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Structural differences of poly(α-ethynylnaphthalene)s obtained with $[Rh(norbornadiene)Cl]_2$ and WCl_6 catalysts: an electron spin resonance and Raman study

Masayoshi Tabata*, Makoto Namioka, Kazuaki Yokota and Hiroki Minakawa
Department of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060, Japan

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Poly(α-ethynylnaphthalene)s were prepared using $[Rh(norbornadiene)Cl]_2$ complex (a stereoregular polymerization catalyst) in triethylamine or alcohol, and WCl_6 (a metathesis catalyst) in toluene. ^1H nuclear magnetic resonance, electron spin resonance and laser Raman spectra of both polymers were measured in order to assign the geometrical structures with respect to the C=C bond in the main chain. Based on these spectral data, it was concluded that the clear spectra differences observed between the two polymers could be explained in terms of geometrical differences, i.e. the Rh complex and WCl_6 catalysts produce polyacetylenes involving *cis–cisoid* and *trans–transoid* sequences, respectively. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(α-ethynylnaphthalene); catalyst; structure)

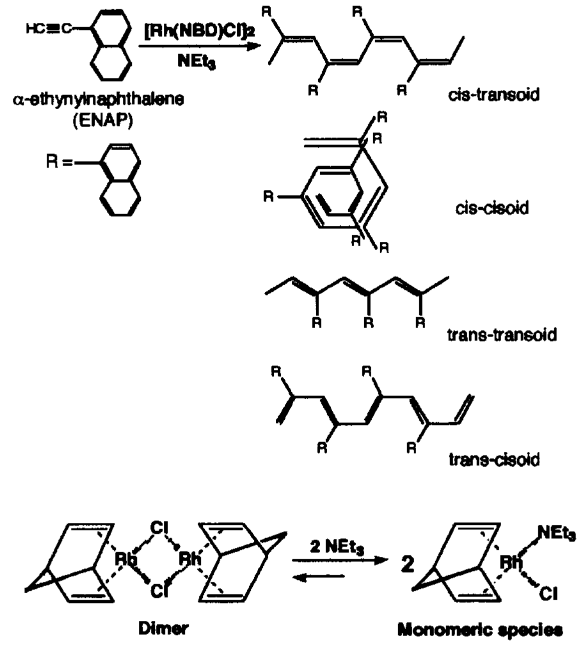
INTRODUCTION

In previous papers[1–5] we have considered the highly stereoregular polymerization of aromatic acetylenes, homologues and alkyl propiolate (HC≡CCOOR), together with the living polymerization of *m*-chlorophenylacetylene catalysed by the Rh complex [Rh (norbornadiene)Cl]$_2$, $[Rh(NBD)Cl]_2$, where either an unusual organic solvent such as triethylamine (TEA) or alcohol was used, and the *cis–transoid* polymers were selectively formed in fairly high yields.

The TEA used as the organic base was considered to work by dissociating the bidentate complex, $[Rh(NBD)Cl]_2$, into monomeric species that may be important initiation species for this polymerization[3,5], as shown in *Scheme 1*.

It has been reported that α-ethynylnaphthalene (ENAP) can be polymerized with $(PPh_3)_3 \cdot NiBr_2$, the Ziegler–Natta catalyst $AlEt_3 \cdot Fe(II)$(dimethyl glyoxime)$_2$Py and metathesis catalysts[6–10] to give rise to poly(α-ethynylnaphthalene) (PENAP) polymer. The geometrical structure has been believed to have the *trans–cisoid* form as shown in *Scheme 1*. It seems, however, that the question of the geometrical form has not been studied in detail, including the structural changes induced by thermal *cis–trans* isomerization, although the pristine polymer structure must depend on the polymerization conditions, e.g. catalyst[6–9], solvent[5] and thermal history such as polymerization temperature.

Recently, we found that there are extremely clear differences between the Raman spectra of the PENAP polymers polymerized with the Rh complex in TEA and the so-called metathesis catalyst WCl_6 in toluene. We finally concluded that the spectral differences can be explained in terms of the geometrical structure as the



Scheme 1

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* To whom correspondence should be addressed

main reason, i.e. the Rh complex produces a PENAP polymer (PENAP-Rh) with a *cis–cisoid* form whereas the WCl_6 catalyst produces PENAP polymer (PENAP-W) with a *trans–transoid* form (see *Scheme 1*). Therefore, in this communication we describe the stereoregular polymerization results of ENAP monomer initiated with the Rh complex catalyst and the WCl_6 catalyst together with characterization of the resulting PENAP polymer using gel permeation chromatography (g.p.c.), ^{1}H n.m.r., electron spin resonance (e.s.r.) and laser Raman spectroscopic methods.

It is worth mentioning here that, in the cases of mono- and disubstituted polyacetylenes, the changes in the structure and properties induced by thermal *cis–trans* isomerization have not previously been investigated in detail using an equivocal assignment method, e.g. a laser Raman method combined with an electron spin resonance method where many radical spins should be generated by a rupture of the *cis* C=C bonds and play an important role in the formation of an organic magnet[11,12]. Furthermore it is necessary to note that mono- and disubstituted polyacetylenes with a complete *trans* π-conjugated structure have also not been prepared to date unlike polyacetylene.

It is considered that the polyacetylenes are potentially important for industrial applications because of recent expectation that such a π-conjugated polymer will exhibit photo- and electrical conductivities as well as ferromagnetism[11,12], non-linear optical (NLO) properties[13,14] and oxygen permeability[15].

EXPERIMENTAL

Synthesis

The α-ethynylnaphthalene (ENAP) was prepared according to the literature[16] from α-acetylnaphthalene by chlorination with PCl_5 and subsequent dehydrochlorination with sodium hydroxide, and obtained as a colourless compound, m.p. 62°C. The Rh complexes $[Rh(NBD)Cl]_2$ and $[Rh(C_8H_{12})\{P(C_6H_5)_3\}_2]PF_6$ (Aldrich) were used without further purification. WCl_6 and $MoCl_5$ (Tokyo Chemical Ltd) were also used as received.

Polymerization

Polymerization was carried out using a specially designed U-type ampoule where two glass inlets with septum caps at the tops of the tube were installed. The Rh catalyst, 0.056 mmol (13 mg), was placed from one side arm into the ampoule and 2.1 mmol (1.0 g) of monomer was introduced from the other side arm with the aid of a hypodermic syringe under a dry nitrogen atmosphere. The solvent, i.e. toluene (7 ml) dried with CaH_2 or triethylamine (TEA) (7 ml) dried by refluxing with benzophenone and sodium, was introduced from both side arms to dissolve the catalyst powder and make the monomer solution followed by the initiation of polymerization at various temperatures for 24 h. The resulting reaction solutions were poured into a large amount of methanol to cause precipitation and the obtained polymer was then filtered. Hot methanol (50 ml) was used to extract the remaining monomer after the polymerization and the resulting polymer was dried under reduced pressure at $\sim 10^{-3}$ Torr at 40°C for 24 h. Polymer yield was estimated by gravimetry. Molecular weights of soluble polymers were measured by gel permeation chromatography using tetrahydrofuran as the eluent, and Asahipac columns, GS-310 and GS-510 with a polystyrene standard.

Spectra

^{1}H n.m.r. spectra were run on a 400 MHz JEOL GX spectrometer in $CDCl_3$ solution with tetramethylsilane (TMS) as the standard signal at 30°C. The laser Raman spectra of polymer powder were recorded with a JEOL JRS 400T using the excitation wavelength of 514.5 nm at room temperature and KBr disc. The e.s.r. spectra in the solid state were measured on a JEOL FE1XG (100 kHz field modulation) at room and liquid-nitrogen temperatures.

RESULTS AND DISCUSSION

Table 1 lists the results of polymerization of α-ethynylnaphthalene (ENAP), which was catalysed by the Rh complex in alcohol and TEA, and by WCl_6 and $MoCl_5$ (metathesis catalysts) in toluene. It is clear that the Rh complex $[Rh(NBD)Cl]_2$ polymerized the ENAP monomer to give rise to the PENAP polymer PENAP-Rh (No. 1) with a violet colour in the highest yield of 86.0% among the catalysts examined. However, the PENAP polymers were insoluble in ordinary solvents when triethylamine or alcohol was used as solvent. On the other hand, the PENAP-W polymers, obtained with the WCl_6 catalyst, were dark brown and soluble in

Table 1 Polymerizations of α-ethynylnaphthalene with Rh complex and metathesis catalysts[a]

No.	Catalyst	Solvent	Temp. (°C)	Yield (%)	M_n	Colour
1	$[Rh(NBD)Cl]_2$[b]	TEA[d]	40	86.0	Insol.	Violet
2	$[Rh(COD)(PPh_3)_2]PF_6$[c]	EtOH	40	75.0	Insol.	Violet
3	WCl_6	Toluene	−20	2.3	30 000	Dark brown
4	WCl_6	Toluene	0	83.4	32 000	Dark brown
5	WCl_6	Toluene	40	84.9	36 000	Dark brown
6	$MoCl_5$	Toluene	40	3.5	2 050	Dark brown

[a] Polymerization time 24 h
[b] NBD, norbornadiene
[c] COD, cyclooctadiene
[d] Triethylamine

toluene, tetrahydrofuran, and chloroform but insoluble in methanol, acetone and n-hexane. The molecular-weight dispersities, M_w/M_n, of the PENAP polymer obtained as soluble polymers were estimated as ca. 2–4 using polystyrene standards.

^1H n.m.r. spectra

Figure 1 shows the ^{1}H n.m.r. spectrum of the soluble PENAP-W polymer observed in $CDCl_3$ solution using tetramethylsilane (TMS) as standard at 30°C. This spectrum is composed of a very broad peak due to protons in the naphthyl group in the range from ~4 ppm to 8.5 ppm together with a very small peak at ca. 5.8 ppm due to the C=C–H proton in the main chain. This is in contrast to the case of poly(*p*-methoxyphenylacetylene) (PMeOPA) polymerized with the $[Rh(NBD)Cl]_2$ catalyst in TEA solvent where a clear and sharp peak due to the C=CH proton was observed[5]. Such linewidth broadenings observed in the n.m.r. spectrum are observed not only when the Ziegler–Natta catalyst but also when the metathesis catalyst were used for the polymerization of acetylene monomers[6–10]. This linewidth broadening is interpreted in terms of the magnetic dipole–dipole interaction between the radical spins and proton spins in the polymer, whose radical spins were generated by rotational disruption of the *cis* C=C bond during and/or after polymerization and by thermal *cis–trans* isomerization.

The incorporation of the resulting *trans* sequence into the *cis* sequence may slow the molecular motion of the main chain due to stiff *trans*-conjugated sequences, spreading the chemical shift distribution to some extent[5–10,17]. This consideration leads us to deduce that the PENAP-W polymer with the broad linewidth in the ^{1}H n.m.r. spectrum has *trans*-conjugated sequences which contain many radical spins stabilized in the π-conjugated system as shown later.

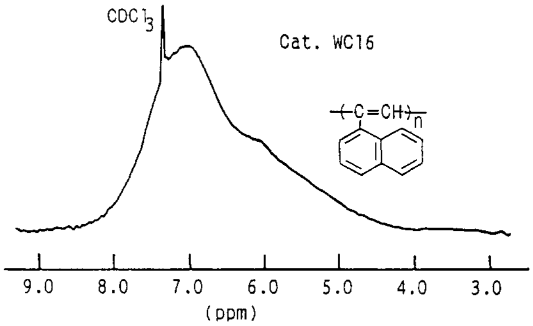


Figure 1 ^{1}H n.m.r. (400 MHz) spectrum of PENAP-W polymer

Two spins per one *cis* C=C double bond should be generated by the rotational rupture of the double bonds in the *cis* PENAP polymer as a biradical during polymerization or when compression was applied to the poly(*o*-methoxyphenylacetylene) (POMPA) polymer[18] or *cis–trans* isomerization was induced by thermal treatment. Of course the π-radicals may function not only as the spin source of the magnetic dipole–dipole interaction but also as the formation of the ferromagnetic, antiferromagnetic, super-paramagnetic and spin-glass polymer as previously predicted[12].

The insolubility of the PENAP-Rh polymer will be explained in terms of the *cis–cisoid* structure with a fairly narrow helicoidal pitch width from which solvation of the polymer chain is prevented, as in the cases of poly(methylpropiolate)[2], poly(*p*-methylphenylacetylene)[3,4] and poly(*p*-chlorophenylacetylene)[5] polymerized with Rh complex and poly(β-ethynylnaphthalene) polymerized with the Ziegler–Natta catalyst[6–9]. It is necessary to mention here that the PENAP with the *cis–transoid* structure is also insoluble in some cases irrespective of a loose helical structure[2]. Therefore the formation of the *cis–transoid* polymer is not always excluded in this case. The *cis–cisoid* form having a perfect 3/1 helix structure is confirmed using wide-angle X-ray scattering in poly(β-ethynylnaphthalene) polymerized with the Ziegler–Natta catalyst whose polymer was not soluble in benzene at all[7]. It seems, however, that not only the broadening in the ^{1}H n.m.r. spectrum but also the insolubility of the PENAP polymers does not allow us to clearly deduce the geometrical structure of the resulting PENAP polymer. Therefore, we performed the structural assignments using e.s.r. and Raman methods as shown below.

E.s.r. study

The radical concentration, linewidth and *g*-value of the PENAP polymers were measured in order to deduce the geometrical structure using the e.s.r. spectrometer. The results are shown in *Table 2*. It is clear that the radical concentration of the PENAP-W polymer polymerized at 40°C is around one magnitude higher than that of the PENAP-Rh polymer polymerized at 40°C, i.e. the former has ca. 1.3×10^{18} spins/g and the latter has ca. 1.0×10^{17} spins/g, respectively. These results suggest that the PENAP-Rh and PENAP-WCl_6 polymers have *cis*- and *trans*-rich forms, respectively.

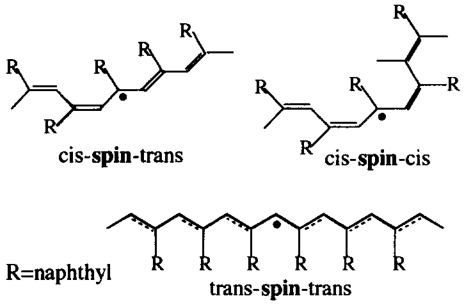
This consideration is also supported by the observed linewidth ΔH_{msl} with temperature dependence, i.e. the

Table 2 E.s.r. parameters of the PENAP polymers polymerized with the Rh complex and WCl_6 catalysts

No. from *Table 1*	Polymer	Spin conc. (spins/g)	*g*-value	ΔH_{msl} (Gauss) R.t.	ΔH_{msl} (Gauss) 77 K	Lit.
1	PENAP-Rh[a]	1.0×10^{17}	2.0028 ± 0.0005	11.7	12.0	–
4	PENAP-W[b]	1.3×10^{18}	2.0024 ± 0.0005	8.9	11.5	–
–	PENAP-Al[c]	$(0.66–3.43) \times 10^{18}$	–	–	–	6–9

[a] Polymerized with $[Rh(NBD)Cl]_2$ at 30°C
[b] Polymerized with WCl_6 at 40°C
[c] Polymerized with Fe(II)$(dgm)_2Py \cdot AlEt_3$ at 25°C

linewidths of the PENAP-Rh polymers showed $\Delta H_{\mathrm{msl}} = 11.7$ Gauss at room temperature and 12.0 Gauss at 77 K, whereas the linewidth of the PENAP-W polymer showed $\Delta H_{\mathrm{msl}} = 8.9$ Gauss at room temperature and 11.5 Gauss at 77 K, respectively. These facts indicate that the unpaired electron stabilized in the PENAP-Rh polymer chain is inmobile because of no temperature dependence for the linewidth; in other words, the spin is localized in the short and restricted conjugated chain, suggesting that the PENAP-Rh polymer has the *cis* structure, i.e. *cis*-**spin**-*cis* or *cis*-**spin**-*trans* form as shown in *Scheme 2*.



Scheme 2

On the other hand, the temperature dependence of the e.s.r. linewidth observed in the PENAP-W clearly indicates that unpaired electrons are stabilized in a fairly long conjugated chain, i.e. *trans*-**spin**-*trans*, where the electrons move around the extended *trans* conjugated chain showing motional or exchange narrowing as reported in the case of polyacetylene[19]. Therefore, it is concluded that the PENAP-W polymer has the *trans–transoid* sequences as has been believed. Thus the e.s.r. parameters support the fact that the PENAP-Rh polymer insoluble in solvent involves the *cis–cisoid* sequence as deduced by the Raman study where the inmobile electrons are stabilized in the main chain, and the PENAP-W polymer involves the *trans–transoid* sequences which stabilize the mobile unpaired electrons in the main chain.

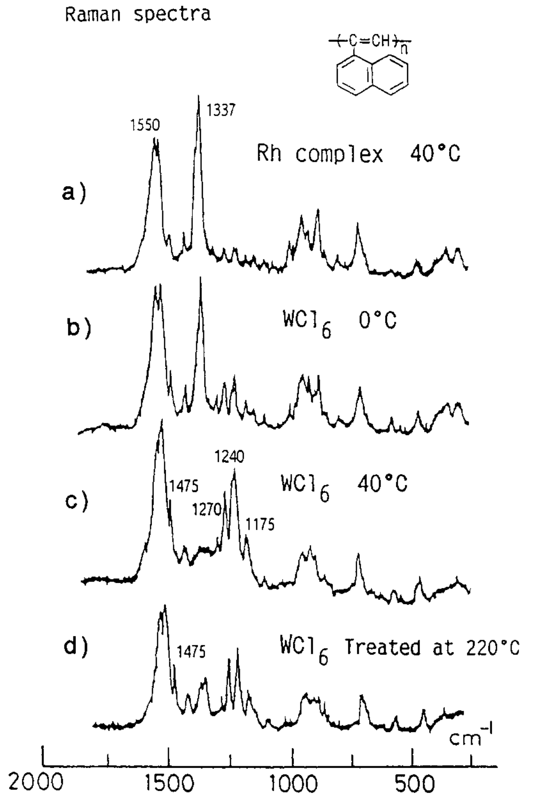


Figure 2 Ar^+ laser Raman spectra of the PENAP polymer: (a) polymerized with $[Rh(NBD)Cl]_2$ in triethylamine at 40°C; (b) polymerized with WCl_6 in toluene at 0°C; (c) polymerized with WCl_6 in toluene at 40°C; (d) PENAP-W polymer polymerized with WCl_6 catalyst at 0°C and heat-treated at 220°C

Raman study

Raman spectra of the conjugated compounds have been used to determine the geometrical structure with respect to the C=C bond together with the estimation of the sequence length of the double bonds in the polyacetylenes[20,21], because the exact band position in the Raman spectra is sensitive to the degree of the length of the conjugated double bonds in polyacetylenes and the excitation wavelength employed. Therefore, the conjugated sequence length and geometrical structure can be estimated if a suitable laser wavelength is used, by which this spectrum is called resonance Raman (RR) spectrum. We examined the structure and double-bond sequence of the PENAP polymers using the RR method with an excitation laser wavelength of the Ar^+ laser at 514.5 nm. The results are shown in *Figure 2* with the spectra observed after the thermal isomerization of the PENAP-Rh at 220°C. The large peak at ca. 1550 cm^{-1} in *Figure 2a* was assigned to that of the naphthalene ring, overlapped with that of *cis* C=C bond in the *cis–transoid* or *cis–cisoid* form. The large peak at 1330 cm^{-1} was assigned to the C–C bond, coupled with the C–H bond in the *cis* polymer which is characteristic for the aromatic polyacetylene having the *cis* form as reported before[22]. *Figures 2b* and *2c* show the spectra of PENAP-W polymers polymerized at 0 and 40°C, respectively. It is clear that the peak at 1337 cm^{-1} decreased with increase of temperature of polymerization and then, inversely, several new peaks centred at 1240 cm^{-1} appeared. The new multiplet can be attributed to the C–C bonds, coupled with the *trans* C–H bonds in the short *trans* conjugated chain sequences because such peaks were observed in the same range of the spectrum of the poly(*p*-chlorophenylacetylene) bearing the *trans–transoid* form whose polymer was topochemically obtained by γ-ray irradiation in the solid state[22].

A small peak at 1475 cm^{-1} observed in each spectrum may be assigned to the fairly long conjugated *trans* sequences as observed in the *trans* poly(*o*-methoxyphenylacetylene) which was converted from *cis* to *trans* form by compression[18]. It seems that such long π-conjugation sequences are generated during polymerization at a higher polymerization temperature or by thermal treatment at 220°C of the PENAP-W polymerized at 0°C, and even in the case of Rh complex polymerization at 40°C to some extent.

The large peak at around 1550 cm^{-1} was also found to be shifted to the lower wavelength side together with a decrease in intensity in the case of the PENAP polymer when the WCl_6 was used to 0 and 40°C, and the PENAP-W polymerized at 0°C was heat-treated up to 200°C, compared to that of the PENAP-Rh polymerized at 40°C. The peak shift will be explained in terms of the decrease of the *cis* component in the PENAP polymers with fairly high *cis* content because *cis–trans* isomerization takes place during the polymerization or by heat-treatment of the PENAP polymer as shown in *Figure 2*. Thus the RR studies support that the PENAP-Rh and PENAP-W polymers have the *cis–cisoid* and *trans–transoid* sequences, respectively. Further, the conclusion based on the RR method is in good agreement with that of the e.s.r. method as mentioned above.

Figure 2 shows that the Raman spectrum of the PENAP-W polymerized at 0°C was nearly identical with that of the PENAP-Rh polymerized at 40°C. This indicates that the WCl_6 catalyst as well as the Rh complex can also be called a stereoregular polymerization catalyst of arylacetylenes like α-ethynylacetylene when the polymerization was carried out at lower temperature although the polymerization mechanism induced by the WCl_6 catalyst[15] must be completely different from that induced by the Rh complex which was recently proposed by us[5].

CONCLUSIONS

The poly(α-ethynylnaphthalene) (PENAP) polymer was stereoregularly obtained with the Rh complex catalyst in TEA solvent to produce the *cis–cisoid* polymer in high yield. Based on the e.s.r. data of the PENAP polymers, it was revealed that the Rh complex and WCl_6 catalysts produce the PENAP polymer with the *cis–cisoid* and *trans–transoid* structures, respectively, where the localized unpaired electron and mobile electron are stabilized in the main chains, respectively. Further the Raman studies led us to conclude that the PENAP-Rh and PENAP-W polymers have the *cis–cisoid* and *trans-transoid* form, respectively.

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