Synthesis and Applications of Polymers Containing Metallacyclopentadiene Moieties in the Main Chain

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Summary: Organometallic polymers containing metallacycles in the main chain were prepared by the reactions of diynes with low-valent organometallic complexes such as $CpCo(PPh_3)_2$, $CP_2Ti(CH_2{=}CHC_2H_5)$, and $(^iPrO)_2Ti(CH_2{=}CHCH_3)$. Their polymer reactions involving the conversion of the main chain structures gave rise to polymers containing functional groups in their main chain repeating units. Design and synthesis of organometallic polymers that potentially serve as novel functional materials are also described.

Keywords: metallacycles; metallocenes; organometallic polymers; polymer reactions; reactive polymers

Introduction

Polymers containing reactive organometallic components in the main chain are potentially useful to create new reactive polymers that can yield organic polymers with versatile main chain functionality. Incorporation of organometallic cores with unique geometry and/or characters such as electrochemical properties may also be useful to design functional materials. Accordingly, we have been working on the synthesis of polymers with organometallic repeating units such as cobaltacyclopentadiene and titanacyclopentadiene moieties in the main chain. This article covers the results obtained recently in our group related to the synthesis and applications of organometallic polymers.

Synthesis of Cobaltacyclopentadiene-Containing Polymers

According to Yamazaki and his co-workers, cobaltacyclopentadiene derivatives are readily accessible by the reaction of $CpCo(PPh_3)_2$ (**1**) and acetylene derivatives.[1] On the basis of the air-stability and moderate reactivity of the cobaltacyclopentadiene derivatives, polymers

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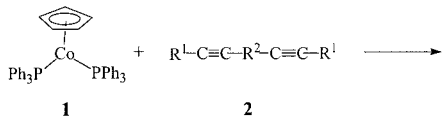
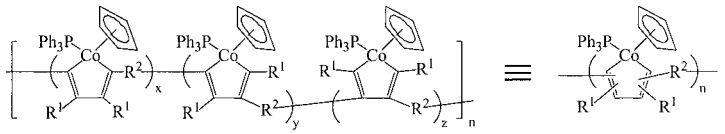
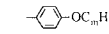
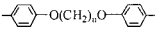
containing the corresponding units are attractive to realize novel kinds of reactive and functional materials. Accordingly, the polymerization of $CpCo(PPh_3)_2$ (**1**) and diynes (**2**) was performed in toluene at 50-60 °C, from which polymers containing cobaltacyclopentadiene moieties in the main chain (**3**) were obtained in high yields (Scheme 1).[2] The brown-colored polymers (**3**) thus obtained are soluble in organic solvents and are stable under air, although they are occasionally contaminated with cyclobutadienecobalt moieties (~10%). In terms of the regiochemistry of the main chain connections at each cobaltacyclopentadiene unit, it is possible to form three regioisomeric units (i.e., the connections through 2,5-, 2,4-, and 3,4-positions of the metallacycles) which can be controlled to some extent by the substituents on the diyne monomers. That is, diynes with less sterically hindered lateral substituents such as **2b** and **2c** gave rise to polymers with a higher content of the 2,5-linkage (**3b**: ~70% and **3c**: ~100%). However, the solubility of the polymers in organic solvents decreased as the 2,5-content increased.



1 **2**



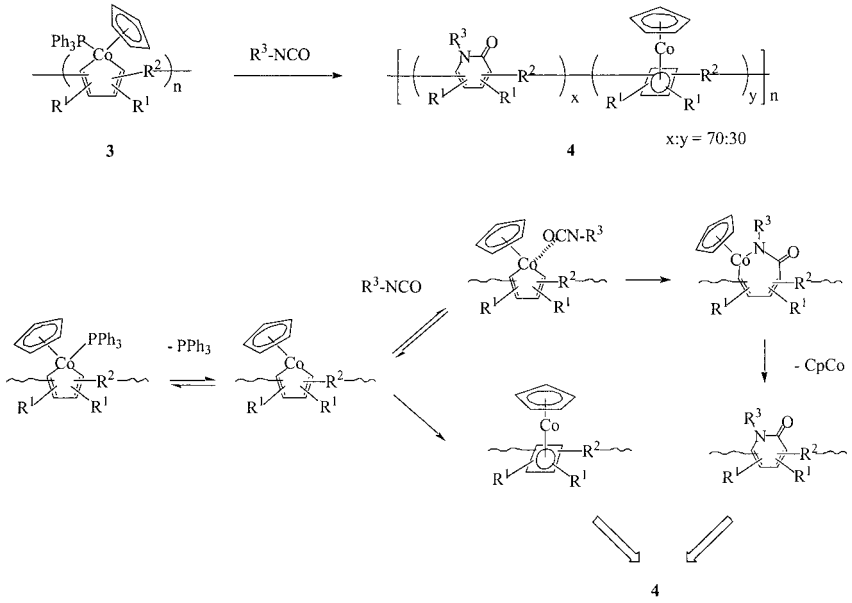
3

	a	**b**	**c**	**d**
R^1 =		-Bu^n	-Me	
R^2 =				

Scheme 1

In accordance with the decomposition temperature of the cobaltacyclopentadiene derivatives (e.g., 193-194 °C for a tetraphenyl substituted cobaltacyclopentadiene[1a]), the organocobalt polymers (**3**) were found to start decomposing at approximately 200 °C by the thermogravimetric

analyses (TGA) and two-step decomposition was observed in all the organocobalt polymers. The first decomposition at about 200 °C can be attributed to the rearrangement of the cobaltacyclopentadiene moieties into the cyclobutadienecobalt which accompanies the elimination of triphenylphosphine (vide infra) and the second one above 400 °C to the decomposition of the organic fragments. No peak for either the glass transition (T_g) nor the melting temperature (T_m) is observable for **3a** in its differential scanning calorimetric (DSC) analysis. Using diynes with flexible spacers (**2d**), it is possible to design organocobalt polymers (**3d**) which exhibit T_g and T_m.[3] The polymers (**3d**) have T_g at -20~130 °C, depending upon the length of the aliphatic spacers. Some of the polymers also exhibit T_m in the range of 60~120 °C.

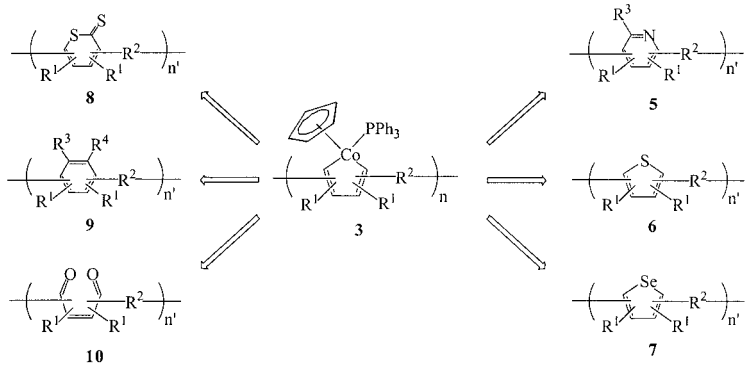


Scheme 2

Conversion into Organic Polymers with Various Main Chain Structures

As mentioned above, the organocobalt polymers are stable under air. However, they serve as novel type of reactive polymers whose main chain can be reconstructed by polymer reactions under appropriate conditions. Conversion of the metallacycle units in the organocobalt polymers

(**3**) into organic functional groups is attainable by the polymer reactions with appropriate reagents. As shown in Scheme 2, polymers having pyridone moieties in the main chain (**4**) were produced from **3** by the reaction with isocyanates at 120 °C.[4] The content of the 2-pyridone moieties reaches about 70% with respect to the starting cobaltacyclopentadiene units. The remaining 30% was found to be η^4-cyclobutadienecobalt moieties as a result of the rearrangement reaction.



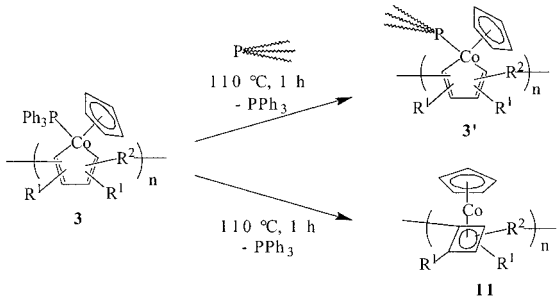
Scheme 3

As summarized in Scheme 3, the organocobalt polymers can be converted into various kinds of polymers with versatile functional groups in the main chain. That is, polymers containing pyridine (**5**), thiophene (**6**), selenophene (**7**), dithiolactone (**8**), phenylene (**9**), and diketone moieties (**10**) were obtained by the reaction with nitriles, sulfur, selenium, carbon disulfide, acetylenes, and oxygen, respectively.[5-10] The organic polymers derived from the organocobalt polymers with fully aromatic main chain systems (e.g., the thiophene-containing polymers from **3a-c**) exhibited the properties of π-conjugated oligomers judging from their UV-vis spectra and the electrochemical properties, probably due to the regio-irregularity of the main chain connection of the organocobalt polymers. The efficiency of these polymer reactions is affected by the reagents and the reaction conditions, which ranged from 70-100%. Even in the cases of polymer reactions that do not proceed in a quantitative fashion, no distinct decrease of the molecular weight of the produced polymers was observed because the lower efficiency of the

polymer reactions does not mean the scission of the main chain of the polymers but the conversion into other structures such as the cyclobutadienecobalt unit.

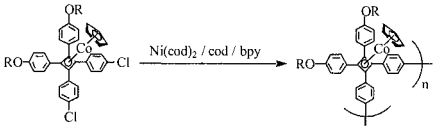
Conversion into Other Organocobalt Polymers

On heating the organocobalt polymers (**3**) in the presence of appropriate ligands such as trialkylphosphines, triphenylphosphine on the organocobalt polymers (**3**) can be replaced quantitatively by the added ligands, by which the properties such as the solubility of the polymers can be modified (Scheme 4).[11]



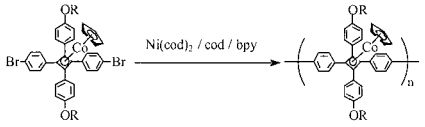
Scheme 4

Without the addition of ligands, the thermal treatment of the polymers (**3**) gave rise to yellow-colored polymers (**11**) containing η^4-cyclobutadienecobalt moieties as a result of the thermal rearrangement reaction.[12] This reaction seems to proceed by the dissociation of the ligand followed by the elimination of the cobalt. The cyclobutadienecobalt-containing polymers (**11**) are also stable under air and soluble in organic solvents such as chloroform, THF, and *N,N*-dimethylformamide (DMF). The polymer (**11a**) produced from **3a** exhibited good thermal stability and the 5% weight loss was observed at 480 °C in its TGA. The cobaltacyclopentadiene-containing polymers with flexible spaces (**3d**) also give rise to cyclobutadienecobalt-containing polymers (**11d**) by the thermal rearrangement. The resulting cyclobutadienecobalt-containing polymers (**11d**) also have T_g and T_m.[3]



12A **13A**

Yellow Viscous Gum
Mesophase *ca.* 58-184 °C
M_n = 8000-13600



12B **13B**

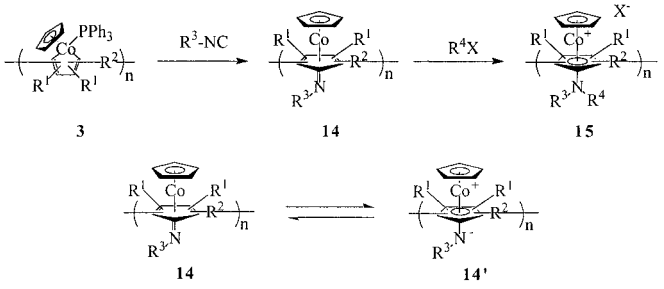
R = -$C_6H_{13}{}^n$ ~ -$C_{16}H_{33}{}^n$

Yellow Powder (partly soluble)
Mesophase *ca.* 156-280 °C
M_n = 16700-22000

Scheme 5

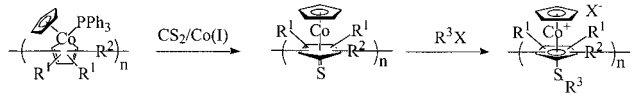
Unique functional materials containing cyclobutadienecobalt moieties might be designed on the basis of their chemical and thermal stability, and of the peculiar square geometry of the cyclobutadiene ligands. Reflecting upon the squarer geometry of the cyclobutadiene moieties, thermotropic liquid crystalline polymers with regioregular main chain connections can be designed by the polycondensation of the regioisomerically pure organocobalt monomers.[13-16] For example, the Ni(0)-promoted dehalogenation polycondensation of both 1,2- and 1,3-regioisomerically pure bifunctional (η^5-cyclopentadienyl)(η^4-cylobutadiene)cobalt complexes (**12A** and **12B**) yields zigzag and rigid rod π-conjugated polyarylenes (**13A** and **13B**), respectively (Scheme 5).[15] Both of these polymers exhibit thermotropic liquid-crystalline behavior, where the zigzag type polymers (**13A**) exhibit thermotropic liquid crystals in lower temperature range and higher solubility in organic solvents compared to the rigid rod type polymers (**13B**). Using a mixture of **12A** and **12B** as a monomer for the polycondensation, the liquid crystalline properties of the polymers could be varied by the ratio of the two isomers.[17] Similar to the cases of the conversion of the organocobalt polymers (**3**) into organic polymers, **3** can also be converted into other organometallic polymers by the reactions with appropriate reagents. Polymers having (η^5-cyclopentadienyl)(η^4-iminocyclopentadiene)cobalt moieties in the

main chain (**14**) were obtained by the reaction with isocyanides (Scheme 6).[18] It is of note that the efficiency of the polymer reaction was quantitative and the polymers produced exhibit a unique solvatochromism. That is, a polymer solution exhibits a reversible color change from purple to red by varying the nature of the solvent (e.g., purple in benzene and red in methanol). This color change might be ascribable to the structural change between the neutral (η^4-iminocyclopentadiene)cobalt (**14**) and the zwitterionic cobalticenium unit (**14'**). The subsequent polymer reaction of **14** with alkyl halides gives polymers containing cobalticenium units (**15**) although the efficiency of the alkylation was not quantitative due to the precipitation of the polymer during the reaction. The electrochemical analysis of **15** suggests the presence of the electronic interaction between the plural organometallic centers.



Scheme 6

It is reported that the reaction of cobaltacyclopentadiene derivatives with carbon disulfide gives unsaturated dithiolactones in moderate yields[1k] by which dithiolactone-containing polymers (**8**) can be produced from **3** as described above. On the contrary, the addition of an equimolar amount of Co(I) complexes such as CpCo(cod) to the reaction system provided an entirely different result. In this case, the dithiolactones were not detected at all but (η^4-cyclopentadiene)cobalt complexes are obtained in excellent yields.[19] On the basis of this reaction, analogous cobalticenium-containing polymers (**16**) are also obtainable by the reaction of the polymers (**3**) with carbon disulfide in the presence of a Co(I) complex, followed by the S-alkylation (Scheme 7).[20]

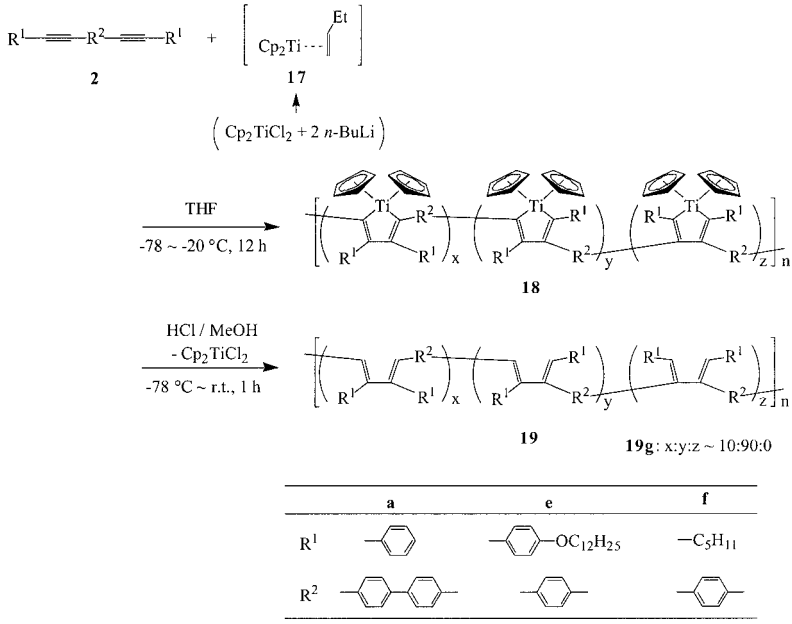


3 16

Scheme 7

Synthesis and Reactions of Titanacyclopentadiene-Containing Polymers

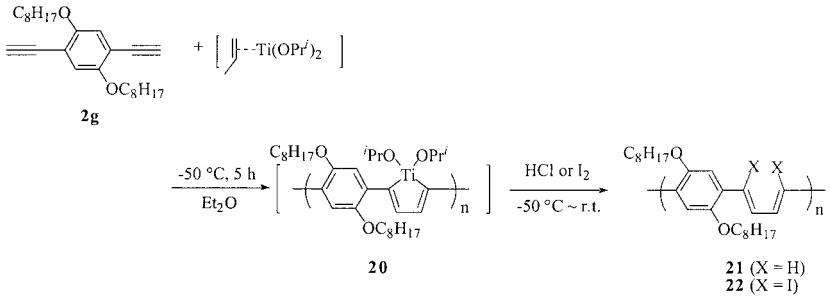
Polymers containing other metallacycle units are attractive for creation of novel reactive polymers leading to versatile organic functional polymers. As described by Tilley et al., zirconacyclopentadiene-containing polymers can be prepared by means of the analogous metallacyclization process between a low-valent bis(cyclopentadienyl)zirconium and diynes. The resulting zirconium-containing polymers also reveal interesting reactivity giving rise to organic polymers diene and heterocyclic moieties in the main chain.[21] Owing to the recent progress of the chemistry of titanacycles,[22] polymers possessing titanacyclopentadiene units are also potentially attractive for the creation of main chain reactive materials. On the basis of the titanacycle formation process described recently by Takahashi et al.,[22a] it is possible to prepare titanacyclopentadiene-containing polymers from diynes (**2**) and a low-valent titanocene derivative (**17**) generated from bis(cyclopentadienyl)titanium dichloride (Scheme 8). The resulting polymers (**18**) are stable at ambient temperature under argon atmosphere.



Scheme 8

The hydrolytic work-up of the polymers (**18**) gives rise to diene-containing polymers (**19**) in moderate yields (M_n ~ 4000). The regioisomeric linkage of the main chain of **18** at the titanacycle moieties must be dependent upon the diynes used and the polymers (**18a** and **18e**) may have statistical distribution of 2,5-, 2,4-, and 3,4-linkages although these units are difficult to be distinguished by the spectroscopic methods. In the case of the polymer (**18f**), the regiochemistry could be determined by the model experiment. That is, the titanacycles obtained from 1-heptynylbenzene, two phenyl substituents are located at the 2,4- and the 2,5-positions (2,4-:2,5- = 90:10) judging from their hydrolysis products. Accordingly, the main chain of the polymer (**18f**) is supposed to be connected through the 2,4- and the 2,5- positions of the metallacycle moieties. Because of the rather low content of the 2,5-connection, an effective linkage for π-conjugation, the polymer (**19f**) produced exhibited a relatively small red shift in the UV-vis spectrum in comparison with the model dienes. The result can also be taken to mean

that the polymer (**18f**) produced from the low-valent titanocene derivative and diyne (**2f**) has the major 2,4- and the minor 2,5- connections through the titanacycle units.



Scheme 9

As shown in Scheme 9, titanacyclopentadiene-containing polymers with a regiospecific main chain connection could be obtained by the polymerization of terminal diynes (**2g**) and a low-valent titanium generated from titanium(IV) isopropoxide.[24] The polymerization proceeds at –78 ~ –50 °C and the polymers produced should be converted into organic polymers without isolation because they are not stable at ambient temperature. According to the report of Yamaguchi et al.,[22b] 1,4-disubstituted dienes are produced in the reaction of terminal acetylenes such as phenylacetylene followed by the hydrolysis. In accordance with their report, the polymerization of terminal diynes such as 1,4-diethynyl-2,5-dioctyloxybenzene (**2g**) gave rise to polymers with regioregular backbone (**20**). The hydrolysis or the iodination of the titanacycle units gave rise to polymers with diene units (**21** and **22**, respectively). For example, the treatment of the polymer (**20**) with iodine provided an iodinated diene-containing polymer (**22**) in 81% yield (M_n = 7,700). Owing to the alkoxy substituents, both the polymers (**21** and **22**) are soluble in organic solvents. The regioregularity of the main chain affects largely on the properties of the diene-containing polymers. The polymer (**21**) produced by the hydrolysis of the titanacyclopentadiene-containing polymer exhibits a clear bathochromic shift of the UV-vis absorption compared to that of a model compound (**23**) (Figure 1). That is, the absorption maximum (λ_{max}) of the polymer (λ_{max} = 470 nm) appeared at longer wavelength by 115 nm than

that of the model compound (λ_{max} = 355 nm). The polymers also exhibit luminescence upon irradiation of the UV-vis light.

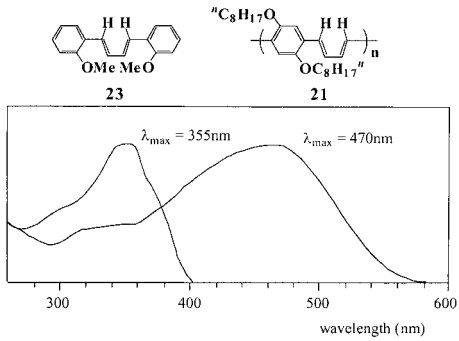
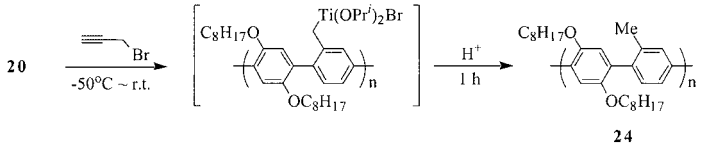


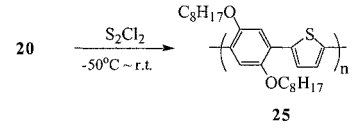
Figure 1. UV-vis spectra of the diene-containing polymer (**21**) and its model compound (**23**) (measured in $CHCl_3$).

Derivatives of poly(p-phenylene) (**24**) are produced by the reaction of the titanacyclopentadiene-containing polymers (**20**) with propargyl bromide (Scheme 10).[25] Similar to the case of the chemical conversion into diene-containing polymers, the polymer reaction proceeds under very mild conditions and yellow powdery polymers produced are soluble in organic solvents (~ 80% yield, M_n~ 5,000). Because of the π-conjugated backbone, the poly(p-phenylene) derivatives (**24**) obtained in this study have the UV-vis absorption in longer wavelength range (λ_{max} = 329 nm) compared to that of model compounds (λ_{max} = 276 nm), p-terphenyl derivatives produced from phenylacetylene derivatives via the titanacyclopentadiene. The polymers also exhibited photoluminescence whose emission maximum also shifts to the longer wavelength region with respect to that of the model compounds.



Scheme 10

Thiophene-containing polymers (**25**) are likewise produced by the reaction of the titanacyclopentadiene-containing polymers (**20**) with sulfur monochloride under mild conditions (Scheme 11).[26] The yield of the soluble fraction was a little lower (~ 50%), because the produced polymers are partially insoluble in organic solvents. As shown in Figure 2, the brown powdery polymers thus obtained exhibit a substantial bathochromic shift in the UV-vis and photoluminescence spectra in comparison with those of the corresponding model compounds, a 2,5-diarylthiophene derivative (**26**).



Scheme 11

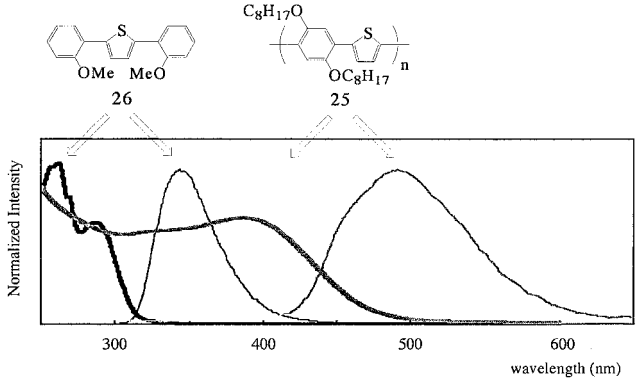
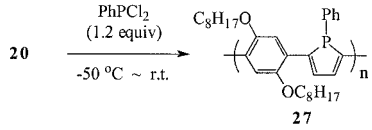


Figure 2. UV-vis (▬) and photoluminescence (—) spectra of the thiophene-containing polymer (**25**) and its model compound (**26**) (measured in $CHCl_3$).

The titanacyclopentadiene-containing polymers (**20**) can be converted into π-conjugated phosphole-containing polymers (**27**) by the reaction with dichlorophenylphosphine (Scheme 12).[27] Similar to the case of the above-mentioned conversion reaction into thiophene-containing polymers, the produced polymers are partially insoluble in organic solvents. The polymers thus obtained revealed λ_{max} at about 500 nm in the UV-vis spectra and the emission

maximum at 600 nm, supporting the π-conjugated character of the resulting phosphole-containing polymers (Figure 3).



Scheme 12

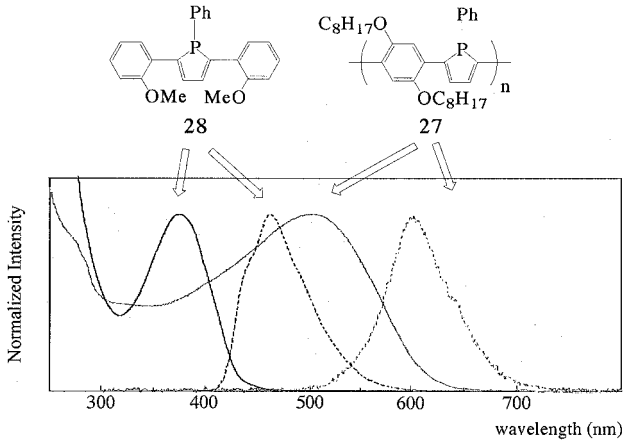


Figure 3. UV-vis (—) and photoluminescence (----) spectra of the phosphole-containing polymer (**27**) and its model compound (**28**) (measured in $CHCl_3$).

Conclusion

Novel polymers possessing reactive sites in the main chain have been successfully prepared by the reactions of diynes with low-valent transition metal complexes such as cobalt(I) and titanium(II). The cobaltacyclopentadiene-containing polymers are stable under air and can be handled as if they are conventional organic polymers. However, they exhibit versatile reactivity under appropriate reaction conditions. That is, the organocobalt polymers serve as reactive precursors for a variety of polymers containing functional groups such as heterocycles, benzene rings, and unsaturated ketones in their repeating unit. The organocobalt polymers can also be

converted to other organocobalt polymers with unique repeating units such as cyclobutadienecobalt and cobalticenium moieties. The titanacyclopentadiene-containing polymers are likewise obtained by the metallacyclization process of diynes with low-valent titanium complexes. Although the two series of the titanacyclopentadiene-containing polymers are not stable under air, they also serve as reactive precursors giving rise to organic polymers with versatile main chain structures.

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