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Studies of Poly-yne Polymers Containing Transition Metals in the Main Chain. 2. Synthesis of Poly[*trans*-bis(tri-*n*-butylphosphine)platinum 1,4-butadiynediyl] and Evidence of a Rodlike Structure

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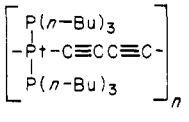
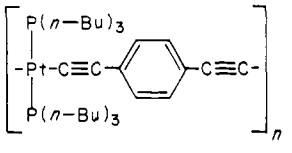
ABSTRACT: The synthesis and characterization of the metal–poly-yne polymers, poly[*trans*-bis(tri-*n*-butylphosphine)platinum 1,4-butadiynediyl] (I) and poly[*trans*-bis(tri-*n*-butylphosphine)platinum 1,4-phenylenediethynylene] (II), are described. The polymers are synthesized by a condensation reaction between a metal chloride and an acetylene or a metal acetylide complex in amines in the presence of cuprous iodide as a catalyst. Studies of their solution properties suggest that the poly-yne polymers have a rodlike structure and the rodlike condition may result as a feature of trans platinum acetylide moieties. The evidence for the rodlike structure rests on (1) an a value of 1.7 in the Mark–Houwink equation, (2) independence of the intrinsic viscosity from solvent for these polymers, and (3) good agreement of the observed polymer size with that calculated based on an ellipsoid of revolution model.

One of the current interests in polymer chemistry lies in multifunctional polymeric materials. In a previous paper[1] we reported a preliminary result on the synthesis of a new class of polymer having a backbone of conjugated poly-yne and platinum metal atoms. Spectral data[1,2] indicated that poly[*trans*-bis(tri-*n*-butylphosphine)platinum 1,4-butadiynediyl] (I) has all-trans configurations at



I



II

platinum moieties and polymer I may be expected to have a rodlike structure. The interest in stiff polymers is growing rapidly in terms of their special properties[3] in both solution and in the solid state. In this paper we wish to report on the synthesis of poly-yne polymers I and II and their solution properties which imply that they have a rigid rodlike structure.

Experimental Section

Apparatus. Infrared spectra were taken on a Hitachi 295 spectrometer and UV spectra were recorded in methylene chloride with a Shimadzu UV 202 spectrophotometer. ^{31}P NMR spectra were run on a JEOL FX100 spectrometer. Intrinsic viscosities were measured using Ubbelohde type viscometers at 25 °C. Gel permeation chromatograms were obtained using a Shimadzu-Du Pont Liquid Chromatograph Model 830 and tetrahydrofuran as the mobile phase at room temperature: column set (packed with polystyrene beads made by Shimadzu-Du Pont) HSG 30 (50 cm) + HSG 60 (50 cm); flow rate 1 mL/min; UV 254 nm detector. Monodisperse polystyrenes from Pressure Chemical Co. were used to calibrate the columns. Partial specific volumes ($\bar{v}$) were measured using a semi-self-filling, Ostwald type of picnometer[4] in toluene at 25 °C.

Preparation of Polymers. Cuprous iodide (7 mg, 0.037 mmol) was added to a deoxygenated solution of *trans*-bis(tri-*n*-butylphosphine)bis(1,4-butadiynyl)platinum[2] (1.3968 g, 2.0 mmol) and dichlorobis(tri-*n*-butylphosphine)platinum (1.3404 g, 2.0 mmol) in 50 mL of diethylamine under a nitrogen atomosphere. The reaction mixture was heated to a gentle reflux with stirring for 1 day and then evaporated to dryness under reduced pressure. In order to remove the cuprous compound, the residue was dissolved in methylene chloride and the resulting solution was filtered by alumina column chromatography. After evaporation of the filtrate, a pale yellow product was collected and purified by repeated precipitation from methylene chloride into methanol. Finally, a benzene solution (100 mL) of the product was frozen and then freeze-dried under reduced pressure to afford a pale yellow polymer of I having $[\eta]$ of 1.20 dL/g (in THF at 25 °C), yield 2.5 g (96%). Anal. Calcd for $C_{28}H_{54}P_2Pt$: H, 8.40; C, 51.92; P, 9.56, Found: H, 8.63; C, 51.89; P, 9.81.

Polymer II was similarly prepared from the condensation reaction between *p*-diethynylbenzene (126 mg, 1.0 mmol) and dichlorobis(tri-*n*-butylphosphine)platinum (671 mg, 1.0 mmol). Similar procedure gave a pale yellow polymer of II having $[\eta]$ of 0.98 dL/g (in THF at 25 °C) in 85% yield. Anal. Calcd for $C_{34}H_{58}P_2Pt$: H, 8.08; C, 56.42; P, 8.56, Found: H, 8.35; C, 56.44; P, 8.28.

Samples for physical measurements were prepared by repeated fractional precipitation from methylene chloride into methanol or *n*-hexane.

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Results and Discussion

Synthesis of Poly-yne Polymers Containing Platinum in the Main Chain. Recently, a variety of polymers containing transition metals have been reported, in most of which transition metals are linked as pendant groups through π bonding as seen in the polymers containing ferrocene or related transition metal complexes.

Previously, we reported[2] a new conventional method for preparation of transition metal acetylide complexes by dehydrohalogenation between metal halides and terminal acetylenes using a cuprous halide as a catalyst in amines. This method has been successively applied to synthesis of the metal–poly-yne polymers and we have obtained polymers containing platinum atoms as the first example in which the transition metal is linked through σ bonds in the polymer backbone.

The general scheme of polymer formation is shown in eq 1. In the case of *p*-diethynylbenzene we can prepare

$$(Bu_3P)_2PtCl_2 + HC{\equiv}CYC{\equiv}CH + NR_3 \xrightarrow{\text{CuX catalyst}} [-Pt(PBu_3)_2C{\equiv}CYC{\equiv}C-]_n + HClNR_3 \quad (1)$$

$$\text{I, Y} = -C{\equiv}C-\underset{\displaystyle PBu_3}{\overset{\displaystyle PBu_3}{\underset{|}{\overset{|}{Pt}}}}-C{\equiv}C-;\ \text{II, Y} = -(C_6H_4)-$$

the polymer from the direct reaction of the acetylene with the metal halide, whereas gaseous butadiyne was once converted to the platinum monomer complex,[2] which is stable in air at room temperature, and then reacted with the metal halide.

The condensation between acetylenes and metal halides was accomplished by use of amines such as diethylamine and piperidine as acid acceptors, but no high molecular weight polymers were formed. We have found that an addition of a catalytic amount of cuprous iodide accelerates enormously the polycondensation and affords high molecular weight polymers. Cuprous bromide and cuprous chloride are also effective for the polycondensation and cuprous iodide is of choice in terms of the high stability in air and easy handling.

Amines are used as acid acceptors. Strongly basic amines such as diethylamine and piperidine are effective for attaining high degree of polymerization although pyridine is not effective. In a polymerization reaction the precipitation of polymers essentially ceases further reaction yielding high molecular weight products. Fortunately, polymers I and II showed high solubilities in amines; especially polymer I dissolved in amines at a high concentration even at room temperature. Polymer II of high molecular weight is also soluble in hot amines. Therefore, amines may be used as acid acceptors and as solvents in these systems.

Since the system containing cuprous halides and amines may act as an oxidant for the oxidative coupling of terminal acetylenes,[5] the polycondesation reaction should be carried out under vacuum or under inert gas atmosphere such as nitrogen and argon.

The condensation took place even at room temperature in diethylamine in the presence of cuprous iodide catalyst, but the reaction proceeded very slowly. For example, the reaction between $(PBu_3)_2Pt(C{\equiv}CC{\equiv}CH)_2$ and $(PBu_3)_2PtCl_2$ yielded polymer I of $\bar{M}_w$ = 70 000 after one month at room temperature, whereas that between *p*-diethynylbenzene and $(PBu_3)_2PtCl_2$ afforded only a low molecular weight product ($\bar{M}_w$ = 8000) due to the relatively low solubility of polymer II in diethylamine at room temperature. The high molecular weight polymer of II was obtained by heating the system and the reaction under reflux of diethylamine gave II of $\bar{M}_w$ = 55 000. For the preparation of polymer I heating the system extremely shortened the reaction time required. Table I shows the time dependence of the degree of polymerization traced by the gel permeation chromatography.

Table I
Time Dependence of the Polymerization between $(PBu_3)_2PtCl_2$ and $(PBu_3)_2Pt(C{\equiv}CC{\equiv}CH)_2$ in $HNEt_2$ in the Presence of CuI under Reflux

time, h	$\bar{M}_w$[a]	$\bar{n}_w$[b]
1	9 000	14
3	18 000	28
6	24 000	37
24	70 000	108

[a] Weight average molecular weight obtained from the GPC analysis. [b] Weight average degree of polymerization calculated based on the equation $\bar{n}_w = \bar{M}_w/648$.

It is obvious that the molar ratio of two reactants strongly affects the degree of polymerization in polycondensation. For attaining high degree of polymerization the monomer purity and the equivalence of reactants are very important. Particularly, the monomer, $(PBu_3)_2Pt(C{\equiv}CC{\equiv}CH)_2$, should be used after careful recrystallization from alcohol because it gradually decomposes in air at room temperature. The polymerization carried out under the optinum conditions, i.e., in the presence of cuprous iodide catalyst in diethylamine under reflux, almost quantitatively gave high molecular weight polymers: I, $\bar{M}_w$ = 70 000; and II, $\bar{M}_w$ = 60 000.

Characterization of the Polymers. The polymers are obtained as pale yellow solids and are stable in air. Polymer I in a solution is, however, somewhat unstable in air and on standing in the sunlight it decomposes slowly with color change from yellow to orange.

Spectral data of the polymers are summarized in Table II along with those of analogous monomeric platinum complexes, which reveal that the polymerization proceeds according to eq 1 without any side reactions. The ^{31}P NMR spectral analysis provides a powerful method which proves configurations around platinum moiety. The spectra of trans configurational phosphorus on platinum bis(acetylide) show a signal at −3.0 to −5.0 ppm and those of the cis configurational one show a signal at +2.0 to +4.0 ppm form 85% phosphoric acid standard. The $^{31}P\{^1H\}$ Fourier transfer NMR spectra of high molecular weight polymer I and II showed large resonances at −4.2 and −3.0 ppm, respectively, attributable to the trans configurational phosphorus with attendant satellites due to coupling with ^{195}Pt ($I = {}^1/_2$, natural abandance 33%). Since no trace of absorption in the region assigned to cis configurational phosphorus was observed in both polymers, it was concluded that polymers I and II have all-trans configurations at platinum moiety and the extended chain structure.

Relation between Viscosity and Molecular Weight. It is well recognized that a rodlike polymer shows a large *a* value in the Mark–Houwink equation (eq 2). For example, poly(γ-benzyl L-glutamate), which is a typical example having rodlike structure in a helicogenic solvent, shows[6] an *a* value of 1.7, while randomly coiled polymers such as polystyrene and polyacrylonitrile have values below one.

$$[\eta] = KM^a \quad (2)$$

In order to obtain evidence of a rodlike structure for polymer I, we have attempted to determine parameter *a* in eq 2 by means of gel permeation chromatography (GPC), since recent developments in GPC have provided a convenient way[7] to determine parameters *a* and *K*. If

Table II
Spectral Data of Metal-Poly-yne Polymers and Monomeric *trans*- and *cis*-Bis(tributylphosphine)dialkynylplatinum Complexes

compd[a]	IR[b] $\nu_{\equiv CH}$, cm^{-1}	IR[b] $\nu_{C\equiv C}$, cm^{-1}	UV[d] λ_{max} (log ϵ), nm	^{31}P NMR[d] δ[e]	^{31}P NMR[d] J_{Pt-P}, Hz
trans-PT(C≡CC≡CH)$_2$	3307	2147	318 (4.39)	−4.7	2279
cis-PT(C≡CC≡CH)$_2$	3315, 4295	2153, 2145	301 (4.22)	+3.7	2269
trans-PT(C≡C-C$_6$H$_4$-C≡CH)$_2$	3280	2098	338 (4.73)	−3.3	2341
cis-PT(C≡C-C$_6$H$_4$-C≡CH)$_2$	3268	2120, 2130	308 (4.75)	+3.3	2248
polymer I	none	2000[c]	384 (4.54)	−4.2	2384
polymer II	none	2095[c]	380 (4.80)	−3.0	2359

[a] PT represents -Pt(PBu$_3$)$_2$- moiety. [b] Nujol mull. [c] Film. [d] In CH_2Cl_2. [e] Negative values of chemical shifts (δ) are in parts per million downfield of external 85% H_3PO_4.

Table III
Intrinsic Viscosity of Polymer I[a]

sample no.	[η], dL/g
I-1	0.484
I-2	0.652
I-3	1.028
I-4	1.204
I-5	2.107

[a] THF, 25 °C.

Table IV
Calculated Values of a[a] by the GPC Method

combination	a	combination	a
(I-1) (I-3)	1.7	(I-2) (I-4)	2.0
(I-1) (I-4)	1.7	(I-2) (I-5)	1.8
(I-1) (I-5)	1.8	(I-3) (I-5)	1.6
(I-2) (I-3)	1.6	(I-4) (I-5)	1.7

[a] $a_{av} = 1.7$.

we take two samples of the same chemical nature but with different viscosities and measure their intrinsic viscosities and GPC traces in the same solvent, parameter a can be calculated through eq 4, subsequently parameter K

$$J_i = [\eta]_i M_i \tag{3}$$

$$\frac{[\eta]_1}{[\eta]_2} = \frac{\sum_i W_{i1} J_i^{a/(a+1)}}{\sum_i W_{i2} J_i^{a/(a+1)}} \tag{4}$$

$$[\eta] = K^{1/(a+1)} \sum_i W_i J_i^{a/(a+1)} \tag{5}$$

through eq 5: where W_i, $[\eta]_i$, and M_i are the weight fraction, viscosity, and molecular weight, respectively, of the ith species.

After making a universal calibration curve for our GPC instrument using polystyrene standards we measured GPC traces for five samples of polymer I with different viscosities listed in Table III. Subsequently, parameter a was calculated using eq 4 for eight sets of a combination of two samples using a computer program. The results are shown in Table IV and an average a value of 1.7 was obtained. Parameter K, then, was determined through eq 5 using an a value of 1.7 and we obtained an average K value of 6.5×10^{-9}. For polymer II, the same procedure afforded an average a value of 1.7 and K value of 2.0×10^{-8}.

By taking values of parameters a and K obtained above, we calculated the weight-average and number-average molecular weight of polymers I and II according to the literature method[7] and compared them with those obtained by the sedimentation equilibrium method[8] as shown in Table V. Deviations up to about 20% for the GPC method may be mainly due to the peak broadening of the chromatogram.[9] Mathematical treatment of the relation between the viscosity and the weight-average molecular weight obtained by the sedimentation equilibrium method yielded an a value in the region 1.5–1.7 for a combination of I-2 and I-5, which showed a good agreement with that obtained above.

Table V
Comparison between Molecular Weights Obtained by the GPC and the Absolute Methods

sample no.	GPC $\bar{M}_w$	GPC $\bar{M}_n$	GPC $\bar{M}_w/\bar{M}_n$	S.E.[a] $\bar{M}_w$
I-2	50 000	34 000	1.5	54 000-60 000
I-5	102 000	68 000	1.5	119 000-122 000
II-4	31 000	22 000	1.4	35 000

[a] Sedimentation equilibrium method (in toluene).[8]

Table VI
Intrinsic Viscosity of Polymer I in Various Solvents[a]

solvent	δ,[b] $(cal/mL)^{1/2}$	H-bonding group	[η]
n-decane	6.6	poor	1.22
n-pentane	7.0	poor	1.25
methylcyclohexane	7.8	poor	1.25
cyclohexane	8.2	poor	1.25
toluene	8.9	poor	1.23
benzene	9.2	poor	1.20
chlorobenzene	9.5	poor	1.23
dichloromethane	9.7	poor	1.19
isopropyl ether	6.9	medium	1.20
tetrahydrofuran	9.1	medium	1.20

[a] $\bar{M}_w = 6.9 \times 10^4$ (from GPC), at 25 °C. [b] Solubility parameter values quoted from ref 11b.

Dependence of Viscosity on Solvents. Polymers I and II show high solubilities in spite of containing a heavy metal in their backbone and in particular polymer I is dissolved in most organic solvents such as hydrocarbons, halogenated hydrocarbons, ethers, and amines but is not soluble in alcohols. This high solubility furnished an opportunity for us to investigate the dependence of viscosity on the nature of solvents and gave us further evidence for the rodlike structure of the polymer.

The intrinsic viscosity of randomly coiled polymers is strongly dependent on the nature of the solvent used. There is a decrease in the viscosity of flexible polymers in poor solvents, while stiff polymers such as cellulose show little change in intrinsic viscosity with changes in the nature of the solvent.[10] However, there are few reports on the systematic investigation of the dependence of viscosity of stiff polymers in a variety of solvents due to their limited solubilities.

Table VII
Calculation of Polymer Size

sample no.	$[\eta]$	$\bar{v}$	P^a	d,[b] Å	L,[b] Å	$\bar{M}_w$	$\bar{n}_w$	L,[c] Å
I-2	0.652	0.79	32	18	702	54 000-60 000	83-91	648-710
I-5	2.107	0.79	64	18	1404	119 000-122 000	184-188	1435-1466

[a] Axial ratio b_1/b_2 of the major axis b_1 to the minor axis b_2 in ellipsoid of revolution. [b] The diameter d and the length L of the equivalent rod to the ellipsoid. [c] The length of the rod calculated from $\bar{M}_w$, L = 7.8 Å × $\bar{n}_w$.

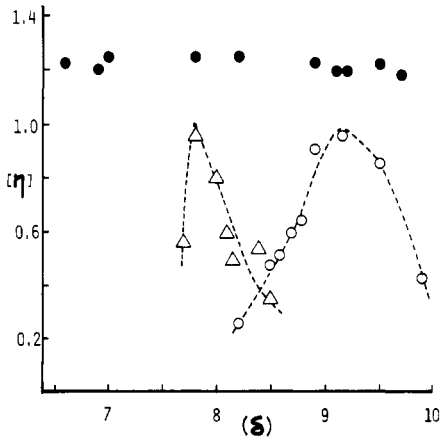

Figure 1. Intrinsic viscosity $[\eta]$ against solubility parameter (δ) plotted according to Table IV and ref 9a: (●) polymer I; (○) polystyrene; (△) polyisobutene.

The results of intrinsic viscosity measurements on polymer I in various solvents are summarized in Table VI, and in Figure 1 the intrinsic viscosity is plotted against the solubility parameter of the solvent employed. Randomly coiled polymers such as isobutylene and styrene exhibit a maximum viscosity in a good solvent and form a bell-shape relation between their viscosities and solubility parameters of solvents,[11] whereas the intrinsic viscosity of polymer I was independent of the solubility parameter in the region 6.6–9.7 $(cal/mL)^{1/2}$ and almost constant. For polymer II we obtained similar results for the intrinsic viscosity measurements in the region 8.9–9.7 $(cal/mL)^{1/2}$, although we were unable to explore as wide a range of solubility parameters due to the low solubility of polymer II. This solution property may indicate that the poly-yne polymers have an essentially uniform shape, i.e., rodlike structure, in those solvents.

Treatment of the Polymer with an Ellipsoid of Revolution Model. We have obtained further evidence for the rigid rodlike structure from a treatment of the poly-yne polymer based on Simha's equation which describes a relation between the viscosity and the size of a prolate ellipsoid of revolution.[12] Thus, calculation of a polymer size according to Simha's equation (eq 6) was

$$[\eta] = \bar{v}\nu(p), \qquad p = b_1/b_2,$$
$$\nu(p) = p^2/15(\ln 2p - \tfrac{2}{3}) + p^2/5(\ln 2p - \tfrac{1}{2}) + \tfrac{14}{15} \quad (6)$$

performed using the measured values of intrinsic viscosity and partial specific volume ($\bar{v}$), giving the axial ratio b_1/b_2 in the ellipsoid of revolution, where b_1 and b_2 stand for the major axis and the minor axis, respectively, which are related to the length L and the diameter d of the equivalent rigid rod by $b_1 = L$ and $b_2 = (^3/_2)^{1/2}d$. The repeat unit in polymer I was assumed to be 7.8 Å in length and 18 Å in width. These dimentions are estimates based on X-ray analytical data for an analogous monomeric acetylide complex of platinum.[13] The results of calculations[14] based on hydrodynamic data for polymer I are shown in Table VII in comparison to those calculated from the sedimentation equilibrium weight-average molecular weights, estimated monomer dimentions, and the assumed rigid rod conformation. An excellent agreement between them strongly suggests that the polymer has a rigid rodlike structure.[15] In summary, the a value of 1.7 in eq 2, although obtained tentatively from the GPC method, and solution properties mentioned above allow us to conclude that the metal–poly-yne polymers have a rodlike structure in solutions.[15] This is supported by the fact that the concentrated methylene chloride solution of polymer I forms an anisotropic phase (liquid crystals) which is recognized under a polarized microscope.[16] It is of interest to note that the rodlike condition of polyamides except some aromatic polyamides[3] is achieved by formation of a helical structure in selected solvents, whereas that of the metal–poly-yne polymers originates as an essential feature of trans platinum acetylide moieties. This may constitute a new class of rodlike polymers.

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(15) The determination of the persistence length which characterizes the rigidity of polymer chains is attempted by Professor H. Fujita and Dr. A. Teramoto at Osaka University.
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