monomers does not depend on the substituents on the phenyl ring but the polymerization solvent used, i.e., the organic base such as triethylamine or DBU enhanced the yields. Table I shows that $[\text{Rh}(\text{NBD})\text{Cl}]_2$ shows higher activity compared with $[\text{Rh}(\text{COD})\text{Cl}]_2$ catalyst although the $[\text{Rh} \text{ bis}(\text{cyclooctadiene})\text{Cl}]_2$ was completely deactive to these monomers.⁹⁾ It was found, interestingly, that *ortho*-methoxyphenylacetylene (OMPA) can be also polymerized with the Rh catalyst irrespective of the steric hindrance at the *ortho* position in the phenyl ring.¹¹⁾

Fig. 1 shows the ^1H NMR spectra of $[\text{Rh}(\text{NBD})\text{Cl}]_2$ observed in CDCl_3 solution at 30°C together with assignments of each peak. The peak at 3.9 ppm due to the olefinic proton in the bidentate Rh complex molecule was found to be splitted into two peaks, i.e., 3.3 and 4.1 ppm when triethylamine was added to the CDCl_3 solution although another peaks due to CH and CH_2 protons of the ligand molecule

Table I. Polymerizations of phenylacetylene and its homologues initiated by Rh complexes in various solvents^a

No.	Monomer	Catalyst	Solvent	Yield (%)	Mw $\times 10^4$	cis (mole%)
1	PA	$[\text{Rh}(\text{NBD})\text{Cl}]_2$	EtOH	83	4.0	100
2	PA	$[\text{Rh}(\text{COD})\text{Cl}]_2$	EtOH	54	7.6	100
3	PA	$[\text{Rh}(\text{NBD})\text{Cl}]_2$	TEA	100	3.5	100
4	PA	$[\text{Rh}(\text{NBD})\text{Cl}]_2$	TEA/ CHCl_3 ^b	9.4	442.0	100
5	<i>m</i> -ClPA	$[\text{Rh}(\text{NBD})\text{Cl}]_2$	TEA/ CHCl_3 ^c	100	50.0	100
6	<i>p</i> -MeOPA	$[\text{Rh}(\text{NBD})\text{Cl}]_2$	THF	81	10.0	34
7	<i>p</i> -MeOPA	$[\text{Rh}(\text{NBD})\text{Cl}]_2$	Benzene	59	0.9	83
8	<i>p</i> -MeOPA	$[\text{Rh}(\text{NBD})\text{Cl}]_2$	TEA	99	6.0	100
9	<i>o</i> -MeOPA	$[\text{Rh}(\text{NBD})\text{Cl}]_2$	DBU	95	— ^d	100
10	<i>o</i> -MeOPA	$[\text{Rh}(\text{NBD})\text{Cl}]_2$	TEA	70	9.1	100

a Polymerization time, 24 hr; Polymerization temperature, 30°C.

b TEA/ CHCl_3 =1/4 (mole ratio).

c $[\text{TEA}]/[\text{Cat}]=100/1$; $[\text{M}]=0.1 \text{ M}$; $[\text{M}]/[\text{Cat}]=1000/1$.

d Insoluble part in THF.

Fig. 1. ^1H NMR (90 MHz) spectra of: (a) $[\text{Rh}(\text{NBD})\text{Cl}]_2$ and (b) TEA solution containing $[\text{Rh}(\text{NBD})\text{Cl}]_2$ (the mole ratio of TEA/ $[\text{Rh}(\text{NBD})\text{Cl}]_2$ is 4/1) observed in CDCl_3 at 30°C .

were not splitted. This splitting can be explained in terms of dissociation of the dimer complex; $[\text{Rh}(\text{NBD})\text{Cl}]_2$ into a monomeric species bearing the triethylamine as a new ligand molecule in order to stabilize the monomeric species by the coordination as shown in Scheme I. Therefore the monomeric species generated by the addition of triethylamine is responsible to the initiation species in this polymerization with which the polyacetylene having high cis-transoid structure was selectively obtained in very high yields. It is also clear that poly(*o*-MeOPA) was obtained in fairly high yield when DBU as one of the strongest organic amine called a super base was used as the polymerization solvent. It is suggested, therefore, that the DBU amine also works as the strong dissociator of the dimer complex catalyst to produce the similar monomeric species as the case of the TEA.^{5),9)}

In our previous paper⁹⁾ it was spectroscopically evidenced that the formation of the monomeric species was induced in triethylamine or tetrahydrofuran solutions because the absorption band corresponding to the monomeric species was clearly observed at a wave length of 380 nm differ from that of the dimer band at 360 nm.

It is also clear that an ultra high molecular weight (UHMW) PPA polymer was obtained when chloroform including triethylamine, i.e., mixed solvent was used as the solvent (see No. 4). In previous paper¹²⁾ we have shown that *m*-chlorophenylacetylene (*m*-CIPA) takes place living like polymerization when the mixed solvent was used as shown in Table I (see No. 5). There is only a few cases of the polymerization system where the geometrical structure, molecular weight,

and molecular weight dispersity (MWD) of polymer can precisely be controlled at the same time.³⁾ This polymerization initiated by the Rh complex-amine catalyst is one of the rare cases.

The cis-transoid content in polyphenylacetylene (PPA) has been estimated using the ratio of the intensity of absorption bands at 760 cm^{-1} and 740 cm^{-1} in the IR spectrum of the polymer. In the case of monosubstituted polyacetylene such as poly(*o*-MeOPA) it was revealed, however, that their peak shapes in the spectral regions were too complicated to estimate the ratio.⁹⁾

Fig. 2 shows the ^1H NMR of P(*p*-MeOPA) synthesized with $[\text{Rh}(\text{NBD})\text{Cl}]_2$ catalyst in various solvents. It is clear that the highest spectral resolution with respect to the vinyl proton, $\text{HC}=\text{C}$ in the main chain was obtained when TEA or ethanol was used as the solvent. By comparison of the peak area at ca. 5.8 ppm due to the vinyl proton in the polymer and total peak area of the spectrum in the polymer the cis to trans ratio were estimated and the results are shown in Table I. Thus the Rh complex is an useful catalyst to give rise polyacetylene with the highest cis-transoid content when amine or alcohol was used as the solvent.

It was found, interestingly, that the cis content decreased with increase of the line width in the ^1H NMR spectrum when the reaction was carried out in THF or benzene solvent as shown in Fig. 2. The line broadening has been explained in terms of the incor-

Fig. 2. ^1H NMR (270 MHz) spectra of P(*p*-MeOPA) synthesized with $[\text{Rh}(\text{NBD})\text{Cl}]_2$ using (a) THF, (b) Benzene, and (c) TEA or ethanol.

poration of the trans extended sequence into the cis sequence which may induce stiffness of the main chains due to the planer trans double bond sequence and then statistically spreads the distribution of each chemical shift of the main chain protons in the polymer.

The line broadening may be correlated with a magnetic dipole-dipole interaction between the proton spin and radical spin.^{9),13),14)} The radical spin is created by the π -bond rupture of the cis C=C double bond during and/or after the polymerization through the cis to trans isomerization where the two π -radical spins as a biradical are created and called soliton when the radical was stabilized in the conjugated chain as shown in Scheme II. If the π -radical spins are stabilized in the trans conjugated chain the trans spins in the polymer can move around as mobile electrons.¹³⁾ On the other hand, the spins stabilized in the cis rich polymer do not move around in the chain due to the restricted conjugated chain sequence, indicating the formation of immobile electron as depicted in Scheme II. Therefore we can easily distinguish the geometrical forms, i.e., cis and trans forms using ESR method.¹³⁾ Because the line width of the ESR spectrum of the mobile electron in the trans rich polymer shows temperature dependence, i.e., motional or exchange narrowing of the line width as reported by us.¹³⁾ On the other hand, the line width of the unpaired electron in the spectrum of the cis rich polymer never exhibits the temperature dependence of the line width due to the immobile electron as depicted in Scheme II.

Fig. 3. Resonance Raman spectra of P(o-MeOPA) polymers observed at room temperature: (a) before compression: (b) after compression at 200 kg/cm².

Fig. 3 shows the laser Raman spectra the P(o-MeOMPA) polymer observed before and after compression, 200 kg/cm² using a KBr manufacturing machine at room temperature. Interestingly, we found that new peaks at 1475, 1485, and 1210 cm⁻¹ were generated but the peak intensity at 980 cm⁻¹ was decreased by the compression. The 1475 cm⁻¹ and 1485 cm⁻¹ peaks can be assigned to the fairly long trans conjugated sequences as reported in the non substituted polyacetylene.¹⁵⁾ The peak at 1210 cm⁻¹ also was assigned to the trans C-C bond coupled with the C-H bond. The lower wavelength peak at 980 cm⁻¹ was assigned to the cis C-H bond.¹⁵⁾ This spectral changes induced by the compression are well explained in terms of the pressure induced cis to trans isomerization.¹¹⁾ Thus the structural difference between cis and trans form of another aromatic acetylenes including the P(*p*-MeOPA) polymer was found to be clearly detected by the Raman spectroscopic method.^{13),14)} In previous paper¹¹⁾ we reported that the P(o-MeOPA) polymer has a pseudo-hexagonal packing structure so called a columnar phase and the diameter of the column was shortened by the compression from 10.39 Å to 9.82 Å. Thus the formation of the pseudo-hexagonal packing structure called columnar phase as a secondary structure is one of the most important feature of the polymers polymerized with the Rh complex as reported by us.^{11),16)}

Fig. 4 shows ESR spectra observed before and after standing at 77 K. The sharp signal with $G=2.0023_5$ and line width, $\Delta H_{msl}=9.5$ Gauss is

Fig. 4. Time dependences in the ESR spectra of PPA polymer observed at 77 K.

assigned to that of the π -radical due to a transition with $\Delta m = \pm 1$, which was produced by the C=C double bond rupture during and/or after the polymerization with Rh complex in the presence of triethylamine (TEA). We found, interestingly, that the very broad signal gradually appeared at lower field sides less than 3200 Gauss when the polymer was kept for prolonged period at 77 K although the signal intensity due to $\Delta m = \pm 1$ at ca. 3300 Gauss did not change. Further we found that the broad peaks changed the intensity, shape, and resonance position with storage time at 77 K as shown in Fig. 4. The broad signals may be ascribed to not inorganic radicals but aggregated π -radical spins, suggesting generation of internal magnetic fields between their spins. Because if the signals are due to inorganic impurity such as ferromagnetic materials, e.g., Fe then the signals never showed such a time dependence as observed in Fig. 4. Therefore we proposed that the broad signals observed at lower magnetic field are ascribed to the aggregated spins formed between the inter and/or intra polymer radical, e.g., the cis and/or trans spins as depicted in Scheme II although the torsion induced rupture of the C=C bonds in the cis or trans polymer may also be considered when the polymer was cooled to less than 77 K because of large thermal contractivity of the polymer. The time dependence in the ESR spectra observed at 77 K may be explained as followed; the polymer polymerized by Rh complex in poor solvent like triethylamine does not have energetically stable conformations at such a lower temperature but metastable ones which need structural relaxations to take a more energetically favorable conformation at such lower temperature. Therefore the polymer chain starts to change the conformations when the polymer was cooled down to 77 K in order to take the new conformation. Then the π -radicals stabilized in the polymer chain may magnetically interact each other

Fig. 5. Magnetic hysteresis curve of PPA polymer observed at 10 K together with the time dependence of magnetic moment observed using 10000 Gauss at 77 K.

between inter and/or intra molecular in order to form some aggregation states which have magnetically different energy levels. Thus the spin aggregations with different internal magnetic fields may show the broad signals at the lower fields.

The magnetic interaction between their spins was inspected using the SQUID instrument. Fig. 5 shows the magnetization curve observed at 10 K together with a figure of the time dependence of magnetization at 77 K. It was found, interestingly, that the PPA polymer shows a magnetic hysteresis curve, i.e., ferromagnetic behavior when the polymer was gradually cooled down to 10 K and kept for more than 12 hr at 10 K. However, the observed coercive field was small (less than 70 Oe). Interestingly we also found that the magnetic moment increased with storage time at 77 K although the magnetic component of the increase in the magnetic moment is not known at present. The increase in the moment means that the magnetic interaction between their spins is induced by the storage of the PPA polymer at 77 K, i.e., the storage of the polymer at 77 K generates the spin ordering states to increase the moment, in other words, time induced magnetic spin order (TIMSO) takes place to generate the ferromagnetic interaction between the radical spins in the PPA polymer which has not been reported before to the best of our knowledge. The more detailed study on the magnetic behavior of the polymer including other polymers is in progress in our laboratory.

Acknowledgment. We thank for the helpful discussion on the polymerization mechanism to Prof. T. Masuda at the Kyoto University. This work was

supported by a Grant-in-Aid for Developmental Scientific Research No. 07455368 in the Japanese Ministry of Education, Science and Culture.

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