2017年3月

関西大学審査学位論文

構造制御したポリマーの合成と人工光合成への応用

Syntheses of Structure-controlled Polymers and their Application to Artificial Photosynthesis

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Kansai University
2017

博士論文要旨

理工学研究科　総合理工学専攻
＜研究領域＞　無機・物理化学
＜学籍番号＞　15D6005
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＜論題＞

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Syntheses of Structure-controlled Polymers and their Application to Artificial Photosynthesis

＜概要＞

現在，化石燃料の枯渇、及びその大量消費による二酸化炭素の増加が地球温暖化の原因となっており、化石燃料に代わる新規クリーンエネルギーの開発が求められている。 そういった背景から水を水素と酸素に分解する人工光合成系の研究が盛んに行われている。人工光合成系の研究を行う上で、三つの実現課題がある：

（1）光エネルギーを効率良く捕集し、反応中心に集める(光誘起エネルギー移動)。

（2）光誘起電子移動反応後の逆電子移動反応を抑制し，効率の良い長寿命電荷分離状態を形成する。

（3）光誘起電子移動反応で生じた電子を次の反応に利用する（多電子酸化還元反応)。

本研究では人工光合成の実現を目指し、構造制御したポリマーの合成及び特性を検討した。また、合成できたポリマーを用いて人工光合成への応用を試した。それらの結果について報告する。

≪各章の要旨≫

CHAPTER 1　新規擬リビング重合法による構造制御したメチルピロール系ポリマーの合成と人工光合成への応用

この章では、新規擬リビング付加縮合重合法を開発した。従来の付加縮合重合と比較し、新規擬リビング付加縮合重合法ではポリマーの構造制御可能になる。また、この新規擬リビング付加縮合重合法を用いて、構造制御したポリマーの性能評価と人工光合成への応用を検討したので、本章で報告する。

Section 1-1. 新規擬リビング付加縮合重合法の開発

通常の付加縮合重合反応では反応がランダムに起こり、ポリマーの構造や分子量などの制御ができない。これに対して、精密重合であるリビング重合法を用いた場合ポリマーの構造や分子量などの制御ができる。本来、付加縮合重合は逐次重合で進行するためリビング重合は本質的に不可能と思われてきた。本節ではモノマー、ダイマーの異なる反応性の

特性を利用して、新規擬リビング付加縮合重合の開発と証明について報告する。

Section 1-2. A,B-ブロック型両親媒性ポリマーを介した異相間のエネルギー移動

新規擬リビング付加縮合重合法を用いて、疎水部にエネルギードナー、親水部にエネルギーアクセプターを有するA,B-ブロック型両親媒性ポリマーを合成した。人工光合成のシステムにおける異相間の反応は重要であり、これを利用して、光化学反応により生成される高エネルギー物質の効率的な分離に利用できる。そこでA,B-ブロック型両親媒性ポリマーを介した異相間のエネルギー移動が起こったことについて報告する。

Section 1-3. 分岐型ポリマーの合成と光捕集系の構築

太陽光を効率よく捕集し反応中心に向かうエネルギー移動を行うことは光合成系の基本プロセスである。天然の光合成では、アンテナクロロフィルと呼ばれる光捕集部分を形成し，各色素間を繰り返しエネルギー移動することによって，反応中心に送られる。本節では、新規擬リビング付加縮合重合法を用いて、分岐部にエネルギードナー、中心部にエネルギーアクセプターを有する分岐型ポリマーを合成した。合成したポリマーを利用して、光合成の最初のステップである多光子捕集を実現するもので、効率の良い光捕集系の構築に成功した。

Section 1-4. 光捕集後の電子移動を可能とする分岐型ポリマーの合成と人工光合成アンテナ反応中心への応用

前節で効率の良い光捕集系の構築を報告した。本節では、光捕集系の続きとして、分岐型ポリマーの中心部にあるエネルギーアクセプターの隣に電子アクセプターを導入した。これにより、エネルギーが分岐部分にあるエネルギードナーから効率良く中心部にあるエネルギーアクセプターに集められ、その後にこのエネルギーを利用して、電子ドナーーアクセプター間の電子移動が起きる。この系では効率的な光捕集と光誘起電子移動を含め、天然光合成のアンテナ反応中心とよく似ている。この結果について報告する。

CHAPTER 2　構造制御したベンゼン型ポリマーの合成と人工光合成への応用

この章では、安定なベンゼン誘導体とアルデヒドの付加縮合重合で、ベンゼン型ポリマーを合成し、高分子ワイヤーとしての電子移動性能を評価した。また、エネルギー準位が異なる2種類のベンゼン型ポリマーを利用し、異なるエネルギー準位を有する新規A,B-ブロック型ポリマーを分子ワイヤーとした多段階電子移動反応も検討したので、本章で報告する。

Section 2-1.　ベンゼン型ポリマーの合成と高分子ワイヤーとしての光誘起電子移動評価

人工光合成系構築には，長寿命電荷分離状態を形成させる事が不可欠である。この課題を達成する方法の一つに，電子ドナーと電子アクセプターをπ-共役系化合物で結合させ，そのπ-共役系を通じて電子をドナーからアクセプターへ送るという，遠距離電子移動系の構築が可能な分子ワイヤーという概念がある。本節ではベンゼン誘導体とアルデヒドの付加縮合体である飛石型共役系ポリマー（ポリマー自体は共役した構造ではないが、共役系分子であるベンゼンが sp^3－炭素で結合し、飛石的に共役系が存在するポリマーである)を高分子ワイヤーに用いた光誘起エネルギー電子移動反応について研究を行った。

Section 2-2.　異なるエネルギー準位を持った高分子ワイヤーの合成と光化学的挙動

長寿命電荷分離状態を形成するため、天然光合成の Z スキームを模倣して、多段階電子移動系の構築が必要となる。ここで光誘起電子移動反応後の逆電子移動を抑制するため、ドナーを有する高エネルギー準位部、アクセプターを有する低エネルギー準位部からなるエネルギーレベルの異なる A,B ブロック型ポリマーを、トリヒドロキシベンゼン及びそのエステルを用いて合成を試みた。この系では、光の照射による励起された電子は高いエネルギー準位部分のドナーから低いエネルギー準位部分のアクセプターへ電子移動ができるが、逆にドナーが低エネルギー準位部にある場合、電子移動が起こらなかった。このことは高分子ワイヤーに電子移動の方向性を持たせたことを意味し、多段階電子移動を発生させ、逆電子移動反応を抑制し、光誘起電子移動反応後の電荷分離状態を長寿命させることにつながることを報告する。

以上

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Section 1-3

Section 1-4

CHAPTER 2

Section 2-1

Abbreviations used in this study are as follows

Mepyr	1-methylpyrrole
BS	benzaldehyde-2-sulfonic acid sodium salt
2-EtPyr	2-ethylpyrrole
PeA	3-perylenecarboxaldehyde
p-TS	*p*-toluenesulfonic acid monohydrate
MePyr-BS	Methylpyrrole type polymer prepared by 1-methylpyrrole with benzaldehyde-2-sulfonic acid sodium salt
iPB	4-isopropylbenzaldehyde
PyA	1-Pyrenecarboxaldehyde
AQ	anthraquinone
MV^{2+}	methylviologen
iPB(Py)-BS(Pe)	A, B-block amphiphilic polymer containing Py unit in the hydrophobic phase and the Pe unit in the hydrophilic phase
iPB(Py)-BS(none)	A, B-block amphiphilic polymer containing Py unit in the hydrophobic phase
iPB(none)-BS(Pe)	A, B-block amphiphilic polymer containing Pe unit in the hydrophilic phase
MePyrA	1-Methyl-2-pyrrolecarboxaldehyde
Py(6)-Pe(1)	Branched polymer indicates that the molar ratio of the Py unit to the Pe unit is 6:1
Py(3)-Pe(1)	Branched polymer indicates that the molar ratio of the Py unit to the Pe unit is 3:1
Py(1)-Pe(1)	Branched polymer indicates that the molar ratio of the Py unit to the Pe unit is 1:1
Py(6)-Pe(0)	Branched polymer indicates that the molar ratio of the Py unit to the Pe unit is 6:0
Py(0)-Pe(1)	Branched polymer indicates that the molar ratio of the

	Py unit to the Pe unit is 0:1
AQA	2-Anthraquinonecarboxaldehyde
Py(6)-Pe(1)-AQ(2)	Branched polymer indicates the molar ratio of the Py, Pe, and AQ units; the ratio in Py(6)-Pe(1)-AQ(2) is 6:1:2
1, 2, 3THB	Pyrogallol (1, 2, 3- trihydroxybenzene)
1, 3, 5THB	Phloroglucinol (1, 3, 5- trihydroxybenzene)
THB (non)	Benzene type polymer prepared by trihydroxybenzene with benzaldehyde-2-sulfonic acid sodium salt
THB (Pe)	Benzene type polymer containing Pe unit
THB (AQ)	Benzene type polymer containing AQ unit
THB (Pe-AQ)	Benzene type polymer containing Pe unit and AQ unit
ester (Pe-AQ)	Ester type polymer containing Pe unit and AQ unit
ester (Pe)- THB (AQ)	A, B-block type polymers having different energy levels containing Pe unit in ester part (high energy level) and AQ unit in THB part (low energy level)
ester (AQ)-THB (Pe)	A, B-block type polymers having different energy levels containing AQ unit in ester part (high energy level) and Pe unit in THB part (low energy level)

GENERAL INTRODUCTION

Fossil fuels and global warming

There are three major forms of fossil fuels: coal, oil and natural gas. All three were formed many hundreds of millions of years ago before the time of the dinosaurs – hence the name fossil fuels. Now, total available energy from fossil fuels is 300 ~ 400 times the total amount of energy by human use.[1] At the same time the science and technology are developing, large amounts of fossil fuel are used. On the other hand, by use of fossil fuel, a huge CO_2 is discharged. At the same time as the reduction of fossil fuels, it has been a rapid increase of the concentration of CO_2 in atmosphere.

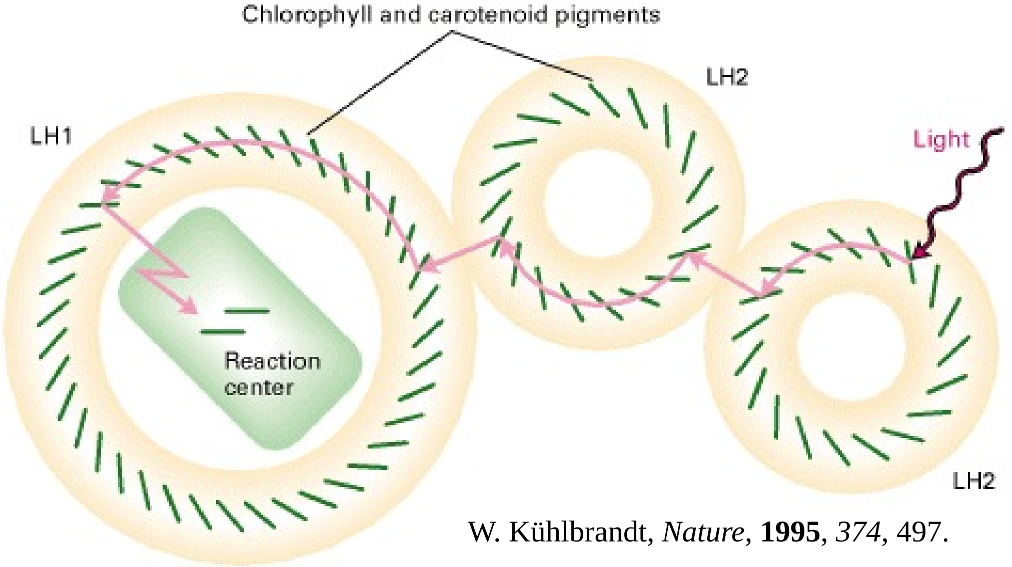
We know the global warming is mostly being caused by human activities, mainly increasing concentrations of greenhouse gases such as methane and CO_2.[2] Changes resulting from global warming may include rising sea levels due to the melting of the polar ice caps, as well as an increase in occurrence and severity of storms and other severe weather events. For the environment, the mitigation of global warming is needed. In order to mitigate global warming, we can reduce greenhouse gas emissions, or absorb greenhouse gas from the atmosphere. There is a large potential for future reductions in emissions by a combination of activities, including: energy conservation and increased energy efficiency; the use of low-carbon energy technologies, such as renewable energy, nuclear energy, and carbon capture and storage.[3-4]

Now, it has attracted attention in solar energy of the renewable energy. Solar energy is radiant light and heat from the Sun that is harnessed using a range of ever-evolving technologies such as solar heating, photovoltaics, solar thermal energy, solar architecture and artificial photosynthesis.[5-8] Artificial photosynthesis light energy conversion systems have been studied worldwide, in order to develop this system, it is essential to understanding the natural photosynthesis system.

Natural photosynthesis

Photosynthesis is a process used by plants to convert light energy into chemical energy that can be used for the organisms’ activities. This chemical energy is stored in carbohydrate molecules which are synthesized from CO_2 and H_20.[9] Photosynthesis occurs in two steps. In the first step, light-dependent reactions capture the light energy and use it to make the energy storage molecules ATP and NADPH. The second step, the light-independent reactions use these products to capture and reduce CO_2. In the light-dependent reaction, efficiently collect the light energy is very important in photosynthesis. Photosynthetic cells contain special pigments to absorb light energy. Different pigments respond to different wavelengths of visible light. In plants, photosynthesis takes place in chloroplasts, which contain the chlorophyll. Chloroplasts are surrounded by a double membrane and contain a third inner membrane, called the thylakoid membrane[10] that forms long folds within the organelle. Chlorophyll, the primary pigment used in photosynthesis, reflects green light and absorbs red and blue light most strongly.[11]The majority of light energy can be available absorbed by the chlorophyll and other pigments.

The absorption of light energy and its conversion into chemical energy occurs in multiprotein complexes, called photosystems, located in the thylakoid membrane. A photosystem has two closely linked components, an antenna containing light-absorbing pigments and a reaction center comprising a complex of proteins and two chlorophyll a molecules. Each antenna contains one or more light-harvesting complexes (LHCs), packed with chlorophyll a and, depending on the species, chlorophyll b and other pigments. LHCs promote photosynthesis by increasing absorption of 680 nm light and by extending the range of wavelengths of light that can be absorbed. Photons can be absorbed by any of the pigment molecules in each LHC. The absorbed energy is then rapidly transferred (in 10^{-9} s) to one of the two chlorophyll a molecules in the associated reaction center, where it promotes the primary photosynthetic charge separation. Within an LHC are several transmembrane proteins whose role is to maintain the pigment molecules in the precise orientation and position that are optimal for light absorption and energy transfer, thereby maximizing the very rapid and efficient process known as resonance transfer of energy from antenna pigments to reaction-center chlorophylls. As depicted in Figure 1, some photosynthetic bacteria contain two types of LHCs: the larger type (LH1) is intimately associated with a reaction center; the smaller type (LH2) can transfer absorbed light energy to an LH1.[12-13]



W. Kühlbrandt, *Nature*, **1995**, *374*, 497.

Figure 1. The structure of the bacterial light-harvesting complex LH2 suggests how absorbed light energy passes through the similar LH1 complex to its final destination, the special pair of bacterionchlorophylls in the reaction centre (RC), where it is used to propel an electron across the membrane.[13]

Then the energy of the light captured by LHCs is funneled to the two chlorophylls in the reaction center, where the primary events of photosynthesis occur. The energy of the absorbed light is used to remove electrons from a donor (H_2O), forming O_2, and then to transfer the electrons to an electron acceptor (quinone), at last transfer the electrons to the cytochrome b_6f complex. This process called photosystem II.[14-15]

$H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Electrons move from the cytochrome b_6f complex electron acceptor through a chain of electron transport molecules in the thylakoid membrane until they reach the ultimate electron acceptor, usually $NADP^+$, reducing it to NADPH. This process called photosystem I.[16]

$NADP^+ + 4H^+ + 4e^- \rightarrow NADPH$

Photosystem II and photosystem I are combined by the cytochrome b_6f complex, to build a multi-step electron transfer mechanism, called the Z scheme shown in Figure 2, to form a long distance and long life charge-separated state, and the electrons are used in the synthesis of NADPH. [17]

$2H_2O + 2NADP^+ \rightarrow 2H^+ + 2NADPH + O_2$

It is convenient to divide the photosynthetic process (light-dependent reaction) in plants into three stages [11, 18, 19]:

(1) Light harvesting which involves the absorption of sunlight to excite electrons in peripheral antennae of the photosynthetic systems and subsequent rapid excitation energy transfer to reaction centers

(2) Photoinduced electron transfer, which generates charge-separated states using this excitation energy.

(3) Using the electrons leading to the reduction of NADP$^+$ to NADPH.

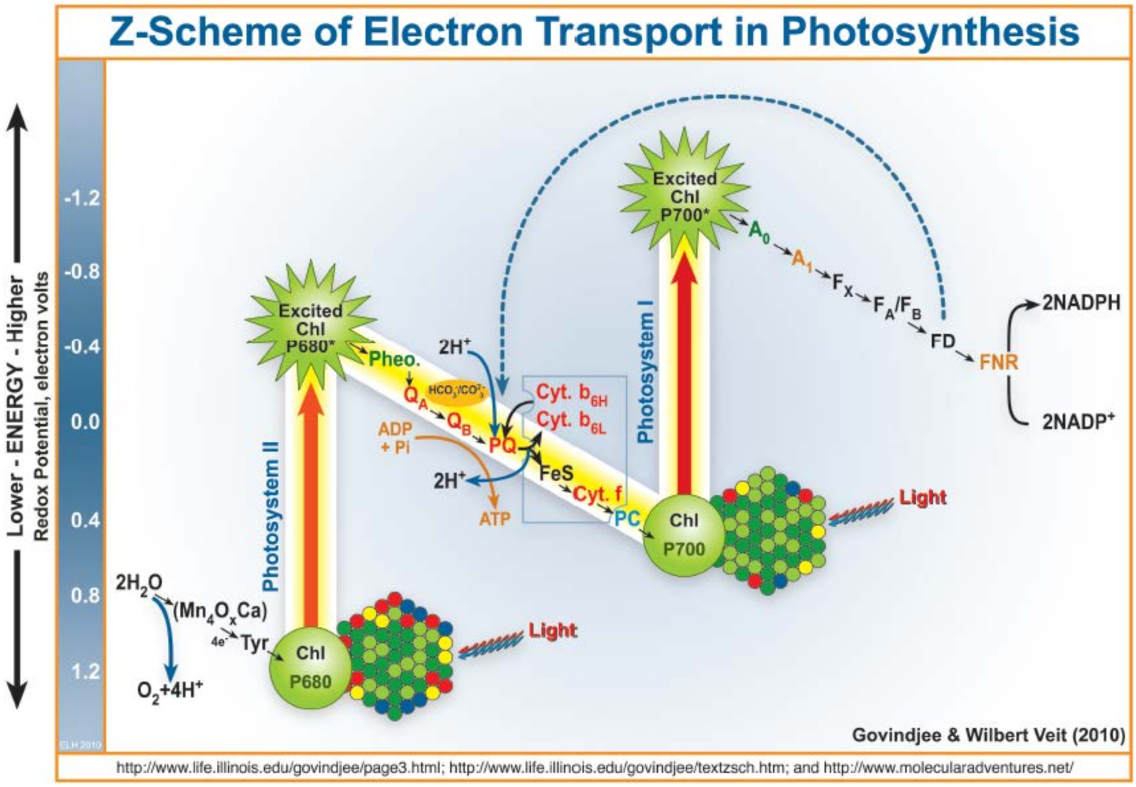


Figure 2. The Z scheme.

Artificial photosynthesis

Artificial photosynthesis is an artificial process that replicates the natural process of photosynthesis. Artificial photosynthesis that liking as natural photosynthesis, converts sunlight, H_2O, and CO_2 into carbohydrates and O_2 by using artificial process. It is commonly used to refer to any scheme for capturing and storing the energy from sunlight.

Since the artificial photosynthesis was first anticipated by Giacomo Ciamician in 1912,[8] the growth of artificial photosynthesis is rapid.[20-24] Now, based on the principle of artificial photosynthesis, there are two types of the artificial photosynthesis systems in the world: (a) Artificial photosynthesis system of water decomposition by using semiconductor; (b) Artificial photosynthesis system of water decomposition by using organic compounds which learning light-dependent reaction in the photosynthesis.

Type (a)

In 1972, Akira Fujishima discovered the photocatalytic properties of titanium dioxide, the so-called Honda-Fujishima effect,[25] which could be used for hydrolysis. In addition, in recent years Panasonic has developed an artificial photosynthesis system which converts CO_2 to organic materials by illuminating with sunlight at an efficiency of 0.2% by using nitride semiconductor and metal catalyst.[26] Toshiba has also developed an artificial photosynthesis technology that converts energy into carbon compounds from carbon dioxide at an efficiency of 1.5% by using multijunction semiconductor and gold nanocatalyst, the highest level yet recorded.[27]

Type (b)

By the study of natural photosynthesis (light-dependent reaction), we know there are three subjects can be used to realize the artificial photosynthesis:

Subject(1) Harvesting photon by the antenna molecules and transferring to the reaction center. (photoinduced energy transfer)

Subject(2) Preventing the charge recombination after the photoinduced electron transfer leading to form a long live charge-separated state efficiently.

Subject(3) Using the charge-separated state to the multi-redox reaction.

Many studies are studying on these subjects. For example, light harvesting[28-34] has been studied on the subject (1). Donor-acceptor systems[35-41] has been studied on the subject (2). Ruthenium complex systems[42-47] has been studied on the subject (3).

The objective of this study

The objective of this study is to realize the artificial photosynthesis by learning light-dependent reaction in the photosynthesis. There are three subjects as mentioned above can be used to realize the artificial photosynthesis. In this study, various kinds of structure-controlled polymers were prepared, and their applications to artificial photosynthesis by using these polymers are examined.

A brief summary for syntheses of structure-controlled polymers and their applications to artificial photosynthesis are as follows:

In **Chaper 1**, involving **Section 1**, **2**, **3**, and **4,** structure-controlled polymers prepared by pseudo-living addition-condensation polymerization of methylpyrrole with aldehyde and their application to study on subject (1) for artificial photosynthesis are described.

In **Chaper 2**, involving **Section 1** and **2**, syntheses of benzene type polymers and their application to study on subject (2) for artificial photosynthesis are described.

Section 1-1. A new type of pseudo-living addition-condensation polymerization

In general condensation-polymerization, e.g., the synthesis of polyesters and polyamides, the reactivities of the dimer, oligomer, and polymer are almost thermodynamically equal to that of the monomer. Therefore, condensation-polymerization is a form of step-growth polymerization, and control of the molecular weight and polymer structure are difficult because of the equal reactivity. In this section, a new type of pseudo-living addition-condensation polymerization was studied. The difference in the reactivity of the monomer and the other mers in the addition-condensation polymerization of pyrrole and aldehyde leads to precision polymerization, which allows for the control of the main structural properties of the polymer as well as the introduction of functional groups by the addition of different aldehydes.

Section 1-2. A, B-block amphiphilic polymer for interphase photoinduced energy transfer

In this section, an A, B-block amphiphilic polymer with energy donors and acceptors, each in a different block was prepared by the pseudo-living addition-condensation polymerization. The ability for a reaction to occur at the interphase is an important component in the construction of an artificial photosynthetic system because it allows for efficient separation of high energy substances generated by photochemical reactions. This type of polymer showed an interphase photoinduced energy transfer in a micellar system.

Section 1-3. Synthesis and characterization of branched polymers and efficient light-harvesting ability

Harvesting photon by the antenna molecules and transferring to the reaction center is the initial step of natural photosynthesis. Antenna chlorophyll, the primary pigment used in photosynthesis, the absorbed energy is rapidly transferred (in 10^{-9} s) between chlorophylls, and then transfer to a molecules in the associated reaction center. In this section, a branched polymer with high and low amounts of energy donors and acceptors was prepared by the pseudo-living addition-condensation polymerization. This type of polymer showed an efficient light-harvesting ability.

Section 1-4. Light-harvesting and electron transfer in a branched polymer for artificial photosynthetic antenna-reaction centers

The initial steps toward designing artificial reaction centers based on efficient light-harvesting have been studied in Section 1-3. In this section, another type of branched polymer was prepared by the pseudo-living addition-condensation polymerization to continue study of artificial photosynthesis. This branched polymer exhibits light-harvesting antenna parts, energy transfer to the polymer center, and electron transfer, as a simple model of an artificial photosynthetic system.

Section 2-1. Syntheses of benzene type step-π-conjugated polymer and study on photoinduced electron transfer

In order to realize the artificial photosynthesis, preventing the charge recombination after the photoinduced electron transfer leading to form a long live charge-separated state efficiently is necessary. For a long live charge-separated state, there is a concept that is capable of molecular wire of long-range electron transfer system. Electron donor and electron acceptor is bound with π-conjugated compound, the electron from the donor through the π-conjugated system to the acceptor, the long range electron transfer can prevent the charge recombination. In this section, we defined a step-π-conjugated polymer which alternately consists of a small π-conjugated molecule as like as a benzene unit and a sp^3-methine carbon. The benzene units have no coplanar each other. Therefore, no strong interaction exists between benzene units; however, superexchange and / or hopping of electrons occur. The polymer can work as a molecular wire with high efficiency electron transfer.

Section 2-2. Synthesis of A, B-block type polymers having different energy levels and study on photoinduced electron transfer

In order to form a long live charge-separated state, a multi-stage electron-transfer system based on Z scheme mimics has been studied. In this section, the long-range photoinduced electron transfer was considered using step-π-conjugated polymers with two different energy level blocks. The structure was controlled that donor was in high energy level part (A-block), and acceptor was in low one (B-block). The macromolecular wire with the different energy levels (A, B-block polymer) suggests an electron transfer with a one-way direction. It can form a long live charge-separated state by using this polymer.

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CHAPTER 1

Structure-controlled polymers prepared by pseudo-living addition-condensation polymerization of methylpyrrole with aldehyde and their application to artificial photosynthesis

Section 1-1

A new type of pseudo-living addition-condensation polymerization

1-1-1. Introduction

Addition-condensation polymerization is generally used in an industrial field of phenol formaldehyde resin, urea-formaldehyde resin, and so on. While in a special field, poly(pyrrolylenemethine) and its derivatives, which were prepared by the addition-condensation polymerization of pyrrole and aldehyde, were studied as narrow-band-gap polymers.[1-9] In our recent study, we showed that the water-soluble narrow-band-gap polymer with band-gap value of less than 0.19 eV[8] and the band-gap values were continuously controlled from 0.3 to 1.1 eV in aqueous solution.[9] This addition-condensation of pyrrole and aldehyde is also very familiar in the field of porphyrin synthesis.[10-13] Lindsey group has been considerably contributed in the porphyrin synthesis. In one of their studies, they showed that the reactivity of α-position of dipyrromethane was much higher than that of pyrrole.[13] This result is very important and interesting in the addition-condensation polymerization. Because this means that the reactivity of dimer, oligomer, and polymer is higher than that of monomer. The different reactivity of monomer and others can lead to a precision polymerization as follows. In the general condensation-polymerization, for example polyesters and polyamides, the reactivity of dimer, oligomer, and polymer is almost thermodynamically equal to that of monomer. Therefore, the condensation-polymerization is a form of step-growth polymerization and the control of molecular weight and polymer structure is difficult because of the equal reactivity. On the other hand, precision polymerizations have been studied in living anionic,[14-15] living cationic,[16-17] living free-radical,[18-21] and living ring-opening metathesis polymerizations.[22-25] These polymerizations are a form of chain-growth polymerization. Here, as a special precision polymerization, living chain-growth polycondensation has been studied.[26-29] In this condensation-polymerization, the reactivity of polymer end group to monomer is higher than that of monomer to monomer. Therefore, monomer preferentially reacts with the polymer end groups. In other words, the different reactivity of monomer and others in the addition-condensation polymerization of pyrrole and aldehyde can lead to the precision polymerization which is able to not only control polymer main structures, but also introduce functional groups by using different aldehydes.

In this section, we show the pseudo-living addition-condensation polymerization of 1-methylpyrrole (MePyr) and some aldehydes. We used MePyr instead of pyrrole because the resulting polymer prepared from MePyr is stable in air while that of pyrrole is not. The linear relationship of the Mw and the added amount of monomers means that this polymerization progresses like a living-polymerization.

1-1-2. Experimental

1-1-2-1. Materials

1-Methylpyrrole (MePyr), benzaldehyde-2-sulfonic acid sodium salt (BS), 2-ethylpyrrole (2-EtPyr), and 3-perylenecarboxaldehyde (PeA) were purchased from Tokyo Kasei Chemical Co., Ltd. *p*-Toluenesulfonic acid monohydrate (p-TS), and other reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. Unless stated otherwise, reagents and solvents were used without purification. 1-Methylpyrrole (Tokyo Kasei Chemical Co., Ltd., Tokyo, Japan) as a monomer was purified by distillation.

1-1-2-2. Measurements

The UV-Vis spectra were recorded on a V-670 spectrophotometer (JASCO).

Fluorescence spectra were recorded on a FP-8300 spectrophotometer (JASCO). ^{1}H-NMR spectra were recorded on a JEOL ECS-400 spectrometer (JEOL) working at 400MHz using TMS as the internal standard. DMSO-d^6 was used as the solvent for the polymer.

1-1-2-3. Polymerization

The polymerization of MePyr and equimolar BS:

MePyr (36.0 mmol) and BS (36.0 mmol) were dissolved in DMF (18 mL). A second solution containing p-TS (1.20 mmol, 18 mL DMF) was added to this solution at 10 °C. The resulting solution was divided into 16 equal parts. After 5 min, a portion of the resulting solution was poured into isopropyl alcohol (45 mL) with potassium hydroxide (KOH, 0.90 mmol). The resulting precipitate was washed with isopropyl alcohol and lyophilized (yield: 0.171 g, 35.0%). Other polymers obtained at different times were similarly prepared.

The pseudo-living addition-condensation polymerization of MePyr with BS by the continuous addition of monomers:

MePyr-BS (8 day) was prepared as follows:
Solution-A: MePyr (5.00 mmol), p-TS (0.167 mmol) in DMF (2.0 mL).
Solution-B: BS (2.5 mmol) in DMF (3.0 mL)
Solution-C: p-TS (1.33 mmol) in DMF (1.5 mL)
Solution-D: BS (17.5 mmol) and MePyr (17.5 mmol) in DMF (20 mL)

Solution-A was stirred (300 rpm) at 10 °C. Solution-B was continuously added to Solution-A for 24 h using a syringe driver (YSP-101, YMC Co., Ltd.). Then, Solution-C and Solution-D were simultaneously and continuously added for 168 h. The reaction was stopped by the addition of a sodium carbonate aqueous solution (5%, 3.2 mL) at 192 h. Isopropyl alcohol (240 mL) was added to the reaction mixture. The resulting precipitate was purified by reprecipitations from two times of DMF/isopropyl alcohol (48 mL/240 mL) and two times of water/isopropyl alcohol (36 mL/240 mL), and then dissolved in water. The polymer was obtained by freeze-drying (3.619 g, 66.7%). The other polymers were similarly prepared.

^{1}H NMR spectrum of MePyr-BS (8 day) polymer: Figure 1-1-2-1 shows the chemical structure and the NMR spectrum of MePyr-BS (8 day) polymer. Although the spectrum broadening is observed in the polymer, it also showed the signals of the polymer proton.

The peaks (6.47, 4.94 and 2.95 ppm) assigned to MePyr protons (a: terminal, b and d). The peaks (7.08 and 7.73 ppm) assigned to BS protons (e and f).

The number-average molecular weight was estimated by the signal intensity ratio of the terminal α-proton (a) and another proton attached to the benzene ring adjacent to the sulfo group (f).

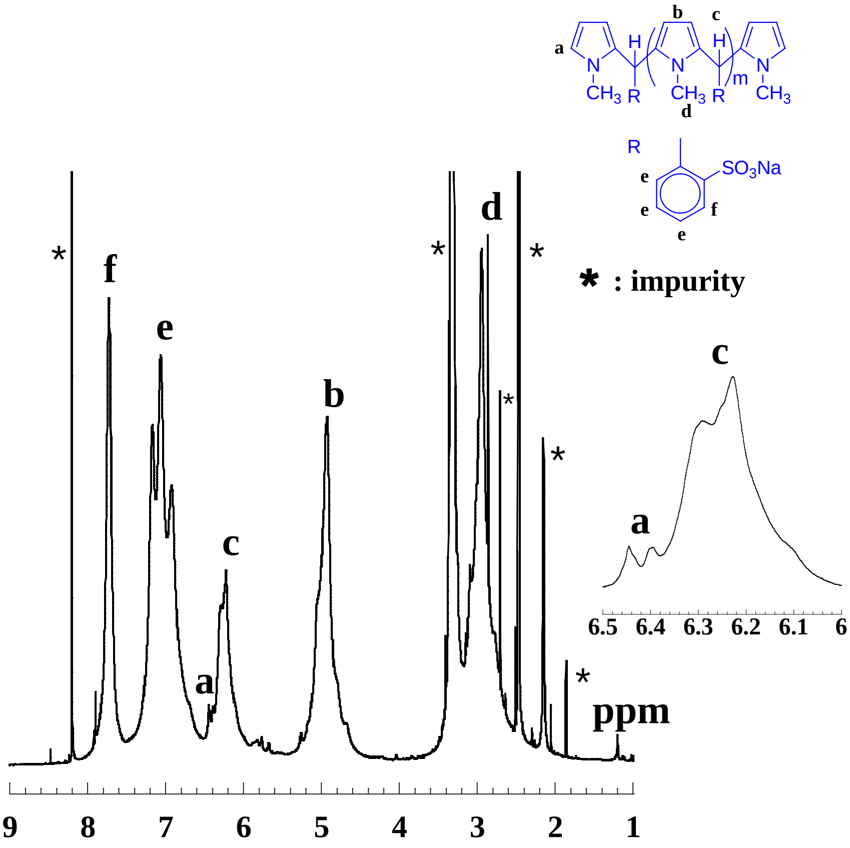


Figure 1-1-2-1. ^{1}H-NMR spectrum of MePyr-BS (8day) polymer in DMSO-d^{6}.

1-1-3. Results and discussion

1-1-3-1. Normal addition-condensation polymerizations of 1-methylpyrrole (MePyr) and aldehydes

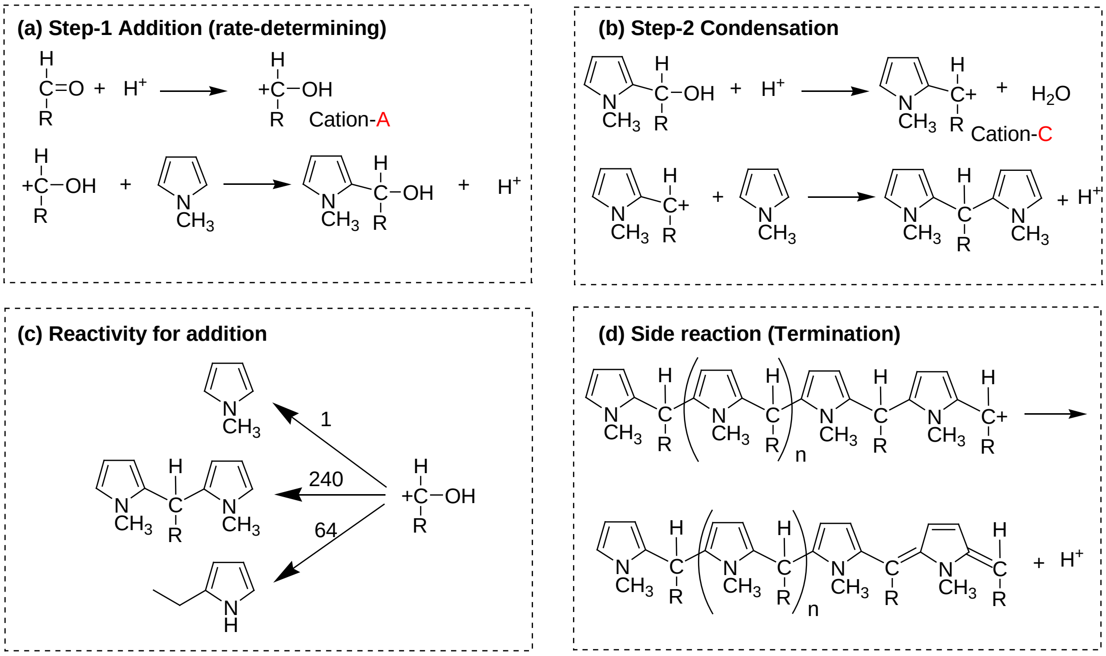
(a) Concept of reaction

Step-1 Addition

In Figure 1-1-3-1a, the reaction starts by proton attack at the oxygen of the formyl group, generating a carbocation (Cation-A). Cation-A then attacks the α-position of MePyr because the electron density is higher at the α-position than the β-position. However, the reactivity of Cation-A is low because it has a hydroxyl group, which is an electron donating group. This lower reactivity leads to a high selectivity for the reaction.

Step-2 Condensation

In Figure 1-1-3-1b, the MePyr-alcohol generated in Step-1 reacts with a proton, which allows water to leave, thus forming a new carbocation (Cation-C). Cation-C also attacks the α-position of MePyr and generates dipyrromethane. Here, the reactivity of Cation-C, which has no hydroxyl group, is much higher than that of Cation-A. Therefore, there is a lower selectivity for the reaction. This higher reactivity leads to a kinetic, rather than thermodynamic, driving force.


(a) Step-1 Addition (rate-determining)

(b) Step-2 Condensation

(c) Reactivity for addition

(d) Side reaction (Termination)

Figure 1-1-3-1. Basic addition-condensation polymerization of 1-methylpyrrole and aldehyde.

(b) Reactivity ratios of dipyrromethane and 2-ethylpyrrole to MePyr in addition

Normal

A solution of MePyr (5.00 mmol) and *p*-toluenesulfonic acid monohydrate (p-TS, 0.167 mmol) was prepared in dimethylformamide (DMF, 2.5 mL) and then mixed with another solution of 3-perylenecarboxaldehyde (PeA, 0.025 mmol, 2.5 mL DMF) at 10 °C. The reaction of PeA with MePyr was then spectroscopically monitored (Figure 1-1-3-2a). This reaction is pseudo-first order because of the excess amount of MePyr. The first order plot is shown in Figure 1-1-3-3. The rate constant estimated from the slope is 4.2×10^{-5} s^{-1}.

1/1000 of the amount of dipyrromethane

MePyr (5.00 mmol), benzaldehyde-2-sulfonic acid sodium salt (BS, 0.005 mmol), and p-TS (0.167 mmol) were dissolved in DMF (2.5 mL) and kept at 10 °C for 30 min. NMR confirmed that no BS remained, indicating a complete conversion. A solution of PeA (0.025 mmol, 2.5 mL DMF) was added to the MePyr solution containing 1/1000 of the amount of dipyrromethane at 10 °C. The reaction of PeA with MePyr and 1/1000 of the amount of dipyrromethane was then monitored by spectroscopic measurement (Figure 1-1-3-2b), and the first order plot is shown in Figure 1-1-3-3a. The rate constant estimated from the slope is 5.2×10^{-5} s^{-1}.

1/100 of the amount of 2-ethylpyrrole

MePyr (5.00 mmol), 2-ethylpyrrole (2-EtPyr, 0.05 mmol), and p-TS (0.167 mmol) were dissolved in DMF (2.5 mL). Another solution of PeA (0.025 mmol, 2.5 mL DMF) was added to the first solution at 10 °C. The reaction of PeA with MePyr and 1/100 of the amount of 2-EtPyr was then spectroscopically monitored (Figure 1-1-3-2c), and the first order plot is shown in Figure 1-1-3-3b. The rate constant estimated from the slope is 6.9×10^{-5} s^{-1}.

Reactivity ratio

The rate constants for MePyr, dipyrromethane, and 2-EtPyr are represented as M, D, and E, respectively.

M = 4.2×10^{-5} s^{-1}

From the 1/1000 of the amount of dipyrromethane system:

0.998 M + 1/1000 D = 5.2×10^{-5} s^{-1}

Therefore, D = 1.0×10^{-2} s^{-1}

The reactivity ratio of D/M = 1.0×10^{-2} s^{-1} / 4.2×10^{-5} s^{-1} = 240

From the 1/100 of the amount of 2-EtPyr system:

M + 1/100 E = 6.9×10^{-5} s^{-1}

Therefore, E = 2.7×10^{-3} s^{-1}

The reactivity ratio of E/M = 2.7×10^{-3} s^{-1} / 4.2×10^{-5} s^{-1} = 64

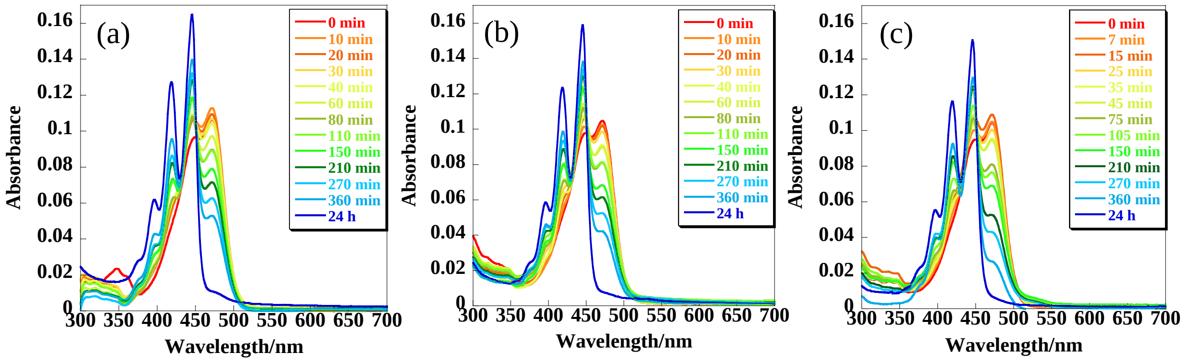


Figure 1-1-3-2. Absorption spectra at different reaction times for PeA (0.025 mmol) with (a) MePyr (5.00 mmol), (b) MePyr (5.00 mmol) and BS (0.005 mmol), and (c) MePyr (5.00 mmol) and 2-EtPyr (0.050 mmol) dissolved in DMF at 25 °C, cell length=1 cm.

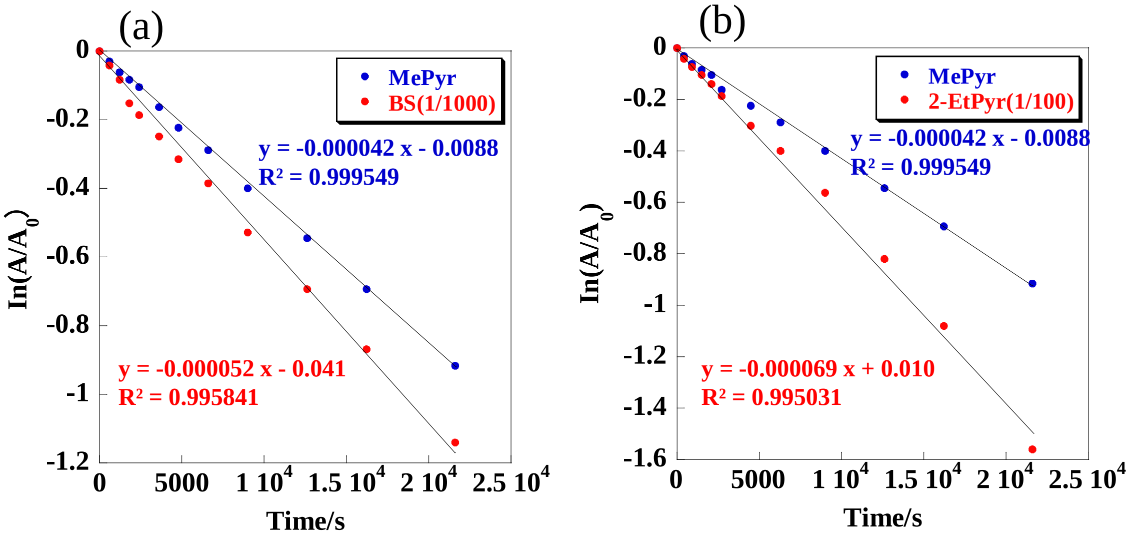


Figure 1-1-3-3. First-order plots for the reaction of PeA (0.025 mmol) with MePyr (5.00 mmol) (a) in the presence and absence of BS (0.005 mmol); (b) in the presence and absence of 2-EtPyr (0.050 mmol).

(c) Polymerization data

The polymerization of MePyr and equimolar BS:

The molecular weight was roughly determined by viscosity and NMR measurements. The number-average molecular weight was estimated by the signal intensity ratio of terminal α-proton and another proton attached to the benzene ring adjacent to the sulfo group (Figure 1-1-2-1). The Mark-Houwink-Sakurada formula was used to relate the viscosity and molecular weight:

$[\eta]=KM^{\alpha}$, $K = 1.21 \times 10^{-3}$, $\alpha = 0.464$.

Here, we used $[\eta]_{sp}/c$ at 0.40 g/dL instead of $[\eta]$ because $[\eta]_{sp}/c$ is almost constant at different concentrations in phosphate buffer (0.025 M KH_2PO_4 and 0.025 M $Na_2HPO_4 \cdot 12H_2O$).

Figure 1-1-3-4a shows the conversion-time curve. The conversion proceeded rapidly until 20 min (conversion of 67%), slowly increased from 20 to 60 min (conversion of 87%), and then became almost constant. Conversely, in the MW-conversion curve shown in Figure 1-1-3-4b, the MW gradually increased until 80% conversion was reached because the propagation reaction is very much like a chain-growth polymerization. Then the MW steeply increased at conversions above 80%, acting more like the step-growth polymerization of polyamide. Finally, the MW became constant because no further reactions occurred between the slow moving, high MW polymers.

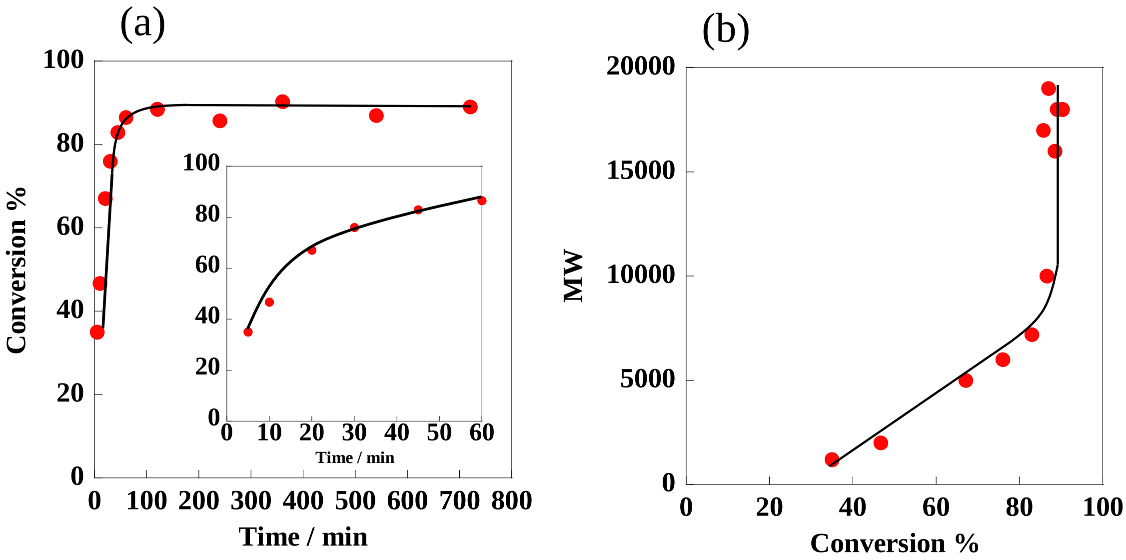


Figure 1-1-3-4. (a) Conversion-time curve and (b) MW-conversion curve of the polymerization of MePyr and BS.

1-1-3-2. Pseudo-living addition-condensation polymerization by continuous addition of monomer

(A) Concept of basic reaction

In the addition-condensation of MePyr and aldehyde in the presence of acid, a rate-determining step is the addition of aldehyde to the α-position of MePyr shown in step-1 in Figure 1-1-3-5b and Figure 1-1-3-1a. The reactivity of following condensation, step-2, is higher than that of step-1. Therefore, the addition occurs with high selectivity. Moreover, the electron density of the α-position of a generated dipyrromethane is higher than that of MePyr. As a result, the reactivity of α-position of generated dipyrromethane is 240 times higher than that of MePyr at 10°C. When the 1% of dipyrromethane generate in the initial sage of the polymerization, the reactivity ratio of dipyrromethane to MePyr becomes about 2.4. In other words, the growing-active-point in Addition (g-A), which is defined as a α-position of dipyrromethane, oligomer, and polymer shown in red-dot in Figure 1-1-3-5 increases at initial stage. However, the g-A immediately becomes almost constant at low concentration because the propagation reaction of the g-A to aldehyde occurs more predominantly than the reaction of MePyr to aldehyde shown in Figure 1-1-3-5d. No reaction of MePyr to aldehyde means no generation of a new g-A. While in the condensation, the growing-active-point in Condensation (g-C) shown in blue-dot in Figure 1-1-3-5 is defined as the carbon attached with hydroxy group generated by addition of aldehyde. The reaction of the g-C to the g-A is thermodynamically preferential. However, this reaction is preventable as follows: The higher reactivity of the g-C means low selectivity. Therefore, the collision of the g-C to MePyr is more important. In the initial and middle stages of the polymerization, the g-C is low concentration as same as the g-A mentioned above. On the other hand, a large amount of MePyr is present in these stages. Moreover, the polymers move slowly because of a high molecular weight (Mw). That is the collision between polymers is very rare. While the collision between polymer and MePyr occurs easily because of the large amount and rapid-moving of MePyr. Therefore, the propagation reaction occurs dynamically and more predominantly than the polymer-polymer reaction does shown in Figure 1-1-3-5e. That is this addition-condensation of MePyr with aldehyde progresses like a chain-growth polymerization in the initial and middle stages. Of course, the polymer-polymer reaction occurs in the final stage shown in Figure 1-1-3-6(iii) because of the low concentration of MePyr. These concepts agree with the experimental result for the polymerization of MePyr and equimolar benzaldehyde-2-sulfonic acid sodium salt (BS) mentioned in 1-1-3-1. In the conversion-time curve shown in Figure 1-1-3-4a, the conversion steeply increased until 20 min (conversion 67%), slowly increased up to 60 min (conversion 87%), and became almost constant. While in the Mw-conversion curve shown in Figure 1-1-3-4b, the Mw gradually increased with the conversion until 80% because of the propagation reaction like the chain-growth polymerization. However, the Mw steeply increased over 80% conversion like the step-growth polymerization of polyamide. Finally, the Mw became constant because of no reaction occurred between high Mw polymers because of very slow-moving.

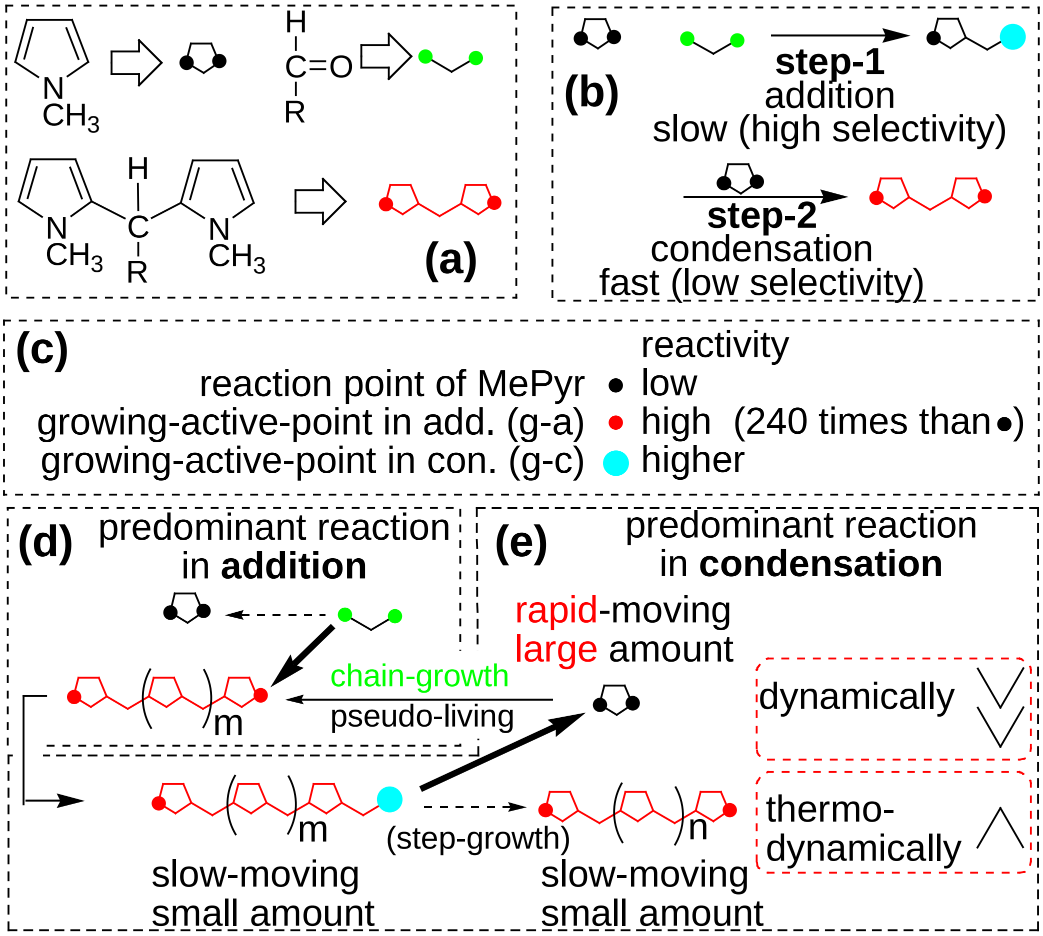


Figure 1-1-3-5. Reaction mechanism of the pseudo-living addition-condensation polymerization of 1-methylpyrrole and aldehyde.

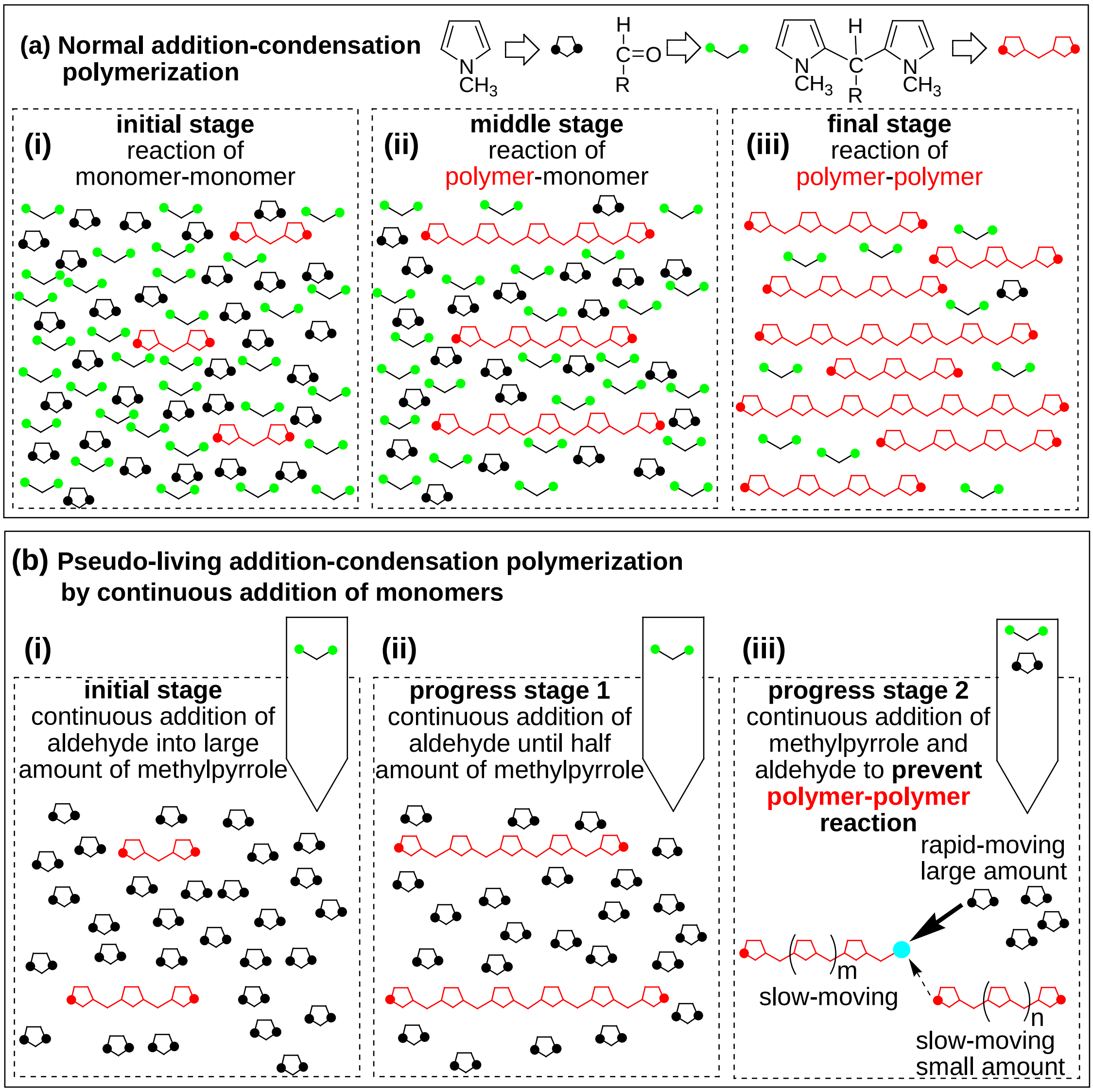


Figure 1-1-3-6. Image for the different reaction systems: (a) normal (b) pseudo-living addition-condensation polymerizations.

(B) Pseudo-living polymerization by continuous addition of monomer

The control of MePyr amount is important in this polymerization. We controlled the MePyr amount as follows.

Initial stage: Aldehyde was slowly added to the excess amount of MePyr. Then dipyrromethane and oligomer generated shown in Figure 1-1-3-6b(i).

Progress stage 1: Continuous addition of aldehyde was conducted until half amount of

MePyr shown in Figure 1-1-3-6b(ii). The added aldehyde with rapid-moving reacted at the g-A predominantly, then the generated g-C was attacked immediately by the large amount MePyr and became the larger g-A illustrated in Figure 1-1-3-5d-e . Moreover, this immediate reaction of the g-C with MePyr is important to prevent the termination which occurs by the side reaction shown Figure 1-1-3-1d.

Progress stage 2: After the half amount addition, both aldehyde and equimolar MePyr were continuously added shown in Figure 1-1-3-6b(iii). The ratio of the g-A to MePyr was kept at almost constant during the polymerization. The polymer-polymer reaction was prevented by the rapid-moving and large amount of MePyr. That is the propagation reaction continues like a living-polymerization under the continuous addition of both monomers.

(C) Polymerization data:

The conversions and molecular weights of the obtained polymers are shown in Table 1-1-3-1. The molecular-weight-distribution of the polymer obtained at 8 days was roughly estimated as follows: the MePyr-BS (8 day) polymer (1.00 g) was dissolved in water (8.0 mL), then the large polymer (0.276 g, 25.4%, MW = 90000 g/mol), middle polymer (0.293 g, 27.1%, MW = 42000 g/mol), and small polymer (0.252 g, 23.2%, Mw = 18000 g/mol) were obtained using 16.6, 24.4, and 33.3 mL of isopropyl alcohol, respectively.

The ratios for the polymer weights are: w_L = 25.4/23.2 = 1.09, w_m = 27.1/23.2 = 1.17, and w_s = 1.

$$M_n = \frac{\Sigma N_i M_i}{\Sigma N_i} = \frac{\Sigma \frac{w_i}{M_i} M_i}{\Sigma \frac{w_i}{M_i}} = \frac{\Sigma w_i}{\Sigma \frac{w_i}{M_i}}$$

$$M_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} = \frac{\Sigma \frac{w_i}{M_i} M_i^2}{\Sigma w_i} = \frac{\Sigma w_i M_i}{\Sigma w_i}$$

$\mathbf{M_n}$ = (1.09 + 1.17 + 1) / [(1.09 / 90000) + (1.17 / 42000) + (1 / 18000)] = 34000

$\mathbf{M_w}$ = (1.09 × 90000 + 1.17 × 42000 + 1 × 18000) / (1.09 + 1.17 + 1) = 51000

$\mathbf{M_w / M_n}$ = 51000 / 34000 = 1.50

Figure 1-1-3-7 shows the Mw-time curve of the polymerization of MePyr and BS. Here, the Progress stage 2 was carried out after 1day. The linear relationship of the Mw and the added amount of monomers means that this polymerization progresses like a living-polymerization.[14-29] The molecular-weight-distribution of the polymer obtained at 8 days was roughly estimated at the value of 1.5. This higher value means that the polymerization is a pseudo-living not an intrinsic living-polymerization with the value of near 1.0.

Table 1-1-3-1. Conversions and molecular weights of the polymers.

	$[\eta]_{sp}$ / C	MW	Conversion %
1 day	0.07	6800	63.2
2 day	0.10	15000	65.9
4 day	0.13	25000	63.5
6 day	0.15	37000	62.7
8 day	0.18	53000	66.7

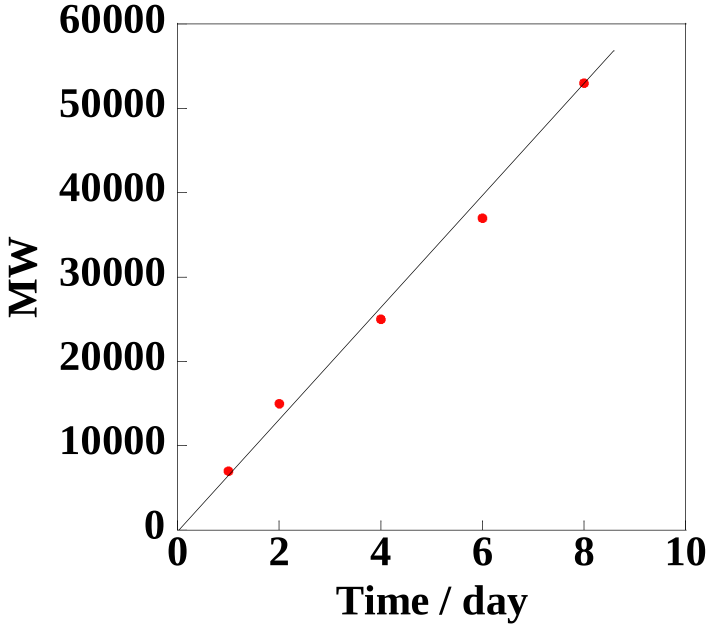


Figure 1-1-3-7. MW-time curve for the pseudo-living addition-condensation polymerization of MePyr and BS with the continuous addition of monomers.

1-1-4. Conclusions

In Section 1, we have shown a new type of pseudo-living polymerization by continuous addition of monomers to the addition-condensation of 1-methylpyrrole and aldehydes. Typically, precision polymerizations, which allow for structure-controlled polymers, are very tedious because they require severe experimental conditions. However, our new synthesis method does not require any special precautions. Additionally, this pseudo-living addition-condensation polymerization is able to control the polymer main structures. The pseudo-living polymerization can lead to the easy preparation of structure-controlled polymers by different monomers.

1-1-5. References

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Section 1-2

A, B-block amphiphilic polymer for interphase photoinduced energy transfer

1-2-1. Introduction

Photosynthesis is carried out by pigments and electron donor and acceptor moieties housed within proteins, which are in turn associated with biological membranes. Typically, these moieties include chlorophylls and their relatives, quinones, and carotenoid. They interact by two basic photochemical processes: energy transfer, and photoinduced electron transfer. For example, antenna systems consisting of chlorophylls, carotenoids, and other pigments collect light and conduct excitation to the reaction center via singlet-singlet energy transfer.[1-4] Then, in photosynthetic reaction centers, excited chlorophyll, resulting from sunlight absorption, donates an electron to nearby chlorophyll, beginning an electron transfer cascade that moves electrons through a series of acceptors to quinones which transforms excitation energy into electrochemical energy in the form of long-lived, transmembrane charge separation is at the heart of photosynthetic energy conversion.[5-8] Accordingly, the ability for a reaction to occur at the interphase can be used in the construction of an artificial photosynthetic system because it allows for efficient separation of high energy substances generated by photochemical reactions.[9-10] In this section, in order to construct the artificial photosynthetic system, an A, B-block amphiphilic polymer with energy donors and acceptors, each in a different block was prepared by the pseudo-living addition-condensation polymerization. An interphase photoinduced energy transfer in a micellar system has been studied.

1-2-2. Experimental

1-2-2-1. Materials

1-Methylpyrrole (MePyr), benzaldehyde-2-sulfonic acid sodium salt (BS), 2-ethylpyrrole (2-EtPyr), 4-isopropylbenzaldehyde (iPB) and 3-perylenecarboxaldehyde (PeA) were purchased from Tokyo Kasei Chemical Co., Ltd. 1-Pyrenecarboxaldehyde (PyA), *p*-toluenesulfonic acid monohydrate (p-TS), Triton X and other reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. Unless stated otherwise, reagents and solvents were used without purification. 1-Methylpyrrole (Tokyo Kasei Chemical Co., Ltd., Tokyo, Japan) as a monomer was purified by distillation.

1-2-2-2. Measurements

The UV-Vis spectra were recorded on a V-670 spectrophotometer (JASCO). Fluorescence spectra were recorded on a FP-8300 spectrophotometer (JASCO). ^{1}H-NMR spectra were recorded on a JEOL ECS-400 spectrometer (JEOL) working at 400MHz using TMS as the internal standard. DMSO-d6 was used as the solvent for the polymer.

1-2-2-3. Polymerization

A, B-block amphiphilic polymer:

Figure 1-2-2-1 shows the schedule for preparing the A, B-block amphiphilic polymer by the continuous addition of the monomer.

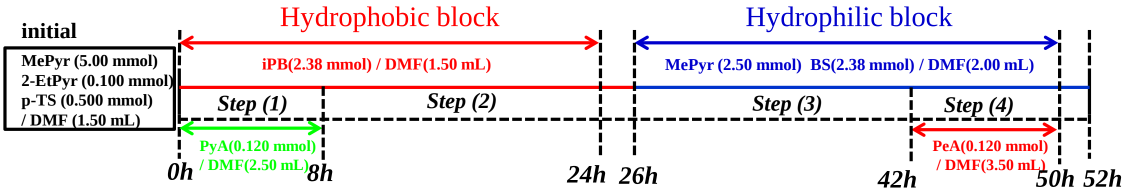

Figure 1-2-2-1. Schedule for the continuous addition polymerization of amphiphilic polymers.

iPB(Py)-BS(Pe) was prepared as follows:

Solution-A: MePyr (5.00 mmol), 2-EtPyr (0.10 mmol), p-TS (0.50 mmol) in DMF (1.5 mL).

Solution-B: 4-isopropylbenzaldehyde (iPB, 2.38 mmol) in DMF (1.5 mL)

Solution-C: 1-Pyrenecarboxaldehyde (PyA, 0.12 mmol) in DMF (2.5 mL)

Solution-D: BS (2.38 mmol) and MePyr (2.50 mmol) in DMF (2.0 mL)

Solution-E: 3-Perylenecarboxaldehyde (PeA, 0.12 mmol) in DMF (3.5 mL)

Solution-A was stirred (300 rpm) at 30 °C. Solution-B was continuously added to Solution-A for 24 h. At the same time, Solution-C was also continuously added for 8 h. At 26 h, the reaction system was cooled to 10 °C. Solution-D was continuously added for 24 h. Then, at 42 h, Solution-E was continuously added for 8 h. The reaction was stopped by the addition of a sodium carbonate aqueous solution (5%, 1.2 mL) at 52 h. Isopropyl alcohol (80 mL) was added to the reaction mixture. The resulting precipitate was purified by two reprecipitations from DMF/isopropyl alcohol (6 mL/80 mL). A mixed solvent (THF:water = 9:1, 40 mL) was added to the resulting precipitate, and the insoluble substance was separated by filtration. The obtained solution was then dried by evaporation. The resulting polymer was dissolved in water (40 mL), and the insoluble part was separated by filtration. The final aqueous solution of the polymer, which is soluble in both THF:water = 9:1 and water, was freeze-dried (0.346 g, yield: 27.5%). The other polymers were similarly prepared.

^{1}H NMR spectrum of A, B-block amphiphilic polymer (iPB(Py)-BS(Pe)): Figure 1-2-2-2 shows the chemical structure and the NMR spectrum of A, B-block amphiphilic polymer. The ratio of the hydrophobic part and hydrophilic part in the A, B-block amphiphilic polymer was 1.2:1, because the intensity ratio of signals of the iPB proton H_h (1.21 ppm) to the BS proton H_f (7.73 ppm) was 7.2:1. The peaks from 7.5 to 8.5 ppm assigned to Py and Pe protons (i and j).

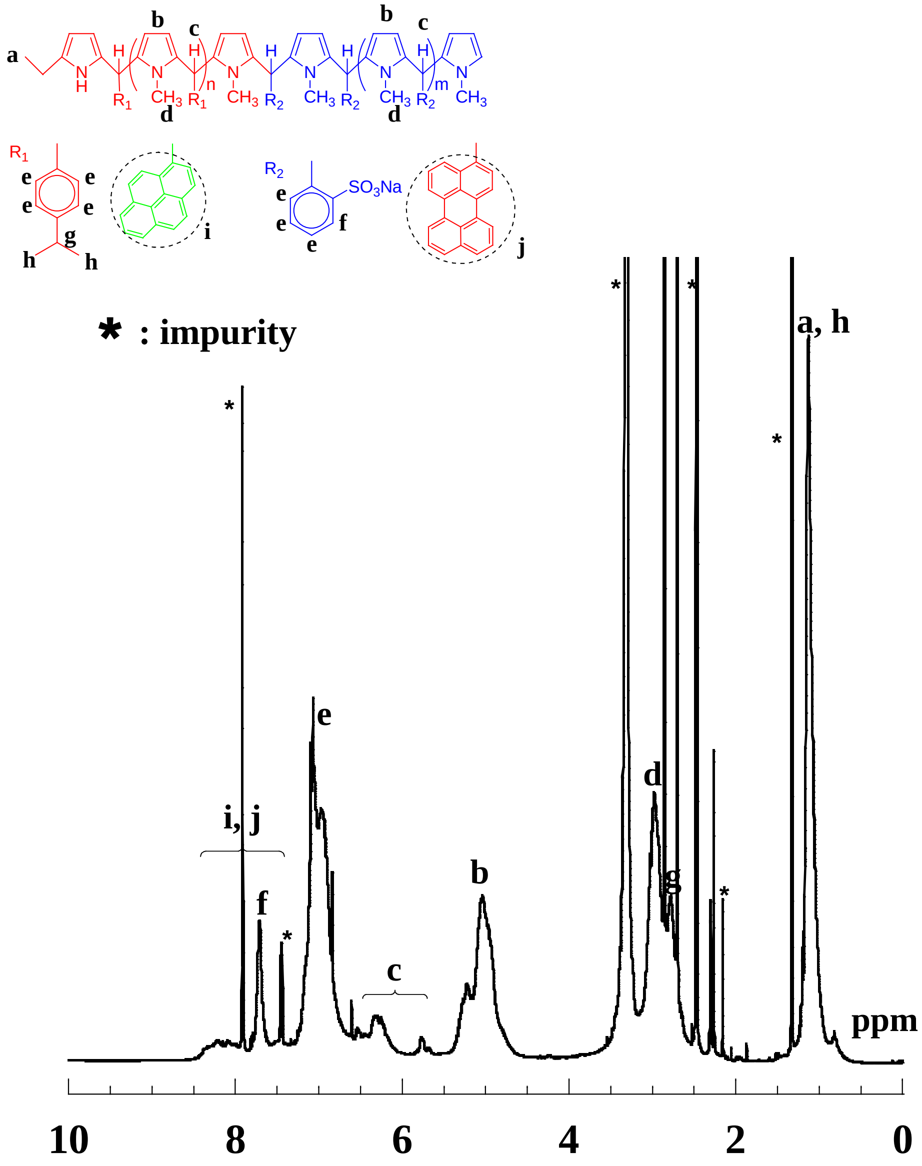

Figure 1-2-2-2. ^{1}H-NMR spectrum of A, B-block amphiphilic polymer in DMSO-d^6.

Preparation of a micellar system:

An amphiphilic polymer (0.010 g) was dissolved in the emulsion solvent (water:toluene = 99:1, 1.0 g) with an ultrasonic homogenizer at 25 °C for 1 min. Then, the resulting solution (0.10 g) was diluted by another emulsion solvent (water:toluene = 99:1, 10.0 g) using an ultrasonic homogenizer for 1 min at 25 °C. An aqueous solution of Triton X (water:Triton X = 9:1, 2.1 g) was added to the solution using an ultrasonic homogenizer for 1 min. Finally, a transparent and stable solution was obtained. The other micellar systems were similarly prepared.

1-2-3. Results and discussion

1-2-3-1. The characteristics of A, B-block amphiphilic polymer

The structures of the aldehydes and 2-ethylpyrrole (2-EtPyr), which was used as the terminal unit, are shown in Figure 1-2-3-1a. The reactivity ratio of 2-EtPyr to MePyr is 64:1 and is discussed in detail in the Section 1-1. Therefore, 2-EtPyr reacted in the initiation stage, and the polymer grew linearly in one direction. The image of preparation and the schedule of addition are shown in Figure 1-2-3-1b and Figure 1-2-2-1, respectively. The sequential addition of monomers to 2-EtPyr and an excess amount of MePyr was conducted in the following order: Step (1), [4-isopropylbenzaldehyde (iPB) and 1-pyrenecarboxaldehyde (PyA)]; Step (2), [iPB]; Step (3), [BS and MePyr]; and Step (4), [BS, MePyr, and 3- perylenecarboxaldehyde (PeA)]. The details are discussed further in the 1-2-2-3.

In order to confirm that the A, B-block amphiphilic polymer existed on the heterophase boundary and the donor and the acceptor existed in different phases, fluorescence quenching was conducted using two quenchers: anthraquinone (AQ) as the toluene-soluble component and methylviologen (MV^{2+}) as the water-soluble component. Two amphiphilic polymers were prepared containing Pe units either in the hydrophobic or hydrophilic phases. The preparation of a micellar system is discussed in 1-2-2-3. Figure 1-2-3-2b shows the fluorescence spectra of iPB(non)-BS(Pe) excited at 420 nm and dissolved in an emulsion solvent at 25 °C with an acceptor: AQ (1.5×10^{-2} M) (red line), MV^{2+} (10^{-4} M) (green line), or without an acceptor (blue line). The fluorescence quenching occurred only in the MV^{2+} system, which suggests that the Pe unit exists in the water phase (Figure 1-2-3-2c). However, the fluorescence quenching occurred only in the AQ system for iPB(Pe)-BS(none) (Figure 1-2-3-3b). The Pe unit exists in the toluene phase (Figure 1-2-3-3c). These results confirm that the A, B-block amphiphilic polymer existed on the heterophase boundary and the donor and acceptor moieties were in different phases.

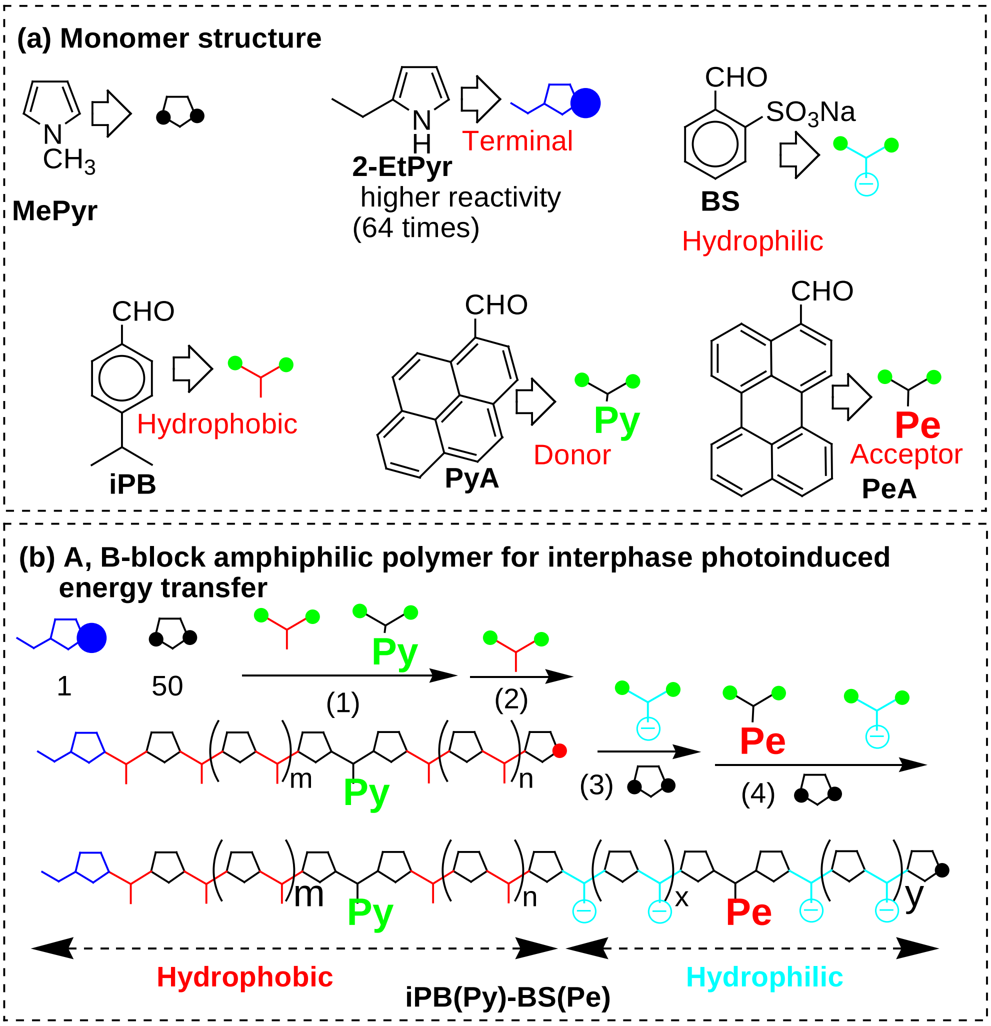

Figure 1-2-3-1. Preparation of structure-controlled polymers by pseudo-living addition-condensation polymerization by the continuous addition of monomers.

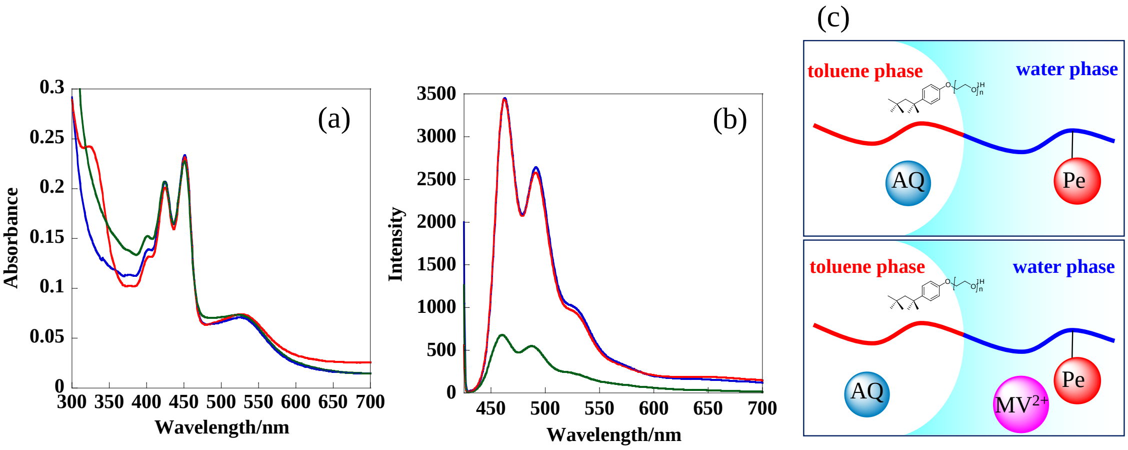

Figure 1-2-3-2. (a) Absorption and (b) fluorescence spectra of iPB(none)-BS(Pe) dissolved in a water/toluene emulsion (118/1) including 1.8% Triton X at 25 °C with acceptor: anthraquinone [1.5 × 10^{-2} M] (red line), methylviologene [10^{-4} M] (green line), or without an acceptor (blue line), [polymer]=0.083 g/L, excited at 420 nm, cell length=1 cm; (c) image of A, B-block amphiphilic polymers in a micellar system.

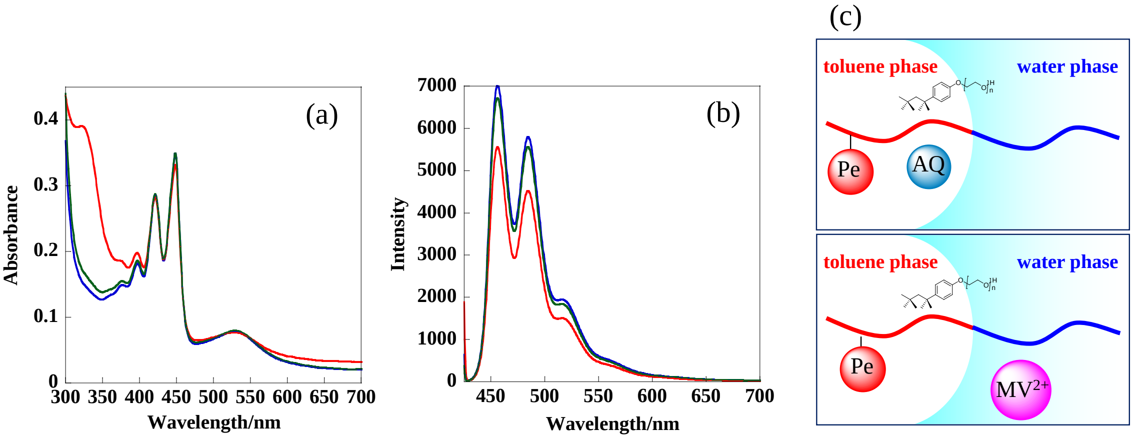

Figure 1-2-3-3. (a) Absorption and (b) fluorescence spectra of iPB(Pe)-BS(none) dissolved in a water/toluene emulsion (118/1) including 1.8% Triton X at 25 °C with acceptor: anthraquinone [1.5 × 10^{-2} M] (red line), methylviologene [10^{-4} M] (green line), or without acceptor (blue line), [polymer]=0.083 g/L, excited at 420 nm, cell length=1 cm; (c) image of A, B-block amphiphilic polymers in a micellar system.

1-2-3-2. A, B-block amphiphilic polymer for interphase photoinduced energy transfer

A fluorescence quenching method was used to provide evidence that the prepared polymer exists at the heterophase boundary with the donor and acceptor groups positioned in the two different phases (shown in Figure 1-2-3-4a). Three reference polymers were made for this purpose: iPB(Py)-BS(Pe), iPB(Py)-BS(none), and iPB(none)-BS(Pe). The abbreviation iPB(Py)-BS(Pe) means that the Py unit is in the hydrophobic phase and the Pe unit is in the hydrophilic phase. Figures 1-2-3-4b, 1-2-3-4c, and 1-2-3-4d show the absorption, fluorescence, and excitation spectra of the polymers, respectively. In the fluorescence spectra (λ_{exc} = 330 nm) in which the Py unit dominates, the fluorescence intensity of iPB(Py)-BS(Pe), which emits around 460 nm, is larger than that of iPB(none)-BS(Pe). Conversely, the intensity of iPB(Py)-BS(Pe), which emits around 400 nm, is smaller than that of iPB(Py)-BS(none). This strongly suggests that the interphase photoinduced energy transfer from the excited Py unit to the Pe unit occurs in the micellar system. In the excitation spectra monitored at 460 nm in which the Pe unit dominates, the intensity at around 330 nm of iPB(Py)-BS(Pe) is larger than that of the other polymers. This result confirms the occurrence of the interphase photoinduced energy transfer.

In Figure 1-2-3-4c, the fluorescence profiles of the Py unit are different from a general emission profile for monomeric Py. This change of the emission profile is due to a solvent effect and/or excimer generation. To clarify the cause of the change, Py-dipyrromethane was prepared, and fluorescence spectra were measured in different mixed solvents of toluene and methanol. The fluorescence profiles changed drastically in different solvents. However, no profile changes were observed at different concentrations (Figure 1-2-3-5 and 1-2-3-6). These results indicate that the unusual spectral profile of the Py unit in Figure 1-2-3-4c reflects the different circumstances, not excimer generation, which are always concentration dependent.

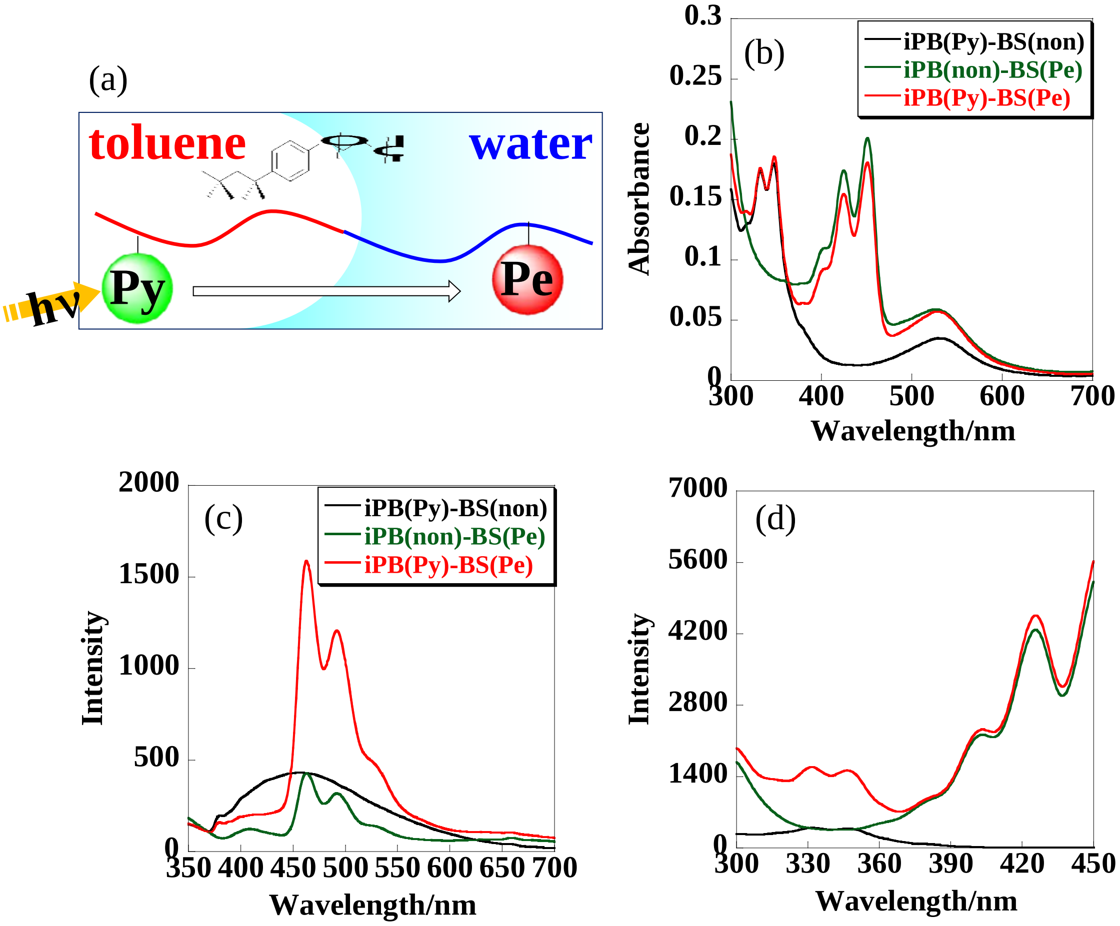

Figure 1-2-3-4. (a) Image of A, B-block amphiphilic polymers in a micellar system, (b) absorption, (c) fluorescence and (d) excitation spectra of the A, B-block amphiphilic polymers containing Py and Pe units dissolved in a water/toluene emulsion (118/1) including 1.8% Triton X at 25 °C, [polymer]=0.083 g/L, (c) excited at 330 nm, (d) monitored at 460 nm, cell length=1 cm.

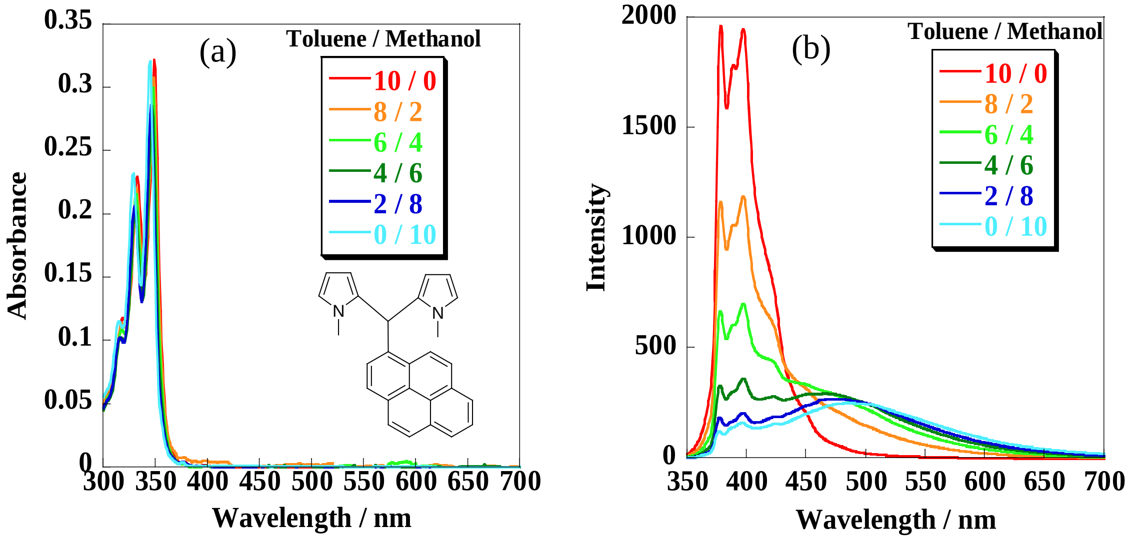

Figure 1-2-3-5. (a) Absorption and (b) fluorescence spectra of Py-dipyrromethane dissolved in mixed solvents (toluene/methanol = 10/0, 8/2, 6/4, 4/6, 2/8, 0/10) at 25 °C. The samples were prepared by the absorbance (0.2) at 330 nm, excited at 330 nm, cell length=1 cm.

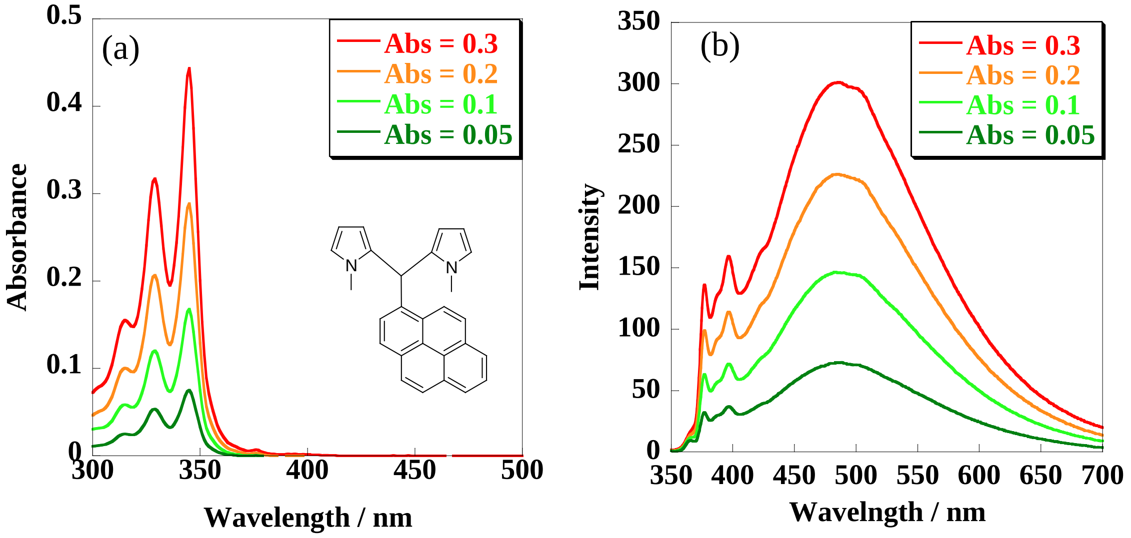

Figure 1-2-3-6. (a) Absorption and (b) fluorescence spectra of Py-dipyrromethane dissolved in methanol at 25 °C. The samples were prepared by the absorbance (0.05), (0.1), (0.2), and (0.3) at 330 nm, respectively, excited at 330 nm (b), cell length=1 cm.

1-2-4. Conclusions

In this section, an A, B-block amphiphilic polymer with energy donors and acceptors, each in a different block was prepared by the pseudo-living addition-condensation polymerization. We confirmed that the A, B-block amphiphilic polymer existed on the heterophase boundary and the donor and the acceptor existed in different phases. This type of polymer showed an interphase photoinduced energy transfer in a micellar system.

1-2-5. References

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Section 1-3

Synthesis and Characterization of branched polymers and efficient light-harvesting ability

1-3-1. Introduction

Harvesting photon by the antenna molecules and transferring to the reaction center is the initial step of natural photosynthesis. Antenna chlorophyll, the primary pigment used in photosynthesis, the absorbed energy is rapidly transferred (in 10^{-9} s) between chlorophylls, and then transfer to a molecules in the associated reaction center. The construction of artificial light-harvesting complexes has received much attention in recent years.[1-21] Efficient transfer of the excitation energy is a key aspect for the construction of effective light-harvesting systems. In light-harvesting systems, energy is absorbed by chromophores and transferred to an acceptor. Porphyrins,[6] polymers,[9] and dendrimers[21] which were used to arrange multiple organic chromophores around acceptor molecules have been studied. However, the synthesis of these systems is very difficult.

In Section 1-1 and 1-2, structure-controlled polymers can be prepared by pseudo-living polymerization, which requires no specific conditions, and the polymer structure is easily controlled by continuous addition of aldehydes has been studied. In this section, a branched polymer with high and low amounts of energy donors and acceptors was prepared by the pseudo-living addition-condensation polymerization. The polymer features a high amount of energy donors in branched parts and a low amount of energy acceptors in centers, it showed an efficient light-harvesting ability.

1-3-2. Experimental

1-3-2-1. Materials

1-Methylpyrrole (MePyr), benzaldehyde-2-sulfonic acid sodium salt (BS), 1-Methyl-2-pyrrolecarboxaldehyde (MePyrA) and 3-perylenecarboxaldehyde (PeA) were purchased from Tokyo Kasei Chemical Co., Ltd. 1-Pyrenecarboxaldehyde (PyA), *p*-toluenesulfonic acid monohydrate (p-TS), and other reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. Unless stated otherwise, reagents and solvents were used without purification. 1-Methylpyrrole (Tokyo Kasei Chemical Co., Ltd., Tokyo, Japan) as a monomer was purified by distillation.

1-3-2-2. Measurements

The UV-Vis spectra were recorded on a V-670 spectrophotometer (JASCO).

Fluorescence spectra were recorded on a FP-8300 spectrophotometer (JASCO).

^{1}H-NMR spectra were recorded on a JEOL ECS-400 spectrometer (JEOL) working at 400MHz using TMS as the internal standard. DMSO-d6 was used as the solvent for the polymer.

1-3-2-3. Polymerization

Branched polymer:

Figure 1-3-2-1 shows the schedule for preparing the branched polymer by the continuous addition of the monomer.

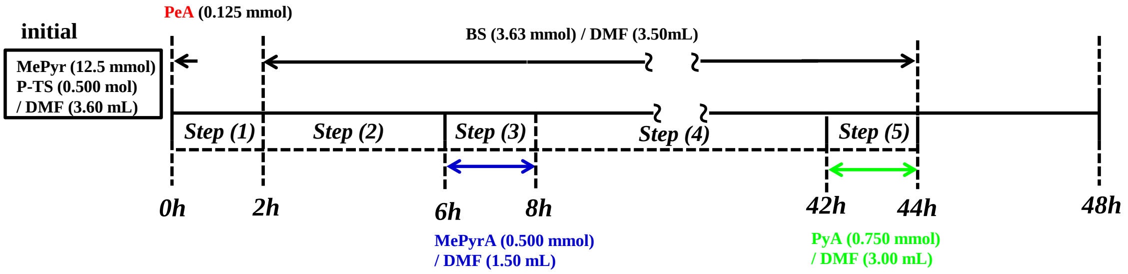


Figure 1-3-2-1. Schedule for the continuous addition polymerization of branched polymers.

Py(6)-Pe(1) was prepared as follows:

Solution-A: MePyr (12.5 mmol), p-TS (0.50 mmol) in DMF (3.6 mL).

Solution-B: BS (3.63 mmol) in DMF (3.5 mL)

Solution-C: 1-Methyl-2-pyrrolecarboxaldehyde (MePyrA, 0.50 mmol) in DMF (1.5 mL)

Solution-D: PyA (0.75 mmol) in DMF (3.0 mL)

3-Perylenecarboxaldehyde (PeA, 0.125 mmol) was added to Solution-A with stirring (300 rpm) at 10 °C for 2 h. Solution-B was continuously added to the reaction mixture for 42 h. At 6 h, Solution-C was continuously added for 2 h. Then, at 42 h, Solution-D was continuously added for 2 h. The reaction was stopped by the addition of a sodium carbonate aqueous solution (5%, 1.2 mL) at 48 h. Isopropyl alcohol (80 mL) was added to the reaction mixture. The resulting precipitate was purified by reprecipitations from two times of DMF/isopropyl alcohol (8 mL/80 mL) and two times of water/isopropyl alcohol (6 mL/80 mL), and then dissolved in water. The polymer was obtained by freeze-drying (0.944 g, yield: 70.4%). Other polymers were similarly prepared.

^{1}H NMR spectra of branched polymers:

Figure 1-3-2-2 shows the chemical structures and the NMR spectra of branched polymers. The peaks from 7.5 to 8.5 ppm assigned to Py and Pe protons (f and g). From Py(0)-Pe(1) to Py(6)-Pe(1), these signals become stronger as the Py content increases.

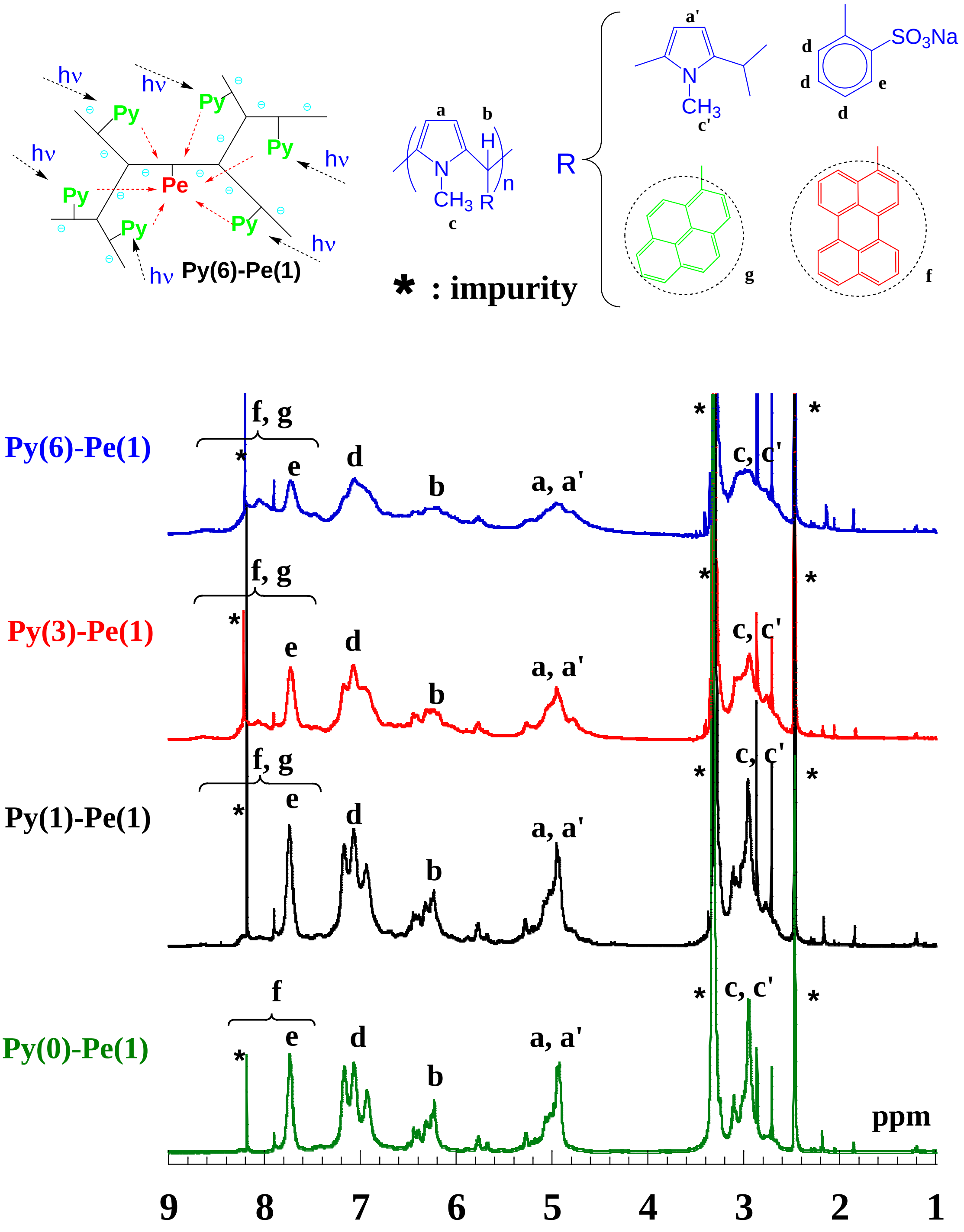


Figure 1-3-2-2. ^{1}H-NMR spectra of branched polymers in DMSO-d^6.

Structure-uncontrolled branched polymer Py(6)-Pe(1) was prepared as follows:

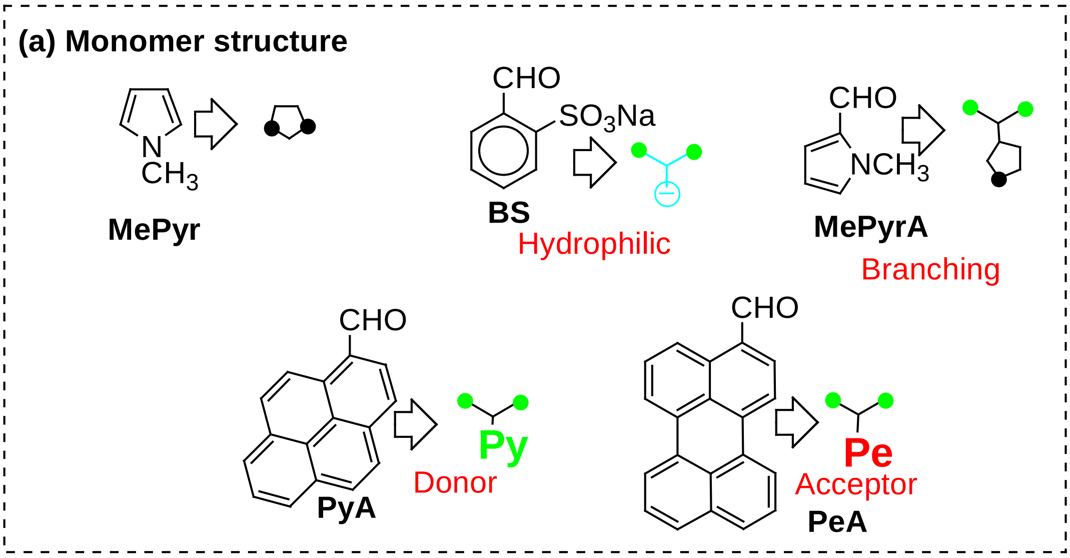
MePyr (5.0 mmol), BS (3.63 mmol), PeA (0.125 mmol), PyA (0.75 mmol), and MePyrA (0.50 mmol) were dissolved in DMF (7.0 mL). A second solution containing p-TS (0.50 mmol, 1 mL DMF) was added to this solution at 10 °C. The reaction was stopped with sodium carbonate aqueous solution (5%, 1.2 mL) after 24 h. Isopropyl alcohol (80mL) was added to the reaction mixture. The resulting precipitate was purified by reprecipitation twice from DMF/isopropyl alcohol (8 mL/80 mL) and twice from water/isopropyl alcohol (6 mL/80 mL), and then dissolved in water. The polymer was obtained by freeze-drying (1.061 g, 75%). Other polymers were similarly prepared.

1-3-3. Results and discussion

1-3-3-1. Branched polymer for light-harvesting

The structures of the aldehydes and 1-methyl-2-pyrrolecarboxaldehyde (MePyrA), which is used as a branching unit, are shown in Figure 1-3-3-1a. The image of preparation and the schedule of addition are shown in Figure 1-3-3-1b and Figure 1-3-2-1, respectively. The sequential addition into an excess of MePyr was conducted in the following order: Step (1), [PeA (at one time addition)]; Step (2), [BS]; Step (3), [BS and MePyrA]; Step (4), [BS]; and Step (5), [BS and PyA]. The details are discussed in the 1-3-2-3.

Light harvesting is the initial step of natural photosynthesis.[22-23] Figures 1-3-3-2, 1-3-3-3a, and 1-3-3-3b show the absorption, fluorescence, and excitation spectra of the prepared polymers, respectively. The abbreviation Py(6)-Pe(1) indicates that the molar ratio of the Py unit to the Pe unit is 6:1. The structural image of Py(6)-Pe(1) is shown in Figure 2c. The absorbance around 330 nm increased with respect to the relative amount of the Py unit (shown in Figure 1-3-3-2). The fluorescence intensity around 460 nm (the emission of the Pe unit) increased almost linearly with respect to the relative amount of the Py unit (shown in Figure 1-3-3-3a). This indicates that the photoinduced energy transfer occurs from the multi donors to one acceptor. In the excitation spectra monitored at 455 nm, the intensity around 330 nm increases with respect to the relative amount of the Py unit. This indicates an efficient light-harvesting mechanism.



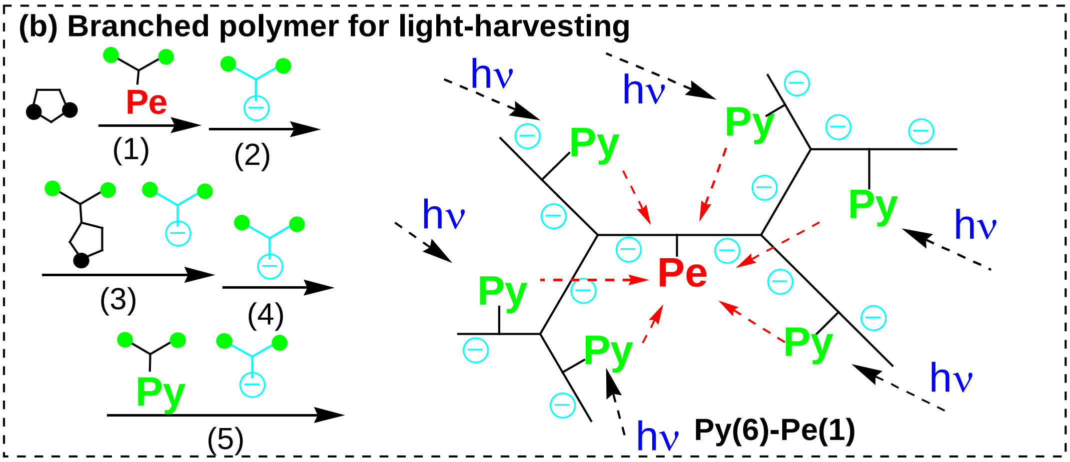


Figure 1-3-3-1. Preparation of structure-controlled polymers by pseudo-living addition-condensation polymerization by the continuous addition of monomers.

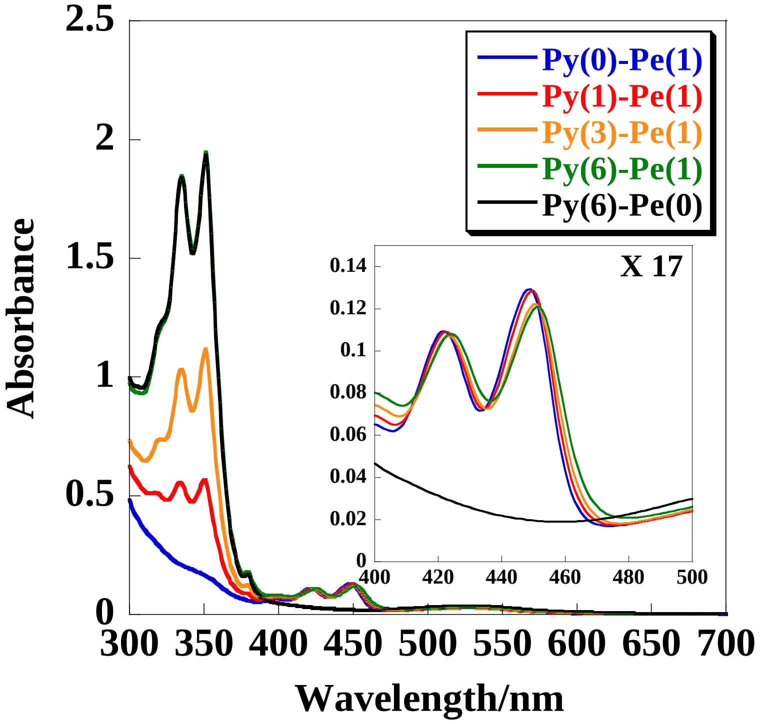


Figure 1-3-3-2. Absorption spectra of branched polymers containing high and low amounts of Py and Pe units dissolved in water at 25 °C, abs (420 nm)=0.1, except Py(6)-Pe(0), cell length=1 cm.

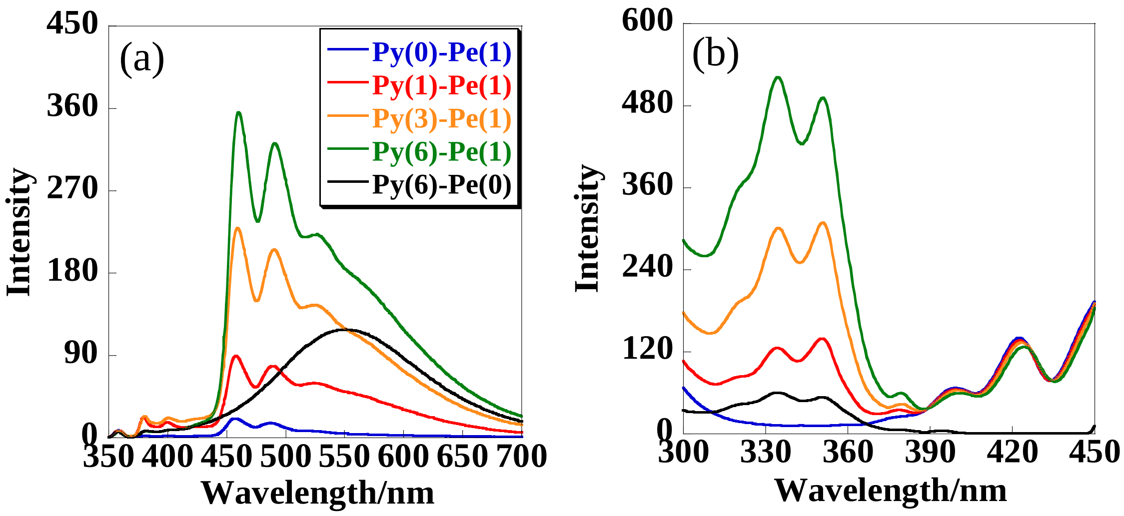


Figure 1-3-3-3. (a) Fluorescence and (b) excitation spectra of branched polymers containing high and low amounts of Py and Pe units dissolved in water at 25 °C, abs(420 nm)=0.01, except Py(6)-Pe(0), (a) excited at 320 nm, (b) monitored at 455 nm, cell length= 1 cm.

1-3-3-2. Energy transfer in structure-uncontrolled branched polymers

In order to clarify the advantage of structure-controlled branched polymers, we compared energy transfer in structure-controlled branched polymers with that in uncontrolled branched polymers.

Figures 1-3-3-5, 1-3-3-4(a), and 1-3-3-4(b) show the absorption, fluorescence, and excitation spectra of the prepared polymers, respectively. In the fluorescence spectra (λ_{exc} = 320 nm) where the Py unit was dominantly excited, the fluorescence intensity of Py(6)-Pe(1) (controlled and uncontrolled), which emitted around 455 nm, was larger than that of Py(0)-Pe(1) (controlled and uncontrolled). In the excitation spectra, which were monitored at 455 nm and dominated by the Pe unit, the intensity of Py(6)-Pe(1) (controlled and uncontrolled) around 330 nm was larger than Py(0)-Pe(1) (controlled and uncontrolled). These results suggest that photoinduced energy transfer occurred from the excited Py unit to the Pe unit both in the controlled and uncontrolled branched polymers. However, energy transfer in controlled branched polymer is more efficient than that in uncontrolled branched polymer.

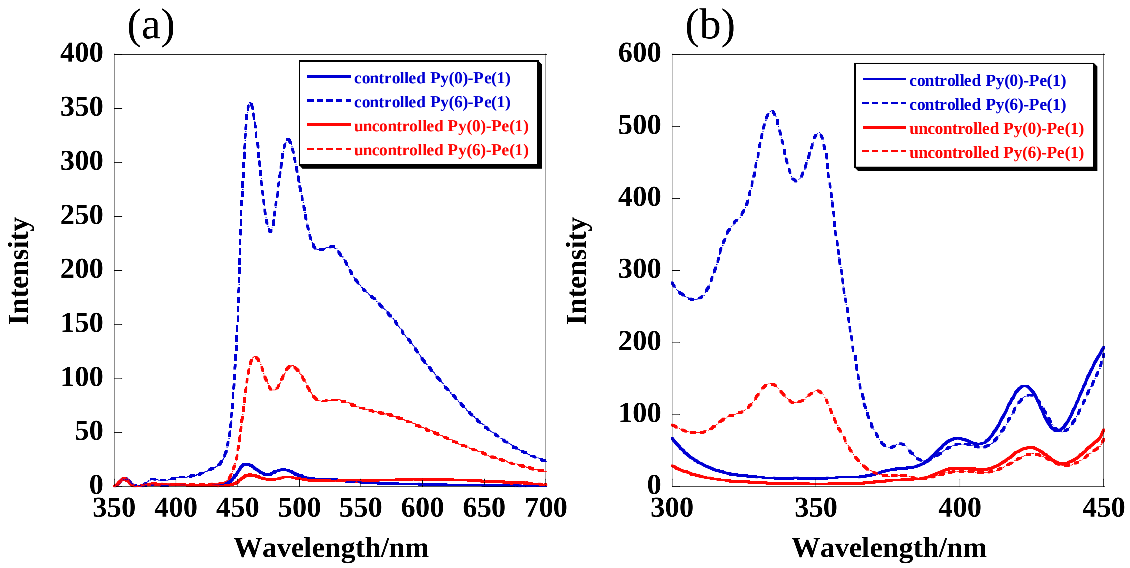


Figure 1-3-3-4. (a) Fluorescence and (b) excitation spectra of controlled (blue line) and uncontrolled (red line) branched polymers dissolved in water at 25 °C, abs(320 nm)=0.1, (a) excited at 320 nm, (b) monitored at 455 nm, cell length= 1 cm.

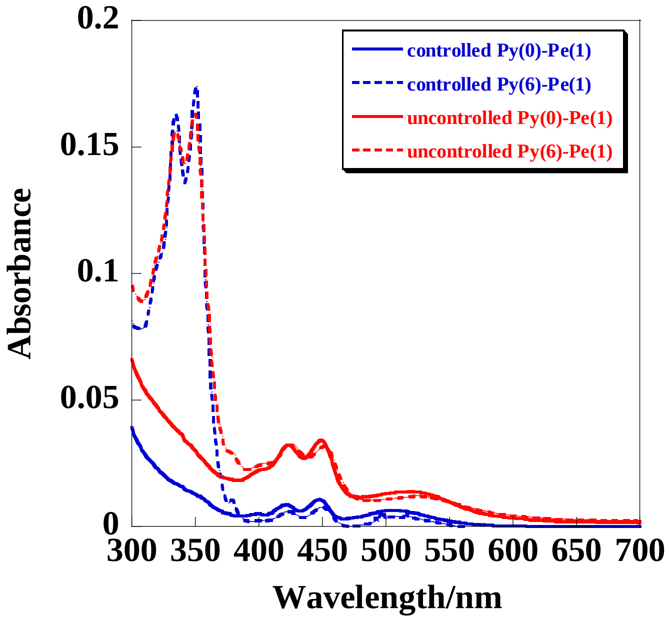


Figure 1-3-3-5. Absorption spectra of controlled (blue line) and uncontrolled (red line) branched polymers dissolved in water at 25 °C, abs (320 nm)=0.1, cell length=1 cm.

1-3-4. Conclusions

In conclusions, a branched polymer with high and low amounts of energy donors and acceptors was prepared by the pseudo-living addition-condensation polymerization. The polymer features a high amount of energy donors in branched parts and a low amount of energy acceptors in centers, it showed an efficient light-harvesting ability.

1-3-5. References

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Section 1-4

Light-Harvesting and Electron Transfer in a branched Polymer for Artificial Photosynthetic Antenna-Reaction Centers

1-4-1. Introduction

Photosynthetic reaction centers are well known to convert light energy into electrochemical energy via photoinduced electron transfer. The conversion of light energy into electrochemical energy during photosynthesis involves two steps: (i) Light harvesting, which involves the absorption of sunlight to excite electrons in peripheral antennae of the photosynthetic systems and subsequent rapid excitation energy transfer to reaction centers; and (ii) photoinduced electron transfer, which generates charge-separated states using this excitation energy.[1-2] Accordingly, it is possible to design and synthesize artificial photosynthetic reaction centers that efficiently convert light energy into electrochemical energy in the form of charge separation.[3-5] In order to construct an artificial photosynthetic system, a variety of antenna mimics, based on porphyrins,[6-7] polymers,[8] and dendrimers,[9-10] have been studied. Furthermore, we recently reported a new type of pseudo-living polymerization that leads to the easy preparation of structure-controlled polymers. Photoinduced energy transfer, especially light harvesting, has been studied in these structure-controlled polymers, in which energy donors in branched parts absorb light and transfer the resulting excitation energy to energy acceptors in reaction centers via singlet-singlet energy transfer. The initial steps toward designing artificial reaction centers based on efficient light-harvesting have been studied[11] in Section1-3.

In order to generate charge-separated states using light energy in artificial reaction centers, porphyrin-fullerene systems have been studied.[12-17] However, the synthesis of porphyrin-fullerene systems is very difficult. In contrast, structure-controlled polymers can be prepared by pseudo-living polymerization, which requires no specific conditions. The polymer structure is easily controlled by continuous addition of aldehydes.[11] In addition, energy transfer in structure-controlled branched polymer is more efficient than that in uncontrolled branched polymer (Section 1-3). Here, we present the preparation of structure-controlled polymer as part of our continuing study of artificial photosynthesis. We attempted to prepare a branched polymer containing anthraquinone (AQ), an electron acceptor, via a pseudo-living addition-condensation polymerization. In photosynthetic reaction centers, excited chlorophyll, resulting from sunlight absorption, donates an electron to nearby chlorophyll, beginning an electron transfer cascade that moves electrons through a series of acceptors to a quinone. In this Section, we report the synthesis and spectroscopic characterization of a branched polymer featuring a high amount of energy donors (pyrene, Py) in the branched parts, and a low amount of energy acceptors (perylene, Pe) in the centers that also bear a Pe-AQ electron donor-acceptor unit. The polymer combines efficient light harvesting (singlet-singlet energy transfer) with photoinduced electron transfer.

1-4-2. Experimental

1-4-2-1. Materials

1-Methylpyrrole (MePyr), benzaldehyde-2-sulfonic acid sodium salt (BS), 1-Methyl-2-pyrrolecarboxaldehyde (MePyrA) and 3-perylenecarboxaldehyde (PeA) were purchased from Tokyo Kasei Chemical Co., Ltd. 1-Pyrenecarboxaldehyde (PyA), *p*-toluenesulfonic acid monohydrate (p-TS), and other reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. Unless stated otherwise, reagents and solvents were used without purification. 1-Methylpyrrole (Tokyo Kasei Chemical Co., Ltd., Tokyo, Japan) as a monomer was purified by distillation.

1-4-2-2. Measurements

The UV-Vis spectra were recorded on a V-670 spectrophotometer (JASCO).

Fluorescence spectra were recorded on a FP-8300 spectrophotometer (JASCO).

^{1}H-NMR spectra were recorded on a JEOL ECS-400 spectrometer (JEOL) working at 400MHz using TMS as the internal standard. DMSO-d6 was used as the solvent for the polymer.

1-4-2-3. Monomer synthesis

2-Anthraquinonecarboxaldehyde (AQA)[18]:

To a suspension of 2-(hydroxymethyl)anthraquinone (2.0 g, 8 mmol) in CH_2Cl_2 (100 mL) was added pyridinium chlorochromate (PCC; 2.6 g, 12 mmol). The mixture was stirred at room temperature for 12 h. Excess PCC was then removed by filtration. The solvent was evaporated under reduced pressure and the residue was washed with water (75 mL) and extracted with CH_2Cl_2 (3 × 75 mL). The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The resulting solid was purified by silica gel chromatography using hexane:CH_2Cl_2 (1:5) as the eluent (yield: 1.180 g, 68 %); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 10.30 (1H, s), 8.86 (1H, d, J = 1.6 Hz), 8.57 (1H, d, J = 8 Hz), 8.45–8.40 (2H, m), 8.37 (1H, dd, J_1 = 8 Hz, J_2 = 1.6 Hz), 7.92 (2H, m).

1-4-2-4. Polymerization

Branched polymer:

Figure 1-4-2-1 shows the schedule for preparing the branched polymer by continuous addition of the monomer.

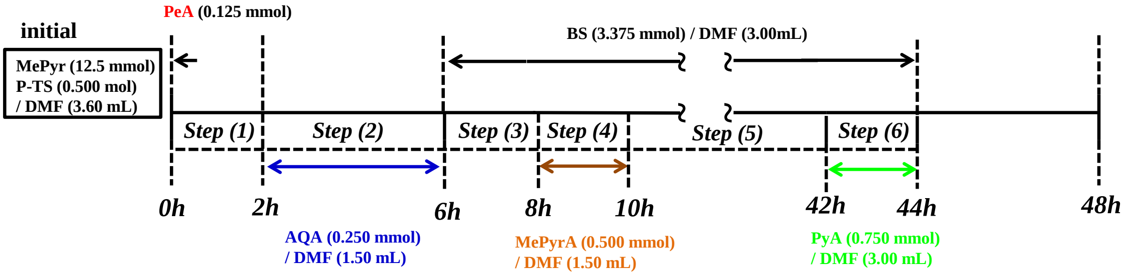

Figure 1-4-2-1. Schedule for the continuous addition polymerization of branched polymers.

Py(6)-Pe(1)-AQ(2) was prepared as follows:

Solution A: 1-Methylpyrrole (MePyr, 12.5 mmol) and *p*-toluenesulfonic acid monohydrate (p-TS, 0.50 mmol) in DMF (3.6 mL).

Solution B: 2-Anthraquinonecarboxaldehyde (AQA, 0.25 mmol) in DMF (2.0 mL).

Solution C: Benzaldehyde-2-sulfonic acid sodium salt (BS, 3.63 mmol) in DMF (3.5 mL).

Solution D: 1-Methyl-2-pyrrolecarboxaldehyde (MePyrA, 0.50 mmol) in DMF (1.5 mL).

Solution E: 1-Pyrenecarboxaldehyde (PyA, 0.75 mmol) in DMF (3.0 mL).

3-Perylenecarboxaldehyde (PeA, 0.125 mmol) was added to Solution A with stirring (300 rpm) at 10 °C for 2 h. At 2 h, Solution B was added continuously for 4 h. Then, Solution C was added continuously for 42 h. At 8 h, Solution D was added continuously for 2 h. Then, at 42 h, Solution E was added continuously for 2 h. The reaction was quenched with sodium carbonate aqueous solution (5%, 1.2 mL) after 48 h. Isopropyl alcohol (80 mL) was added to the reaction mixture. The resulting precipitate was purified by reprecipitation twice from DMF/isopropyl alcohol (8 mL/80 mL) and twice from water/isopropyl alcohol (6 mL/80 mL), and then dissolved in water. The polymer was obtained by freeze-drying (yield: 0.933 g, 69.6 %). Other polymers were similarly prepared.

^{1}H-NMR spectrum of branched polymer. Figure 1-4-2-2 shows the chemical structures and an example NMR spectrum for the branched polymers. Peaks from 7.5 to 8.5 ppm were assigned to Py, Pe, and AQ protons (g, f, and h). However, the contents of Py, Pe and AQ units in the polymer could not be determined because of spectral broadening and overlapping peaks.

Reduction of anthraquinone that in the branched polymer

An aqueous solution (abs(420 nm) = 0.1) of Py(6)-Pe(1)-AQ(2) (1.0 g) was prepared by diluting with water (9.0 g) at 25 °C. Sodium borohydride ($NaBH_4$, 0.010 g) was added to the resulting solution (3.0 g). After 2 h, spectroscopic measurement of the solution containing $NaBH_4$ was carried out. Solutions of other polymers were similarly prepared under the same measurement conditions.

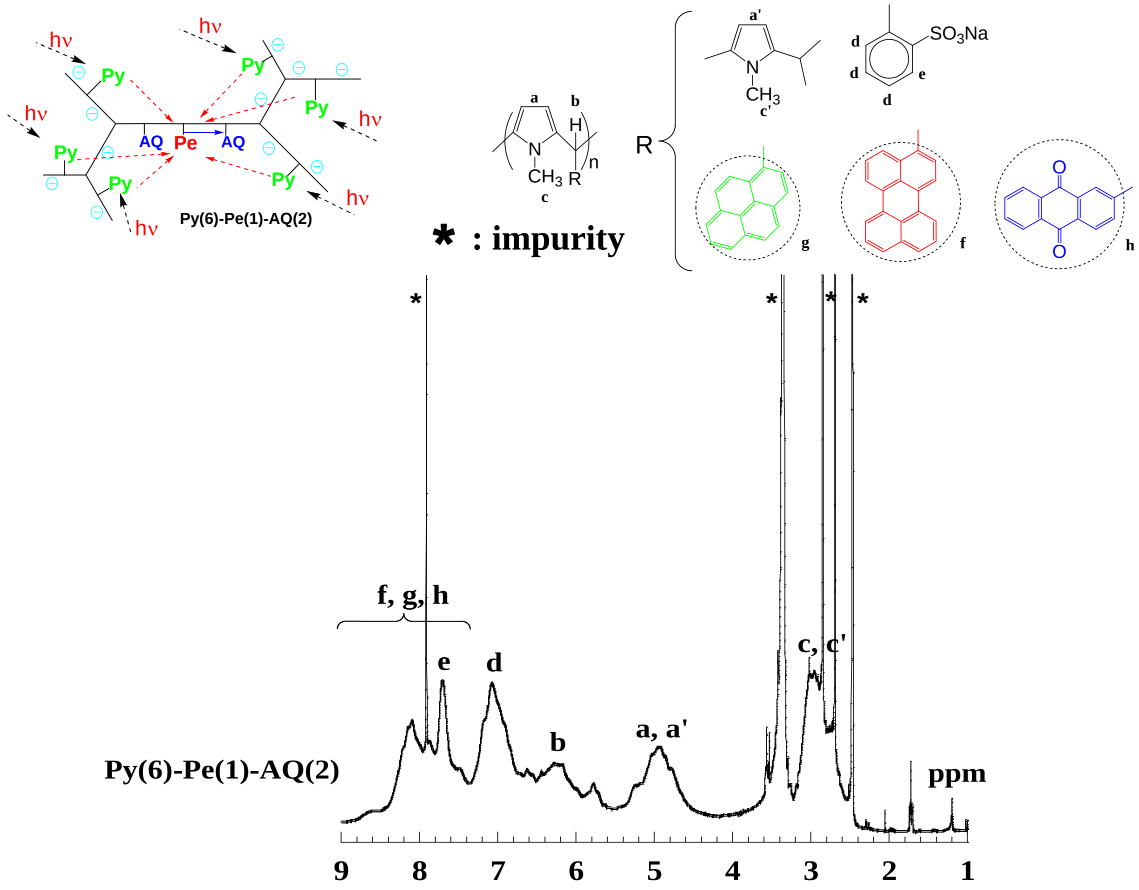

Figure 1-4-2-2. ^{1}H-NMR spectra of a branched polymer in DMSO-d^6.

1-4-3. Results and discussion

1-4-3-1. Light-Harvesting and Electron Transfer in a branched Polymer

Branched polymers were prepared by the pseudo-living addition-condensation polymerization of 1-methylpyrrole (MePyr) and an aldehyde. The structures of the aldehydes and 1-methyl-2-pyrrolecarboxaldehyde (MePyrA), which was used as a branching unit, are shown in Figure 1-4-3-1a. The preparation and schedule of addition are shown in Figures 1-4-3-1b and 1-4-2-1, respectively. Sequential addition into excess MePyr was conducted in the following order: Step (1), one-time addition of 3-perylenecarboxaldehyde (PeA); Step (2), 2-anthraquinonecarboxaldehyde (AQA); Step (3), benzaldehyde-2-sulfonic acid sodium salt (BS); Step (4), BS and MePyrA;

Step (5), BS; and Step (6), BS and 1-pyrenecarboxaldehyde (PyA). Three reference polymers were prepared for this purpose: Py(6)-Pe(1)-AQ(2), Py(6)-Pe(1)-AQ(0), and Py(0)-Pe(1)-AQ(0). This notation indicates the molar ratio of the Py, Pe, and AQ units; e.g., the ratio in Py(6)-Pe(1)-AQ(2) is 6:1:2. The structure of Py(6)-Pe(1)-AQ(2) is depicted in Figure 1-4-3-1c.

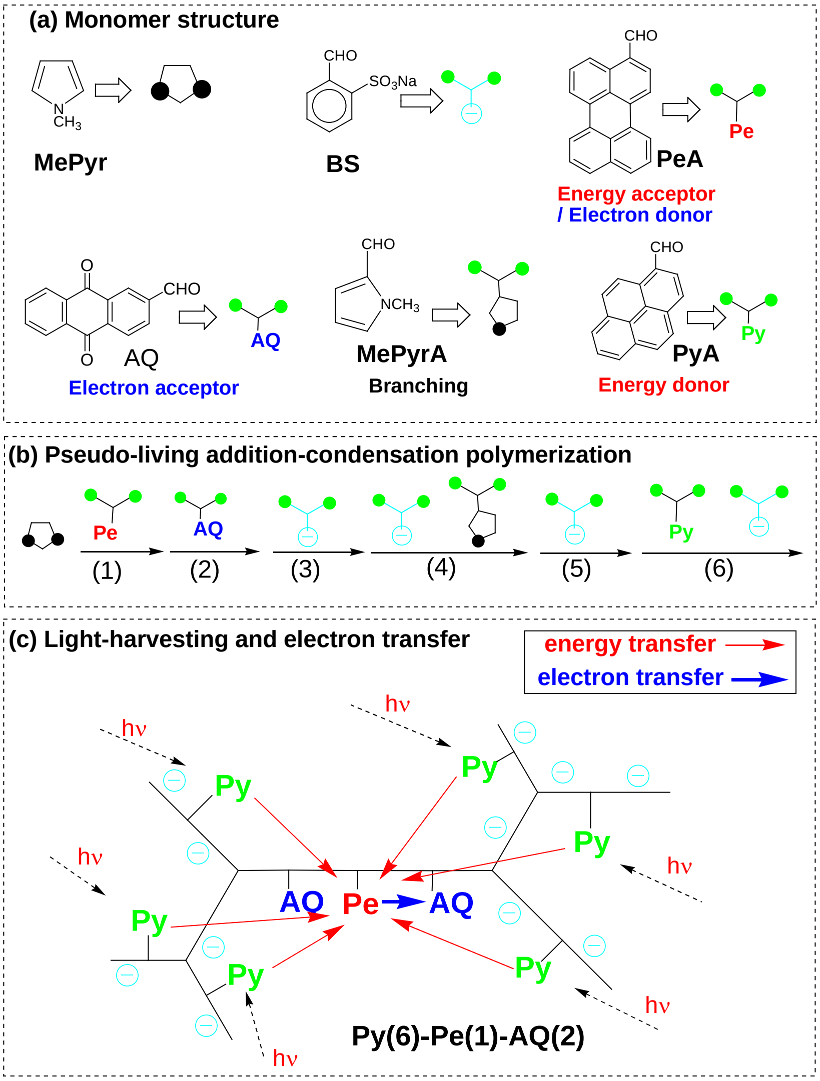

Figure 1-4-3-1. Preparation of structure-controlled branched polymers for light harvesting, energy transfer, and electron transfer model by pseudo-living addition-condensation polymerization with the continuous addition of monomers.

Figures 1-4-3-3a, 1-4-3-2a, and 1-4-3-2b show the absorption, fluorescence, and excitation spectra of the prepared polymers, respectively. In the absorption spectra, Py unit bands appeared around 330 nm, while Pe unit bands appeared around 420 nm. In the fluorescence spectra (λ_{exc} = 320 nm), which were dominated by the Py unit, the fluorescence intensity of Py(6)-Pe(1)-AQ(0), which emitted around 455 nm, was larger than that of Py(0)-Pe(1)-AQ(0). In the excitation spectra, which were monitored at 455 nm and dominated by the Pe unit, the intensity of Py(6)-Pe(1)-AQ(0) around 330 nm was larger than those of the other polymers. This indicates that photoinduced energy transfer occurred from multiple donors to one acceptor and that an efficient light-harvesting system had been prepared (Figure 1-4-3-6(a)). In contrast, the fluorescence intensity (λ_{exc} = 320 nm) of Pe in polymer Py(6)-Pe(1)-AQ(2) was quenched in comparison with polymer Py(6)-Pe(1)-AQ(0), which lacked the AQ acceptor. In the fluorescence spectra (λ_{exc} = 420 nm, Figure 1-4-3-3b), which were dominated by the Pe unit, the fluorescence intensity of Pe in Py(6)-Pe(1)-AQ(2) was also quenched. This result suggests that electron transfer from the electron donor (Pe) to the electron acceptor (AQ) had occurred. These fluorescence (λ_{exc} = 320 and 420 nm) and excitation spectra results suggested that photoinduced energy transfer occurred from the excited Py unit to the Pe unit, and that electron transfer occurred from the Pe unit to the AQ unit. Although, there is a possibility that electron transfer occurred from a part of the excited Py units to the AQ units (Figure 1-4-3-6(b)).

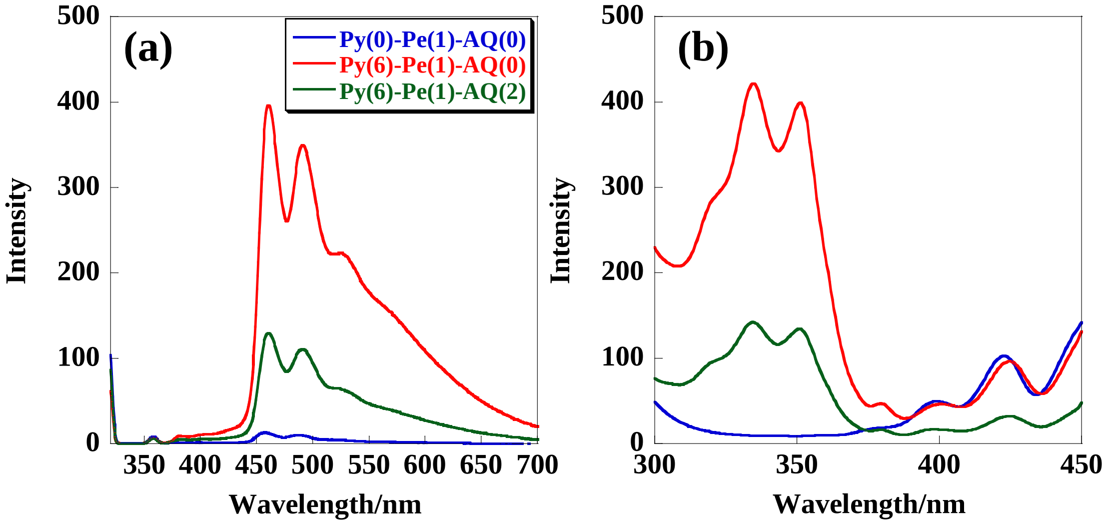

Figure 1-4-3-2. (a) Fluorescence and (b) excitation spectra of branched polymers dissolved in water at 25 °C; abs(420 nm) = 0.01, (a) excited at 320 nm, (b) monitored at 455 nm, cell length = 1 cm.

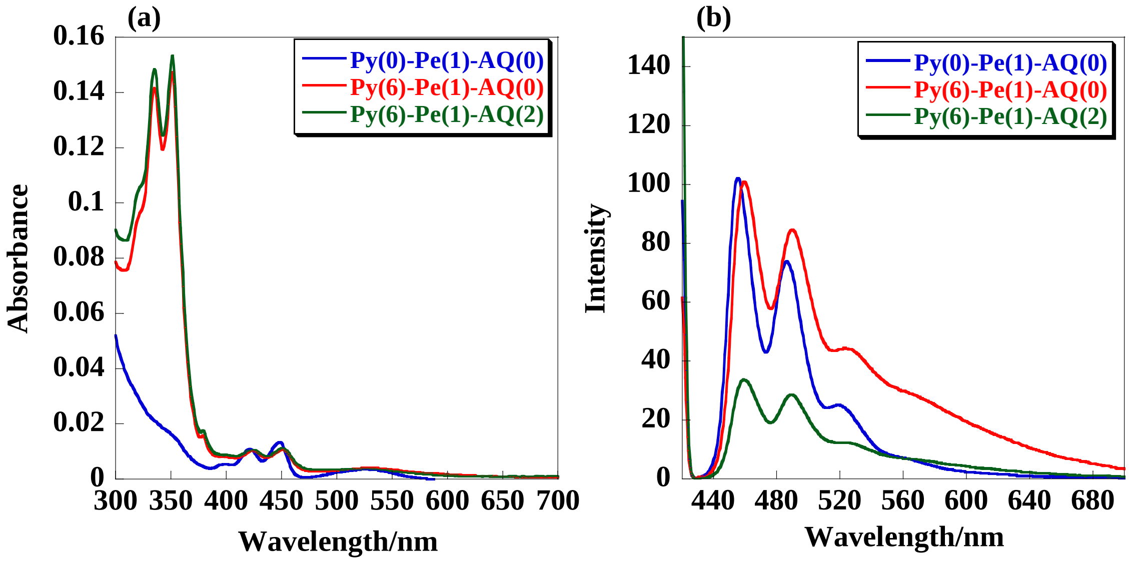

Figure 1-4-3-3. (a) Absorption and (b) fluorescence spectra of branched polymers dissolved in water at 25 °C; abs (420 nm) = 0.01, (b) excited at 420 nm, cell length = 1 cm.

Moreover, to prove electron transfer from Pe to AQ, the AQ units in the polymers were reduced with sodium borohydride ($NaBH_4$; further details are given in the 1-4-2-4). Figures 1-4-3-4(a) and 1-4-3-4(b) show the fluorescence and excitation spectra of the prepared polymers treated with $NaBH_4$. In the fluorescence spectra (λ_{exc} = 320 nm), which were dominated by the Py unit, the fluorescence intensity of reduced Py(6)-Pe(1)-AQ(2), which emits around 455 nm, was similar to that of Py(6)-Pe(1)-AQ(0) and Py(0)-Pe(1)-AQ(0). In the excitation spectra monitored at 455 nm, the intensity of reduced Py(6)-Pe(1)-AQ(2), at around 330 nm, was increased to that of Py(6)-Pe(1)-AQ(0). After reduction, Py(6)-Pe(1)-AQ(2) was an efficient light-harvesting system, as seen for Py(6)-Pe(1)-AQ(0). In the fluorescence spectra (λ_{exc} = 420 nm, shown in Figure 1-4-3-5(b), which were dominated by the Pe unit, the fluorescence intensity of reduced Py(6)-Pe(1)-AQ(2) was similar to those of Py(6)-Pe(1)-AQ(0) and Py(0)-Pe(1)-AQ(0). Therefore, reduction of the AQ unit caused electron transfer in Py(6)-Pe(1)-AQ(2) to disappear. This also suggested that photoinduced energy transfer occurred from excited Py units to Pe units, and that electron transfer occurred from Pe units to AQ units.

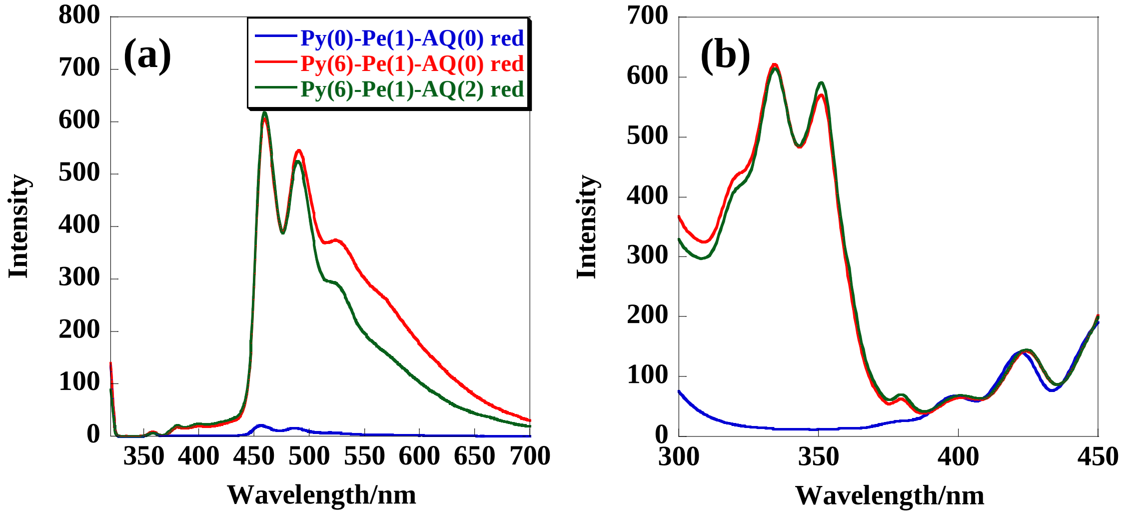

Figure 1-4-3-4. (a) Fluorescence and (b) excitation spectra of branched polymers treated with $NaBH_4$ dissolved in water at 25 °C; abs(420 nm) = 0.01. (a) excited at 320 nm, (b) monitored at 455 nm, cell length = 1 cm.

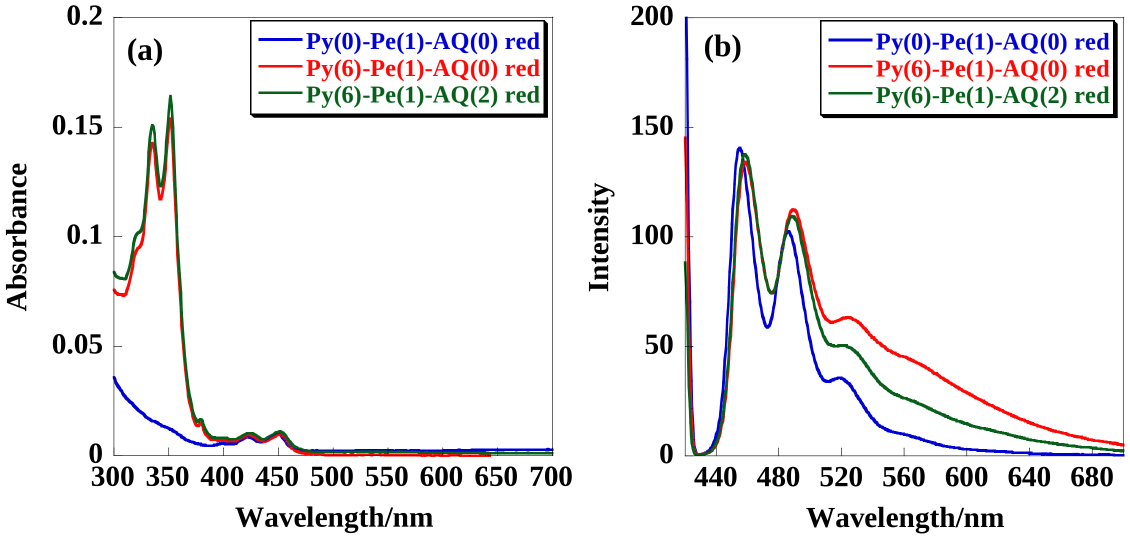

Figure 1-4-3-5. (a) Absorption and (b) fluorescence spectra of branched polymers with $NaBH_4$ dissolved in water at 25 °C; abs(420 nm) = 0.01, excited at 420 nm, cell length = 1 cm.

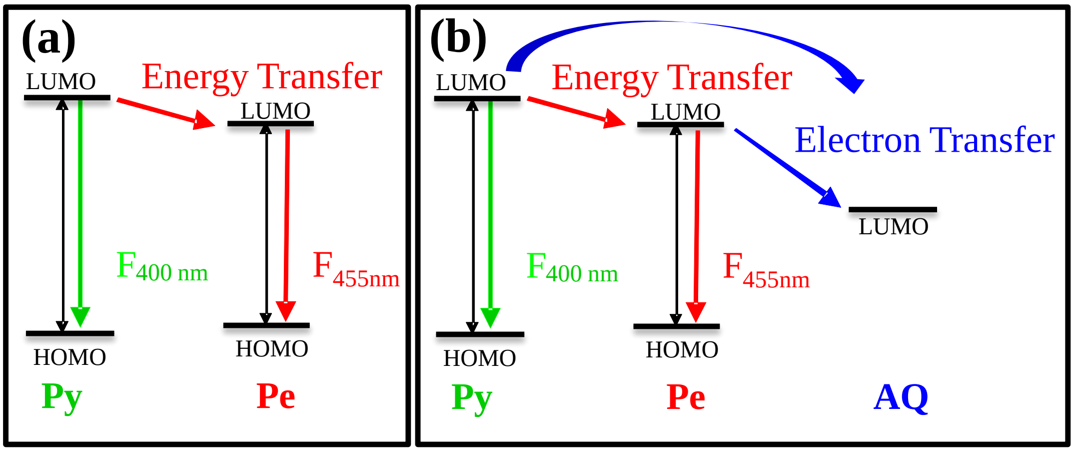

Figure 1-4-3-6. Energy and electron transfer mechanisms described in this paper: (a) energy transfer occurs from the excited Py to Pe; (b) energy transfer occurs from the excited Py to Pe, and electron transfer occurs from Pe to AQ.

1-4-4. Conclusions

In conclusions, we prepared a branched polymer, which integrates singlet-singlet energy transfer and photoinduced electron transfer, by pseudo-living addition-condensation polymerization. The polymer, which features a high amount of energy donors (Py) in branched parts and a low amount of energy acceptors (Pe) in the centers, also bears Pe–AQ electron donor-acceptor units similar to those seen in natural photosynthetic antenna-reaction center complexes.

1-4-5. References

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CHAPTER 2

Syntheses of polymers prepared from trihydroxybenzene with aldehyde and their application to artificial photosynthesis

Section 2-1

Syntheses of step-π-conjugated polymer from trihydroxybenzene with aldehyde and study on photoinduced electron transfer

2-1-1. Introduction

The conversion of light energy into electrochemical energy during photosynthesis involves two steps: (i) Light harvesting, which involves the absorption of sunlight to excite electrons in peripheral antennae of the photosynthetic systems and subsequent rapid excitation energy transfer to reaction centers; and (ii) photoinduced electron transfer, which generates charge-separated states using this excitation energy.[1-2] The design and development of light-harvesting, and electron transfer will make it possible to realize an efficient artificial photosynthetic system.[3-5] The light-harvesting have been studied in chapter 1.[6-7] In photosynthetic reaction center proteins, transfer electron over long distances using stepwise electron hopping reactions between redox cofactors. [8-12] Synthetic electron donor-acceptor systems have been prepared to study the dependencies of electron transfer rate constants on donor-acceptor distance.[13-15] For electron transfer from A_1 to A_2 efficiently (Figure 2-1-1-1), it is necessary to slow down the K_{b1}. For slowing down the K_{b1}, the electron transfer distance between D_1 and A_1 needs to be long. In order to change the distance between D_1 and A_1, molecular wire can be used. A molecular wire is often described as a molecular bridge that is able to move charge efficiently over many chemical bond lengths. Accordingly, D-B-A systems allow us to study the structural and electronic requirements for transitioning between superexchange and charge hopping.[13-22]

In this section, we defined a step-π-conjugated polymer which alternately consists of a small π-conjugated molecule as like as a benzene unit and a sp^3-methine carbon. The benzene units have no coplanar each other. Therefore, no strong interaction exists between benzene units; however, superexchange or hopping of electrons occurs. The step-π-conjugated polymer can work as a molecular wire with high efficiency electron transfer (Figure 2-1-1-2).

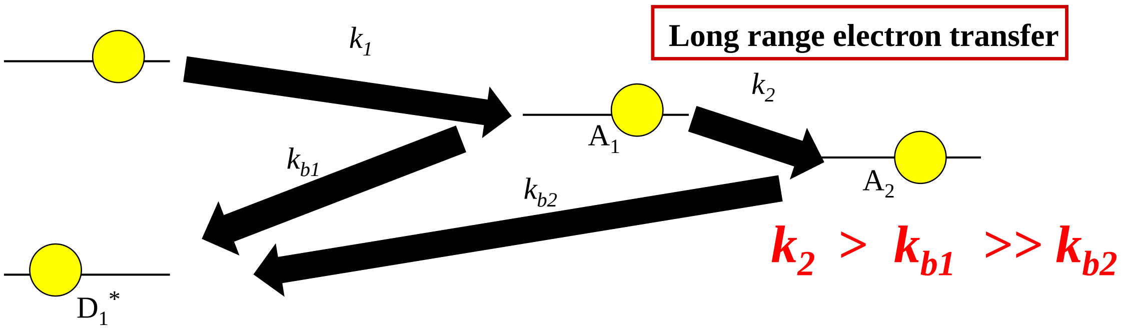


Figure 2-1-1-1. Long range electron transfer to prevent the charge recombination.

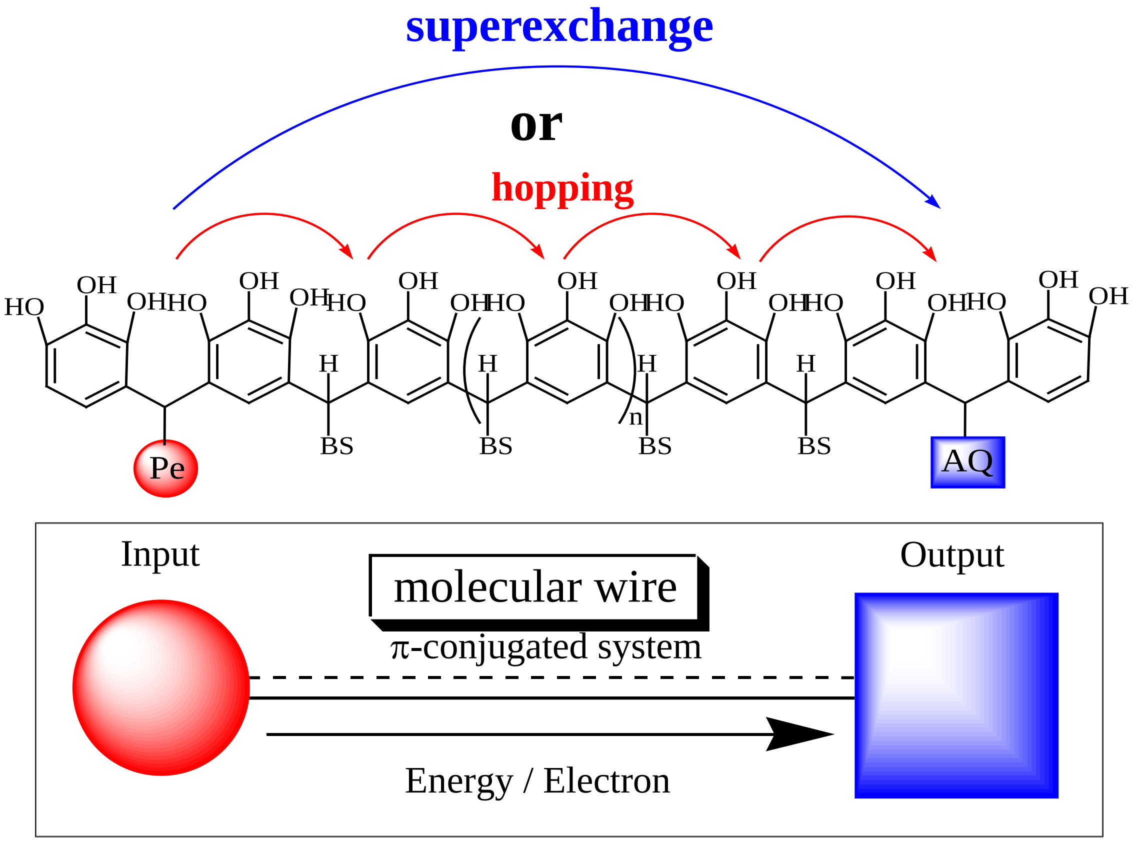


Figure 2-1-1-2. Concept of THB type molecular wire.

2-1-2. Experimental

2-1-2-1. Materials

Benzaldehyde-2-sulfonic acid sodium salt (BS), and 3-perylenecarboxaldehyde (PeA) were purchased from Tokyo Kasei Chemical Co., Ltd. Pyrogallol (1, 2, 3-trihydroxybenzene (1, 2, 3THB)), phloroglucinol (1, 3, 5- trihydroxybenzene (1, 3, 5THB)), *p*-toluenesulfonic acid monohydrate (p-TS), and other reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. Unless stated otherwise, reagents and solvents were used without purification.

2-1-2-2. Measurements

The UV-Vis spectra were recorded on a V-670 spectrophotometer (JASCO).

Fluorescence spectra were recorded on a FP-8300 spectrophotometer (JASCO).

^{1}H-NMR spectra were recorded on a JEOL ECS-400 spectrometer (JEOL) working at 400MHz using TMS as the internal standard. DMSO-d6 was used as the solvent for the polymer.

2-1-2-3. Polymerization

The polymerization of THB (non) polymer:

Synthesis of THB (non) polymer is shown in Scheme 2-1-2-1.

1, 2, 3 THB (10.0 mmol) and BS (12.0 mmol) were dissolved in water (5.0 mL). A second solution containing p-TS (1.0 mmol, 1 mL water) was added to this solution at 25 °C. After 24 h, isopropyl alcohol (120 mL) was added to the reaction mixture. The resulting precipitate was purified by reprecipitations from three times of water/isopropyl alcohol (12 mL/120 mL), and then dissolved in water. The polymer was obtained by freeze-drying (0.611 g, 75%).

The polymerization of THB polymer containing electron donor (Pe) or electron acceptor (AQ):

Syntheses of THB (Pe/ AQ) polymers are shown in Scheme 2-1-2-1.

THB (Pe) was prepared as follows:

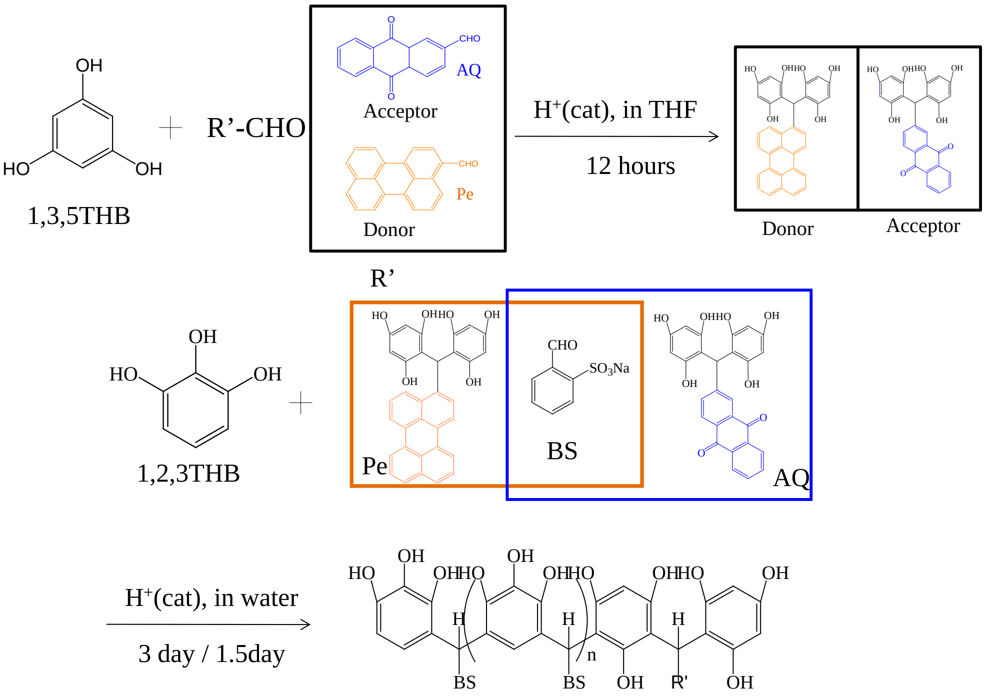
Solution-A: 1, 3, 5 THB (0.60 mmol), PeA (0.30 mmol) in THF (7.5 ml)
Solution-B: p-TS (1.0 mmol) in THF (0.5 ml)
Solution-C: 1, 2, 3 THB (4.70 mmol), BS (6.0 mmol) in water (8.5 ml)

Solution-B was added to Solution-A at 25 °C. After 12 h, Solution-C was added to the reaction mixture. Then after 24 h, THF in mixture solution was distillation by evaporation. The resulting solution was kept at 25 °C for 72 h. THF (80 mL) was added to the reaction mixture. The resulting precipitate was purified by reprecipitations from two times of water/THF (8.0 mL/80 mL) and two times of water/isopropyl alcohol (6.0 mL/240 mL), and then dissolved in water. The polymer was obtained by freeze-drying (0.286 g, 70%). THB (AQ) polymer was similarly prepared.

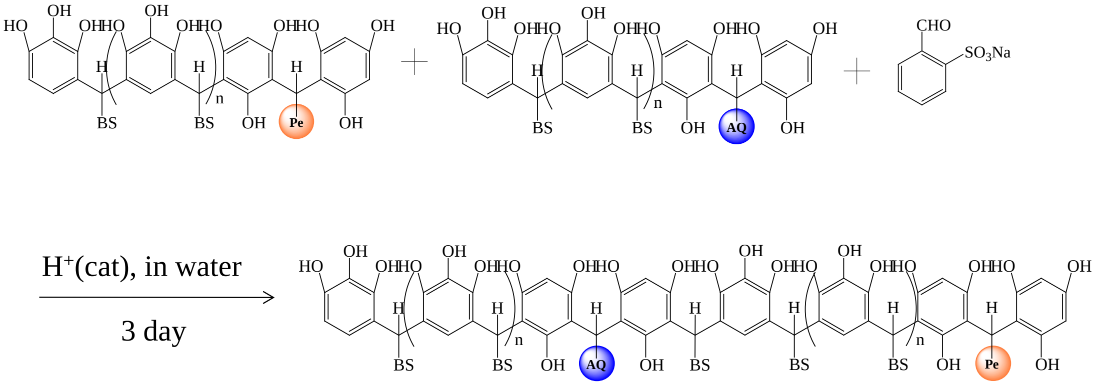
The polymerization of THB polymer containing electron donor (Pe) and electron acceptor (AQ):

Synthesis of THB (Pe-AQ) polymer is shown in Scheme 2-1-2-2.

THB (Pe) (0.2 g), THB (AQ) (0.6 g), and BS (0.1 g) were dissolved in water (3.0 mL). A second solution containing p-TS (0.50 mmol, 1 mL water) was added to this solution at 25 °C. After 72 h, isopropyl alcohol (120 mL) was added to the reaction mixture. The resulting precipitate was purified by reprecipitations from two times of water/isopropyl alcohol (12 mL/120 mL), and then dissolved in water. The polymer was obtained by freeze-drying (0.745 g, 80%). THB (Pe-non) polymer was similarly prepared.



Scheme 2-1-2-1. THB polymers containing Pe and AQ units prepared by continuous addition of aldehydes.



Scheme 2-1-2-2. Synthesis of two component macromolecular wire prepared by THB(Pe) polymer, THB(AQ) polymer and aldehyde(BS).

2-1-3. Results and discussion

2-1-3-1. Polymerization data

The molecular weight was roughly determined by viscosity measurement. The Mark-Houwink-Sakurada formula was used to relate the viscosity and molecular weight:

$[\eta] = KM^{\alpha}$, $K = 5.73 \times 10^{-5}$, $\alpha = 0.751$.

Here, we used $[\eta]_{sp}/c$ at 0.40 g/dL instead of $[\eta]$ because $[\eta]_{sp}/c$ is almost constant at different concentrations. The conversions and molecular weights of the obtained polymers are shown in Table 2-1-3-1. Figure 2-1-3-1 showed the absorption spectra of THB polymers. Electron donor (Pe) and electron acceptor (AQ) were introduced into the THB polymers by the absorption spectra.

Table 2-1-3-1. Conversions and molecular weights of THB polymers.

	$[\eta]_{sp}/C$	MW	Conversion %
THB (Pe)	0.041	6000	70
THB (AQ)	0.090	18000	73
THB (non)	0.092	18000	75

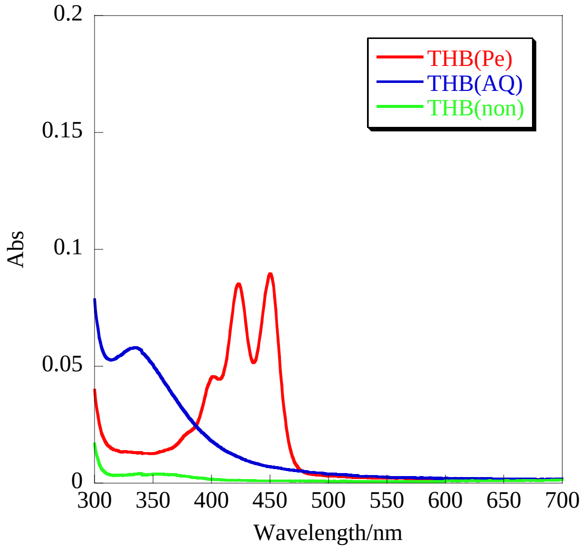


Figure 2-1-3-1. Absorption spectra of THB polymers containing Pe and AQ units dissolved in water with 5 % triton X, cell length = 1 cm.

2-1-3-2. The chemical stability for oxidation of MePyr type polymer and benzene type polymer

MePyr type polymer is easy to be oxidized,[23-24] and partial oxidation of polymers leading to the energy trap (Figure 2-1-3-2). On the other hand, the main chain of benzene type polymer synthesized by stable benzene ring, it is difficult to be oxidized. Oxidation test of MePyr tpye polymer and benzene type polymer was carried out. Chloranil was used to the oxidation.

Figure 2-1-3-3 showed the absorption spectra of MePyr type and THB type polymers oxidized by chloranil oxidant. In the absorption spectra of MePyr type polymers, long wavelength range bands were observed by oxidation reaction. On the other hand, in the absorption spectra of THB type polymers, there is no absorption bands over 700 nm. This suggested that THB type polymers were found to be a good oxidation resistance than MePyr type polymers.

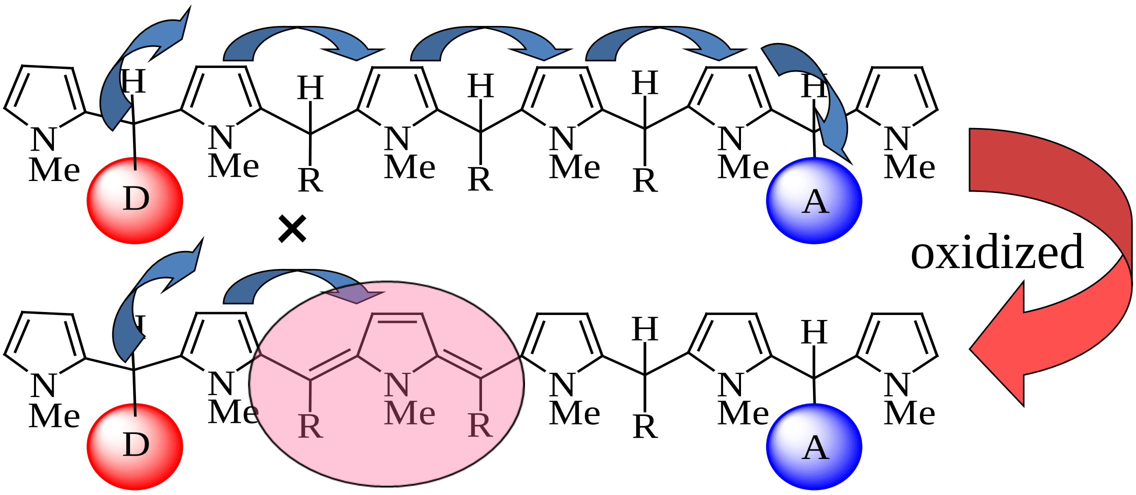


Figure 2-1-3-2. Partial oxidation of MePyr type polymers leading to the energy trap.

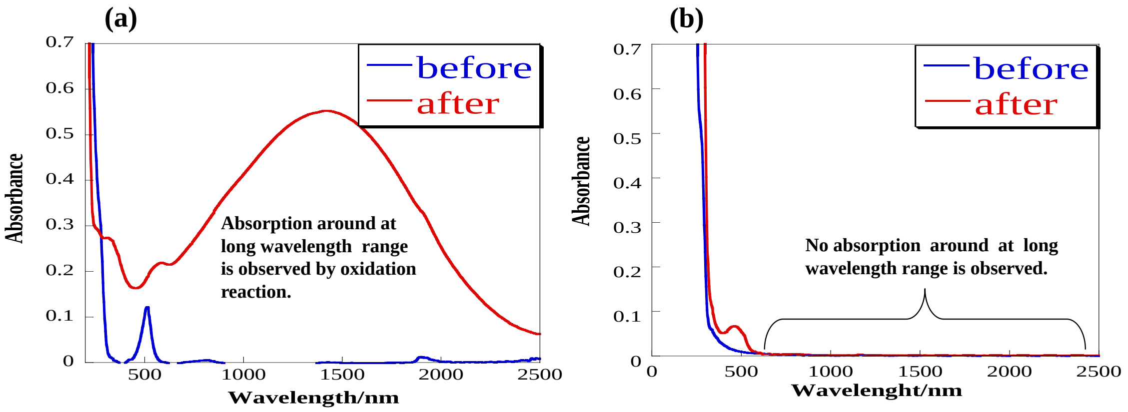


Figure 2-1-3-3. Absorption spectra of (a) MePyr type and (b) THB type polymers oxidized by chloranil, [polymer] = 4 g/L, cell length = 0.1 mm.

2-1-3-3. Electrochemistry, and Energy level diagram

In order to evaluate the photoinduced electron transfer in THB (Pe-AQ), cyclic voltammograms of the monomers were measured (Figure 2-1-3-4 and 2-1-3-5). Moreover, the band gaps of monomers were observed by using absorption spectra. The potentials of the monomers are summarized in Table 2-1-3-2.

On the other hand, the highest occupied molecular orbital (HOMO) of the THB polymer was estimated from the ionization potential by ultraviolet photoelectron spectroscopy in air (surface analyzer, model AC2, Riken Keiki, Co., Ltd., Japan). The ionization potential measurement (Figure 2-1-3-6) and band gap measurement spectrum (Figure 2-1-3-7) results show the HOMO level of the THB polymer is -5.69 eV, and band gap is 5.25eV. Then the energy level diagram shows in Figure 2-1-3-8. The LUMO-LUMO energy gap between Perylene and THB polymer is >1eV, this suggested that the electron transfer from Pe to AQ maybe proceed by the superexchange mechanism.[22]

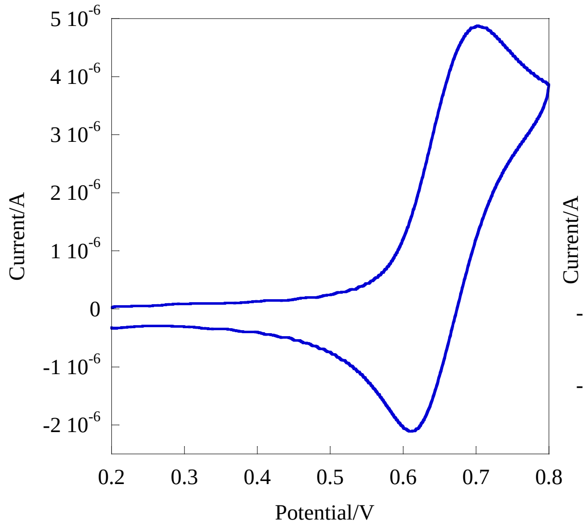


Figure 2-1-3-4. Cyclic voltammograms of Perylene on Pt electode in 0.1 M TBuAPF6 in propylene carbonate at a sweep rate 0.05 V/s.

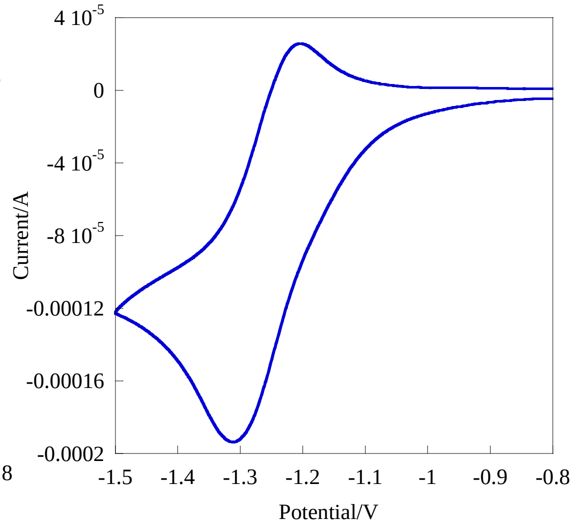


Figure 2-1-3-5. Cyclic voltammograms of anthraquinone on Pt electrode in 0.1 M TBuAPF6 in DMF at a sweep rate 0.05 V/s.

Table 2-1-3-2. Electrochemical Properties of the monomers.

	$E_{(Ox)}$	$E_{(Red)}$	E	E(ev)	
Pe / Pe$^{\cdot+}$ vs. (Ag / Ag$^+$)	**0.63**	**0.69**	**0.66**	**-5.62**	**HOMO**
AQ / AQ$^{\cdot-}$ vs. (Ag / Ag$^+$)	**-1.24**	**-1.29**	**-1.26**	**-3.70**	**LUMO**

With Fc as an internal reference, for which $E_{1/2}$ (Fc$^+$/Fc) = - 4.8 eV vs. (Ag / Ag$^+$).

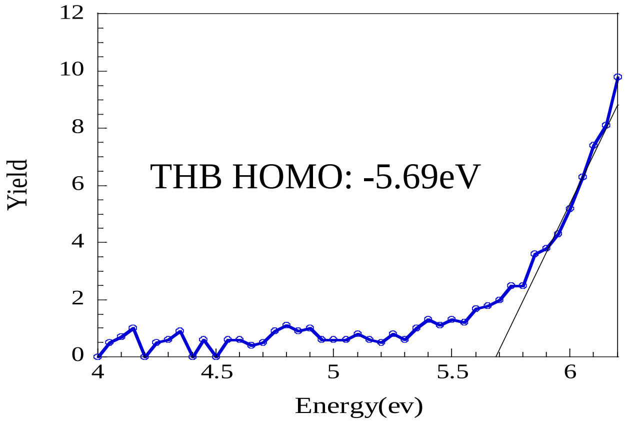


Figure 2-1-3-6. Ionization potential of THB polymer.

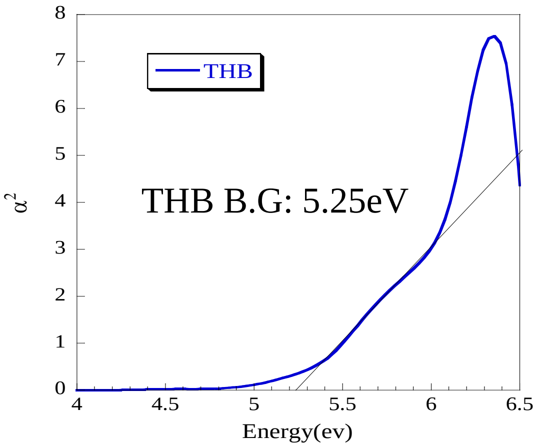


Figure 2-1-3-7. Band gap of THB polymer.

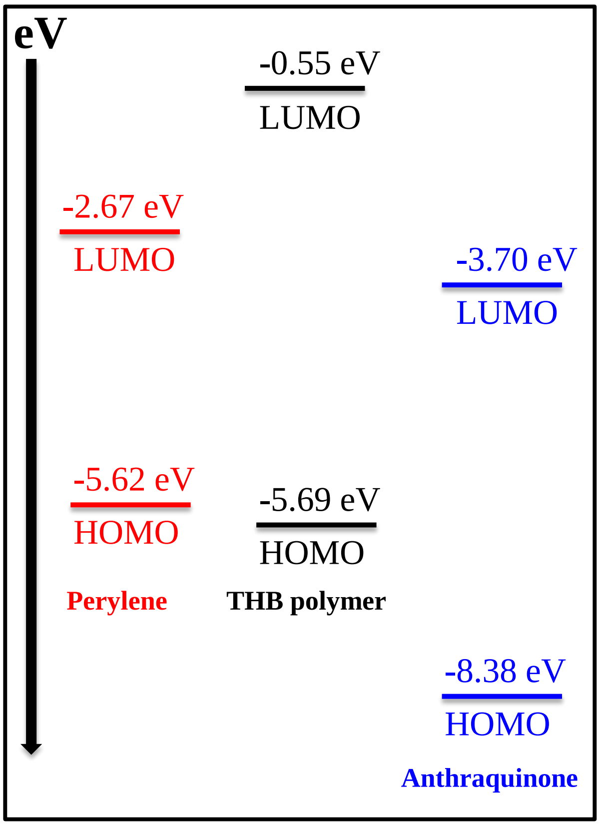


Figure 2-1-3-8. Energy level diagram showing the Pe, THB polymer, and AQ.

2-1-3-4. Steady-State Spectroscopy

Figures 2-1-3-9a and b show the absorption, and fluorescence spectra of the prepared polymers, respectively. In the absorption spectra, AQ unit bands appeared around 350 nm, while Pe unit bands appeared around 420 nm. In the fluorescence spectra (λ_{exc} = 420 nm), which were dominated by the Pe unit, the fluorescence intensity (λ_{exc} = 420 nm) of Pe in polymer THB (Pe-AQ) was quenched in comparison with polymer THB (Pe-non). This result suggested that electron transfer from the electron donor (Pe) to the electron acceptor (AQ) occurred via the macromolecular wire. On the other hand, comparing from the fluorescence spectra of the mixture of THB (Pe) and THB (AQ) and the reference mixture of THB (Pe) and THB (non), no difference of fluorescence intensity for Pe is observed. In other words, no electron transfer occurs between the polymers (Figure 2-1-3-10).

Moreover, to prove electron transfer from Pe to AQ, the AQ units in the polymers were reduced with sodium borohydride ($NaBH_4$). Figures 2-1-3-11a and b show the fluorescence and excitation spectra of the prepared polymers treated with $NaBH_4$. In the fluorescence spectra (λ_{exc} = 420 nm), the fluorescence intensity of reduced THB (Pe-AQ), was similar to that of THB (Pe-non). Because of no electron transfer occurred in the reduced THB (Pe-AQ). Therefore, reduction of the AQ unit caused electron transfer in THB (Pe-AQ) to disappear. This result also suggests that AQ in the polymer works as an electron acceptor.

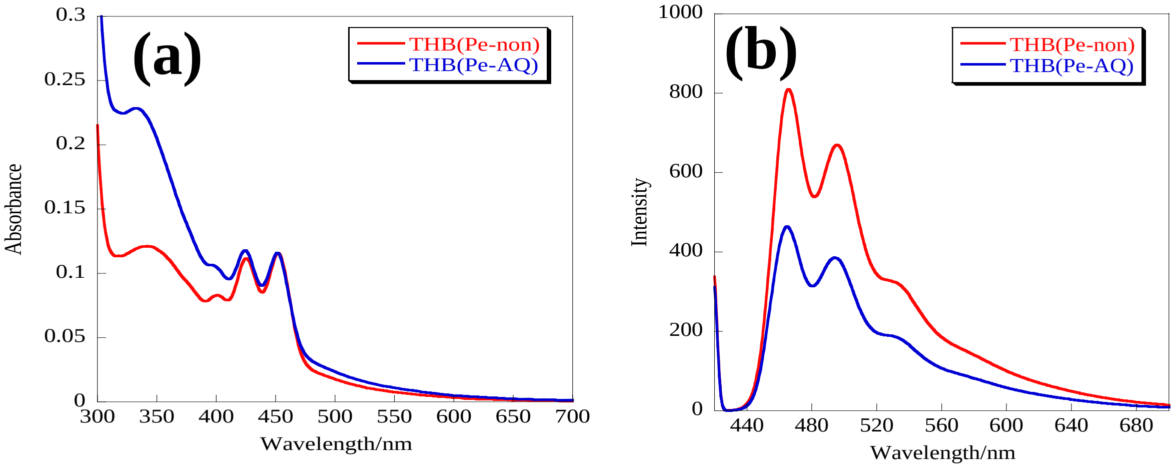


Figure 2-1-3-9. (a) Absorption and (b) fluorescence spectra of THB polymers dissolved in water with 0.1% triton X at 25 °C; abs (420 nm) = 0.01, (b) excited at 420 nm, cell length = 1 cm.

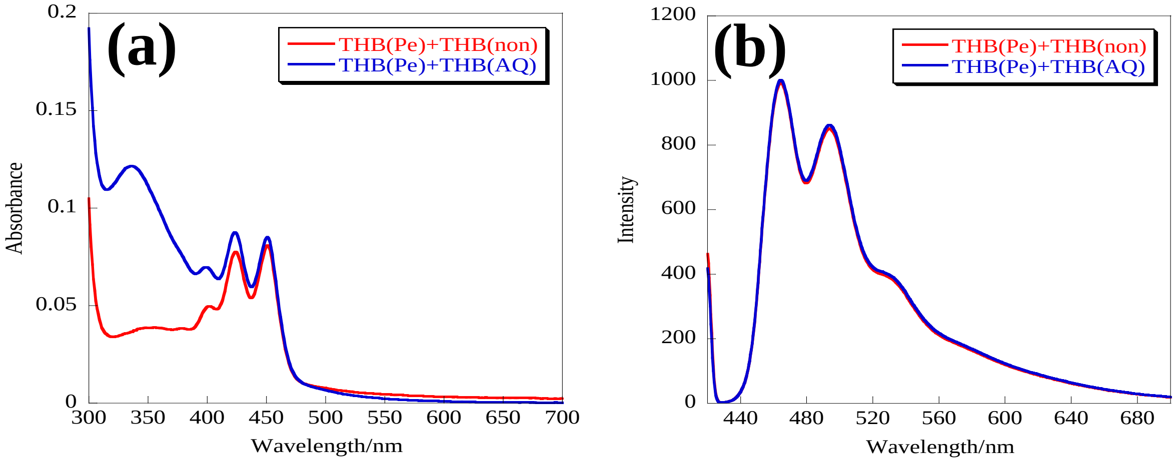


Figure 2-1-3-10. (a) Absorption and (b) fluorescence spectra of THB polymers dissolved in water with 0.1% triton X at 25 °C; abs(420 nm) = 0.01, excited at 420 nm, cell length = 1 cm.

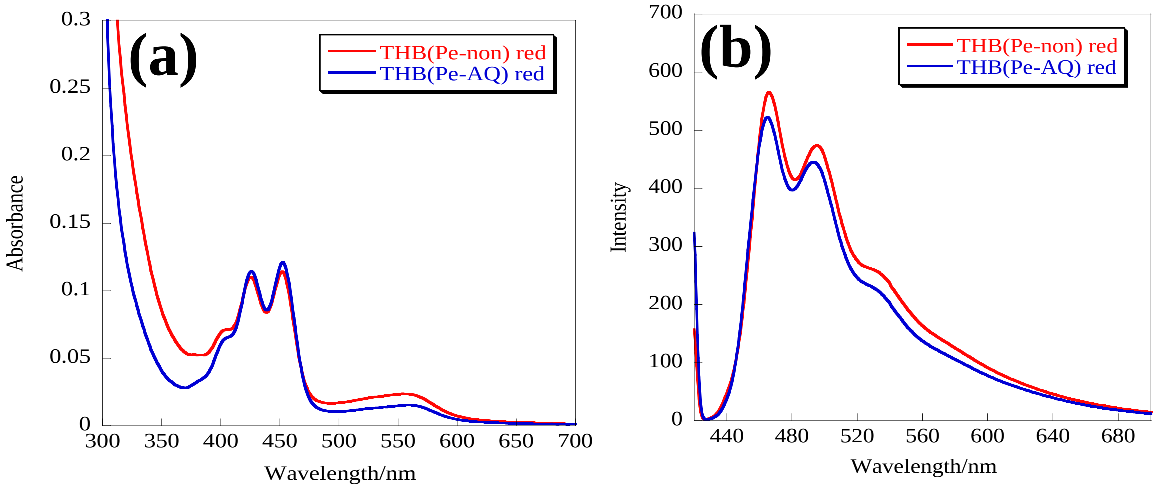


Figure 2-1-3-11. (a) Absorption and (b) fluorescence spectra of THB polymers with $NaBH_4$ dissolved in water with 0.1% triton X at 25 °C; abs(420 nm) = 0.01, excited at 420 nm, cell length = 1 cm.

2-1-3-5. Femtosecond Transient Absorption Spectral Studies

Figure 2-1-3-12 shows the transient spectra of THB (Pe-AQ) and the mixture of THB (Pe) and THB (AQ) in water with 0.1 % triton X at different time using a 388 nm laser light with a 150 fs pulse width as excitation source. Comparing from the transient spectra of THB (Pe-AQ) and the mixture of THB (Pe) and THB (AQ), the spectra profile of the polymers were different. The reason of the spectra difference should be the charge-separated state of $Pe^{\cdot +}$ and $AQ^{\cdot -}$ having been formed in THB (Pe-AQ).

In future, we plan to measure the rate constants of energy and electron transfer, and explore the detailed mechanism in the polymer.

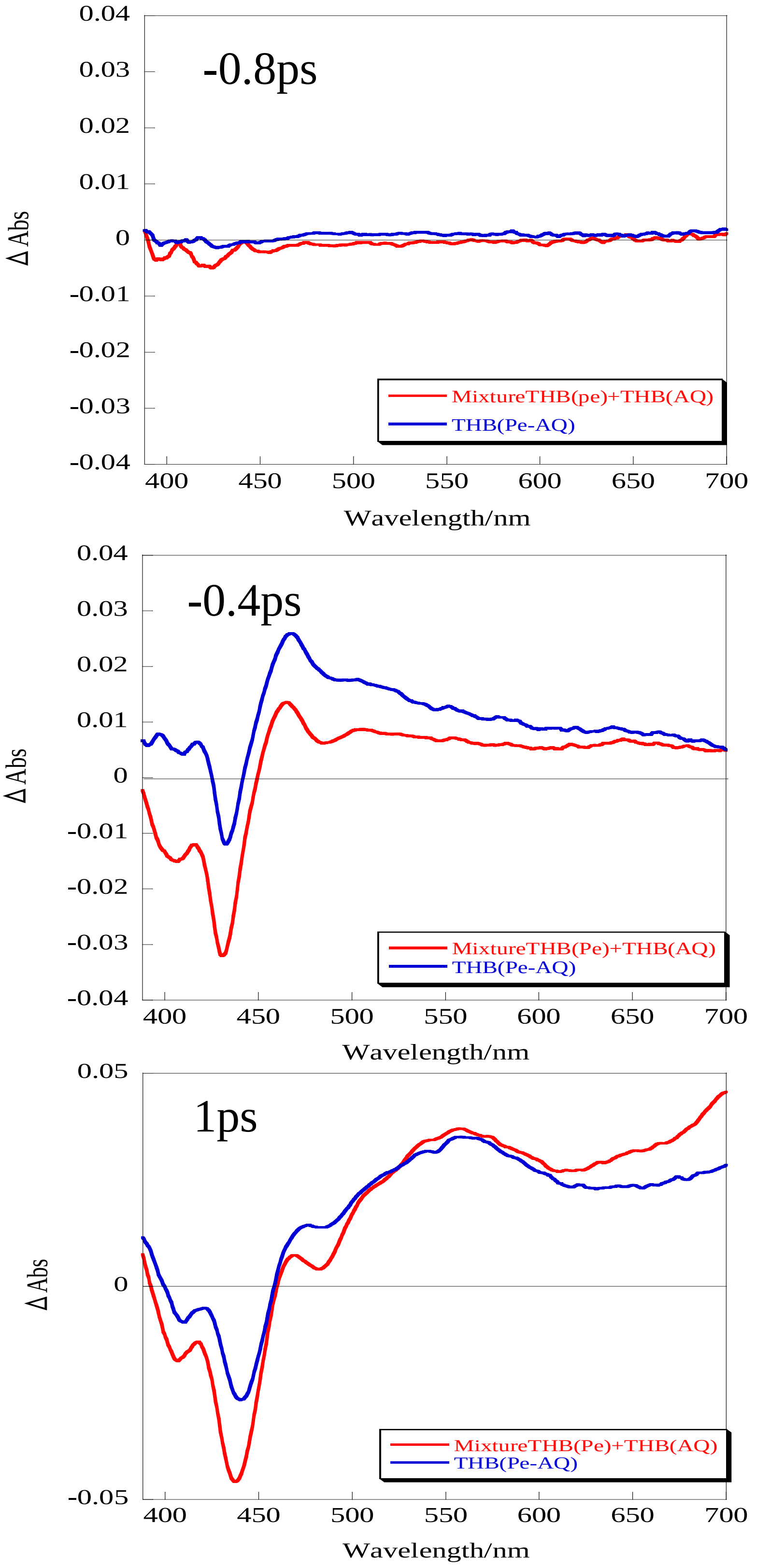


Figure 2-1-3-12. Transient Absorption spectra of THB polymers containing Pe and AQ, dissolved in water with 0.1% triton X, cell length = 0.5mm, excited at 388nm; [polymer]=24g/l, time = -0.8ps, -0.4ps, and 1ps.

2-1-4. Conclusions

In conclusion, comparing from the steady-state fluorescence of the polymer THB (Pe-AQ) and the reference polymer THB (Pe-non), the fluorescence of Pe in THB (Pe-AQ) is quenched. The transient spectra of THB (Pe-AQ) and the mixture of THB (Pe) and THB (AQ), the difference between the polymers has been found. This result suggests that the electron transfer occurs from electron-donor (Pe) to electron-acceptor (AQ) via the macromolecular wire.

The LUMO-LUMO energy gap between Pe and THB polymer is > 1eV, so the electron transfer from Pe to AQ maybe proceed by the superexchange mechanism.

2-1-5. References

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Section 2-2

Synthesis of A, B-block type polymers having different energy levels and study on photoinduced electron transfer

2-2-1. Introduction

As is well know there are three subjects to realize the artificial photosynthesis (learning from the light-dependent reaction of photosynthesis) : (1) Harvesting photon by the antenna molecules and transferring to the reaction center (photoinduced energy transfer); (2) Preventing the charge recombination after the photoinduced electron transfer leading to form a long live charge-separated state efficiently; and (3) Using the charge-separated state to the multi-redox reaction.[1-2] The initial steps toward designing artificial reaction centers (subject (1)) based on efficient light-harvesting[3-8] have been studied in chapter 1. In order to realize the artificial photosynthesis, forming a long live charge-separated state (subject (2)) is very important. In order to form a long live charge-separated state, it is necessary to prevent the charge recombination. In order to form a long live charge-separated state, a multi-stage electron-transfer system based on Z scheme mimics has been studied.[9-13] In Section 2-1, THB type macromolecular wire was used to the long range electron transfer has been studied. In this section, the long-range photoinduced electron transfer was considered using THB type macromolecular wire with two different energy level blocks. The structure was controlled that donor was in high energy level part (A-block), and acceptor was in low one (B-block). The macromolecular wire with the different energy levels (A, B-block polymer) was suggested an electron transfer with a one-way direction (Figure2-2-1). It can form a long live charge-separated state by using this polymer.

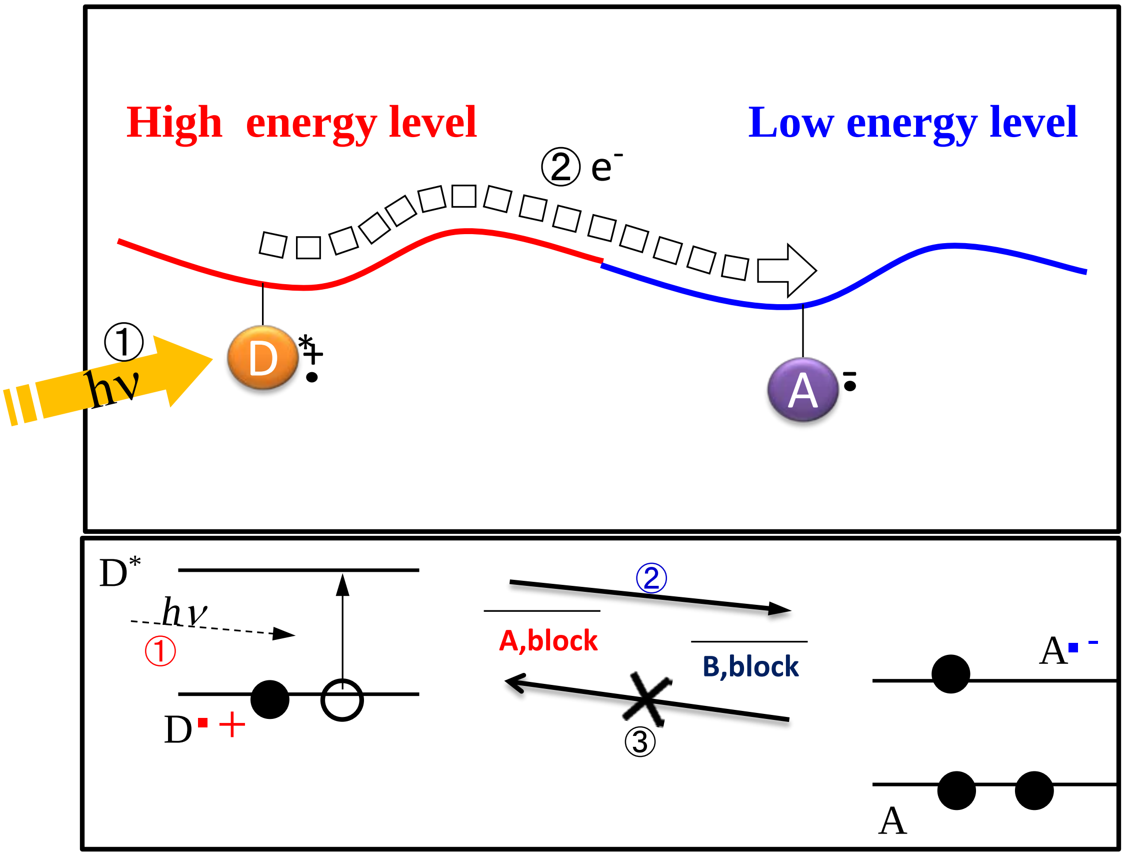


Figure 2-2-1. Image of electron transfer with two component macromolecular wires having different energy levels for effective charge separation.

2-2-2. Experimental

2-2-2-1. Materials

Benzaldehyde-2-sulfonic acid sodium salt (BS), 3-perylenecarboxaldehyde (PeA), and acetyl chloride were purchased from Tokyo Kasei Chemical Co., Ltd. Pyrogallol (1, 2, 3THB), phloroglucinol (1, 3, 5THB), *p*-toluenesulfonic acid monohydrate (p-TS), and other reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. Unless stated otherwise, reagents and solvents were used without purification.

2-2-2-2. Measurements

The UV-Vis spectra were recorded on a V-670 spectrophotometer (JASCO).
Fluorescence spectra were recorded on a FP-8300 spectrophotometer (JASCO).
^{1}H-NMR spectra were recorded on a JEOL ECS-400 spectrometer (JEOL) working at 400MHz using TMS as the internal standard. DMSO-d6 was used as the solvent for the polymer.

2-1-2-3. Polymerization

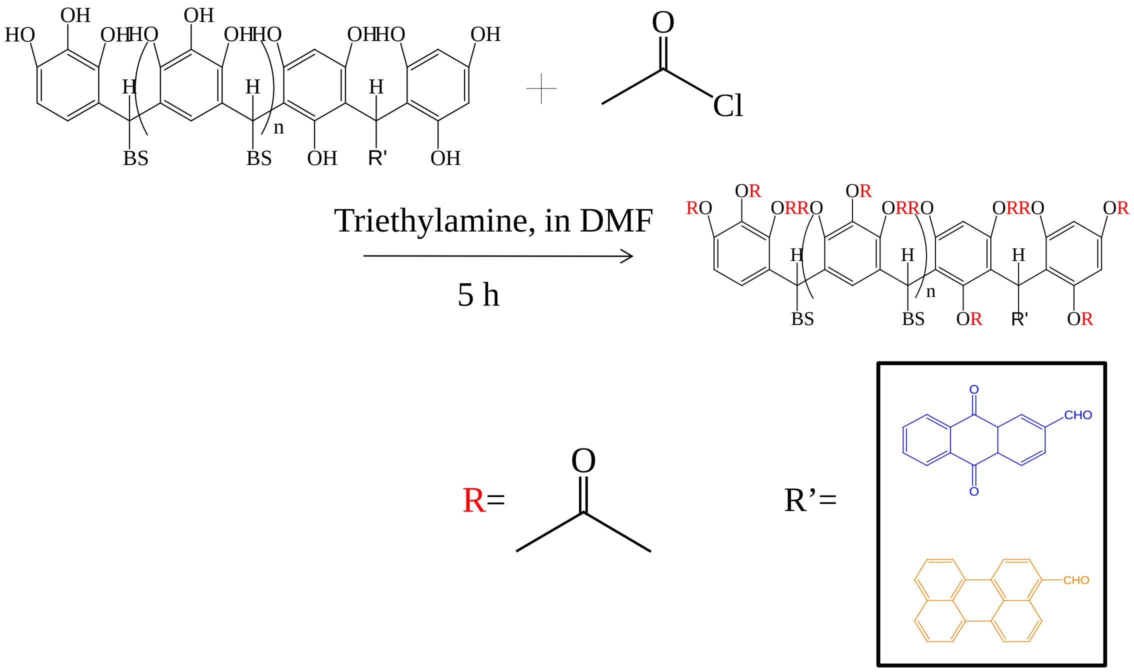
Syntheses of the ester polymers:

Syntheses of ester polymers are shown in Scheme 2-2-2-1.

THB (Pe-AQ) (0.50 g, prepared in Section 2-1) was dissolved in DMF (5.0 mL). Triethylamine (24 mmol) was added to this solution. The resulting solution was stirred at 25 °C. Then, a solution containing acetyl chloride (24 mmol, 3.0 mL DMF) was continuously added to resulting solution for 30 min. After 6 h, the insoluble substance in reaction mixture was separated by filtration. Isopropyl alcohol (80 mL) was added to the obtained solution. The resulting precipitate was purified by reprecipitations from two times of water/isopropyl alcohol (4 mL/80 mL), and then dissolved in water. The polymer was obtained by freeze-drying (0.302 g). The other polymers were similarly prepared.

^{1}H NMR spectra of ester polymer and THB polymer:

Figure 2-2-2-1 shows the chemical structures and the NMR spectra of ester polymer and THB polymer. Although the spectrum broadening is observed in the polymer, it also showed the signals of the polymer proton. Comparing from the spectra of ester polymer and THB polymer, the peaks (around 7.0 ppm) in ester polymer become weaker as the hydroxy content disappeared because of ester reaction. On the other hand, the peaks (around 2.0 ppm) in ester polymer become stronger as increasing the methyl content.



Scheme 2-2-2-1. Synthsis of ester polymers containing Pe and AQ units.

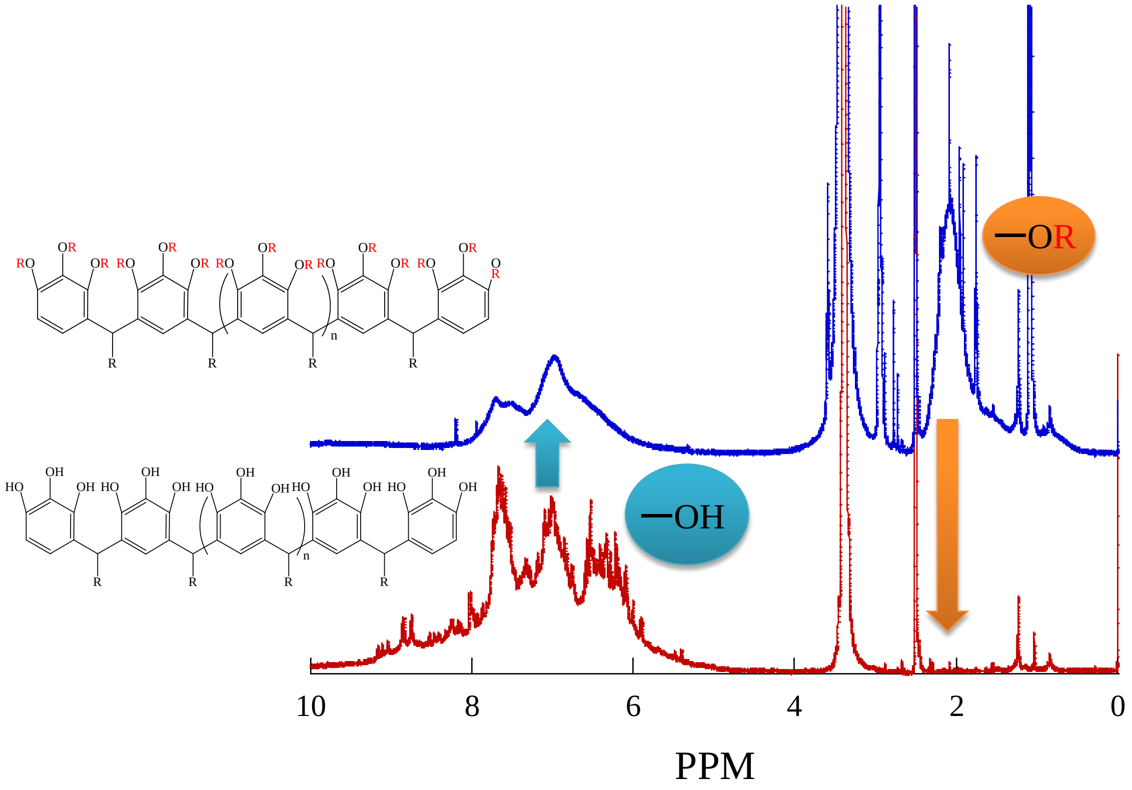
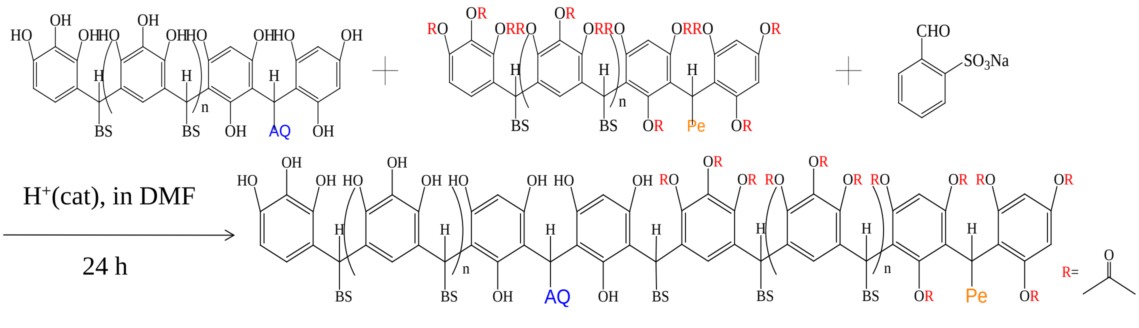


Figure 2-2-2-1. ^{1} H -NMR spectrum of THB polymer and ester polymer in DMSO-d^6.

Synthesis of A, B-block type polymers having different energy levels:

Syntheses of A, B-block type polymers are shown in Scheme 2-2-2-2.

Ester (Pe) (0.2 g), THB (AQ) (0.6 g), and BS (0.1 g) were dissolved in DMF (4.0 mL). A second solution containing p-TS (0.50 mmol, 1 mL DMFr) was added to this solution at 25 °C. After 24 h, isopropyl alcohol (40 mL) was added to the reaction mixture. The resulting precipitate was purified by reprecipitations from two times of water/isopropyl alcohol (3 mL/40 mL), and then dissolved in water. The polymer was obtained by freeze-drying (0.782 g, 80%). The other polymers were similarly prepared.



Scheme 2-2-2-2. Synthesis of two component macromolecular wire prepared by THB polymer, ester polymer and aldehyde(BS).

2-2-3. Results and discussion

2-2-3-1. The properties of the ester polymers

Energy level diagram:

The ionization potential measurement (Figure 2-2-3-1) and band gap measurement spectrum (Figure 2-2-3-2) results show the HOMO level of the ester polymer is -5.02 eV, and band gap of the ester polymer is 5.14eV. While the HOMO level and band gap of THB polymer have been studied in Section 2-1. Based on these, energy level diagram is formed (Figure 2-2-3-3).

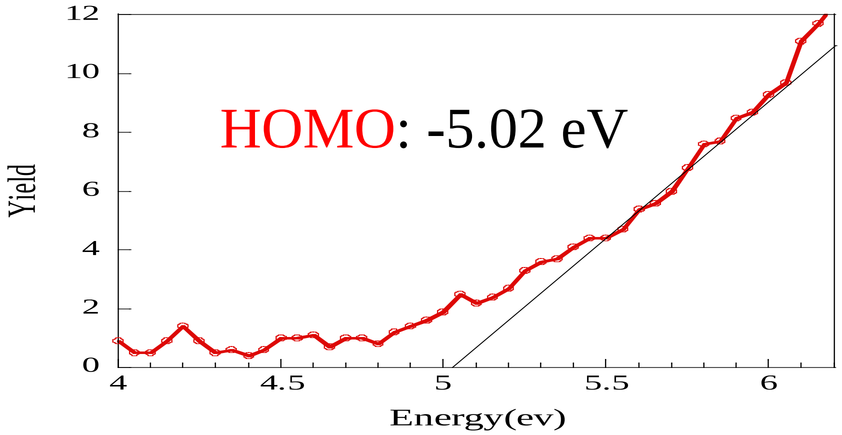


Figure 2-2-3-1. Ionization potential of ester polymer.

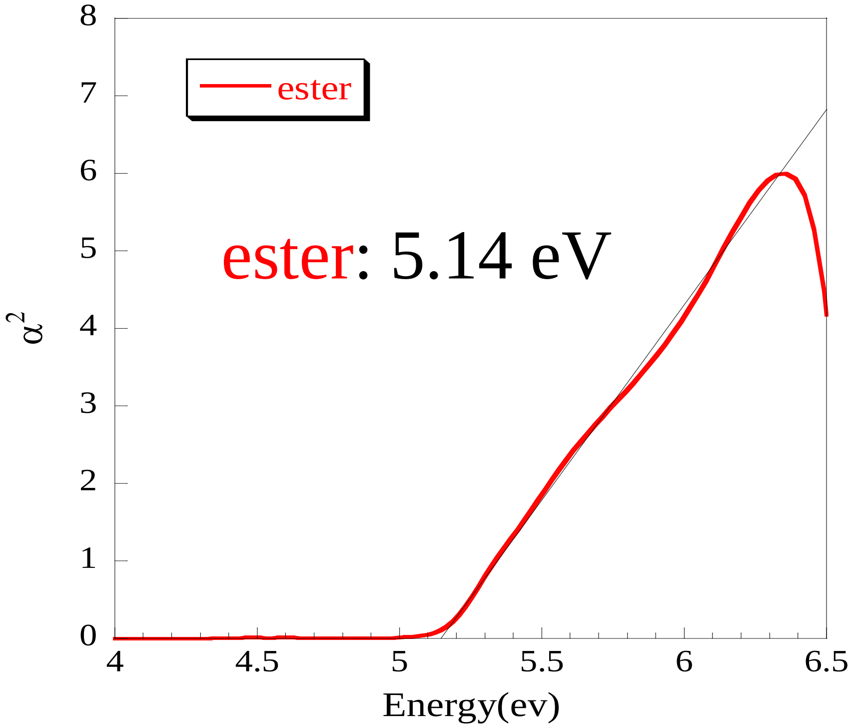


Figure 2-2-3-2. Band gap of ester polymer.

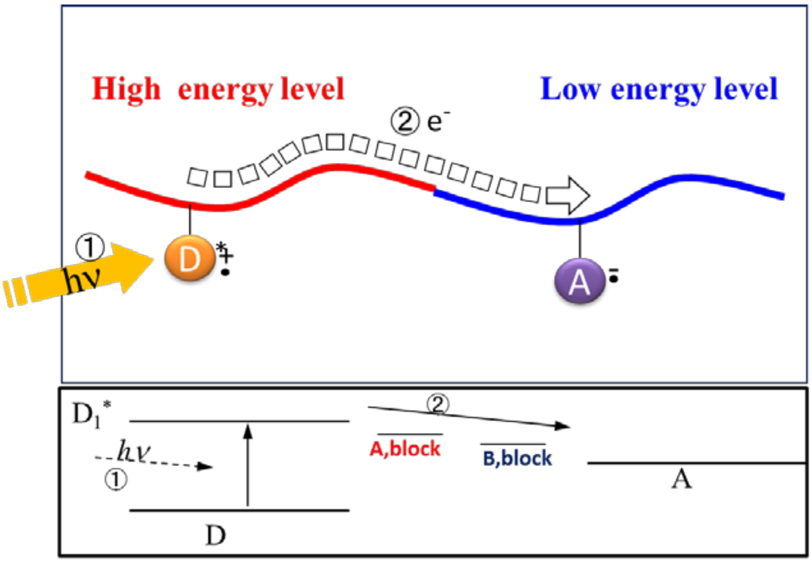


Image of electron transfer with two component macromolecular wires having different energy levels for effective charge separation.

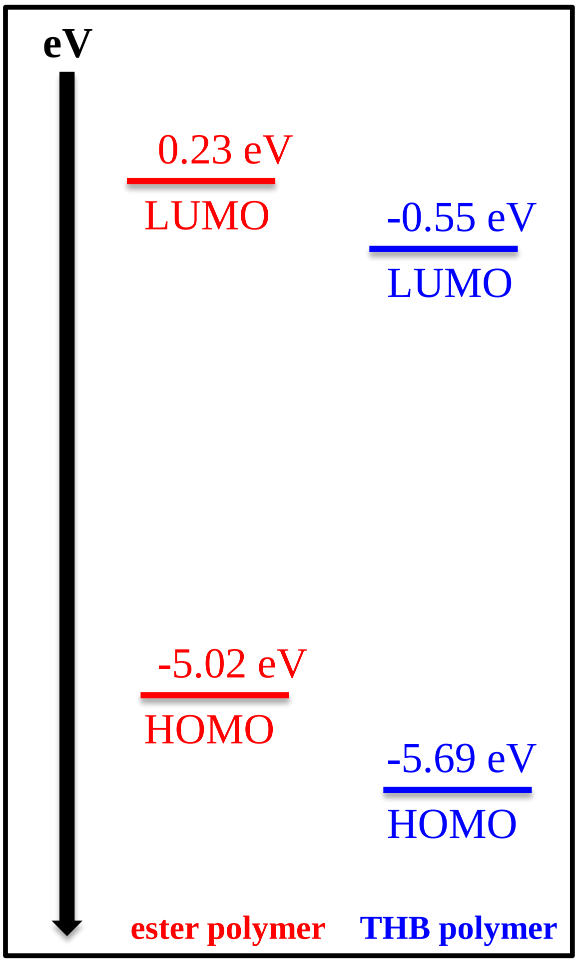


Figure 2-2-3-3. Energy level diagram showing the ester and THB polymers.

Steady-State Spectroscopy

Figures 2-2-3-4a and b show the absorption, and fluorescence spectra of the prepared polymers, respectively. In the absorption spectra, the absorption bands of AQ unit appeared around 350 nm, while the absorption bands of Pe unit appeared around 420 nm. In the fluorescence spectra (λ_{exc} = 420 nm), which were dominated by the Pe unit, the fluorescence intensity (λ_{exc} = 420 nm) of Pe in polymer ester (Pe-AQ) was quenched in comparison with polymer ester (Pe-non), which lacked the AQ acceptor. This result suggested that electron transfer from the electron donor (Pe) to the electron acceptor (AQ) had occurred. Accordingly, ester polymer also can work as a macromolecular wire.

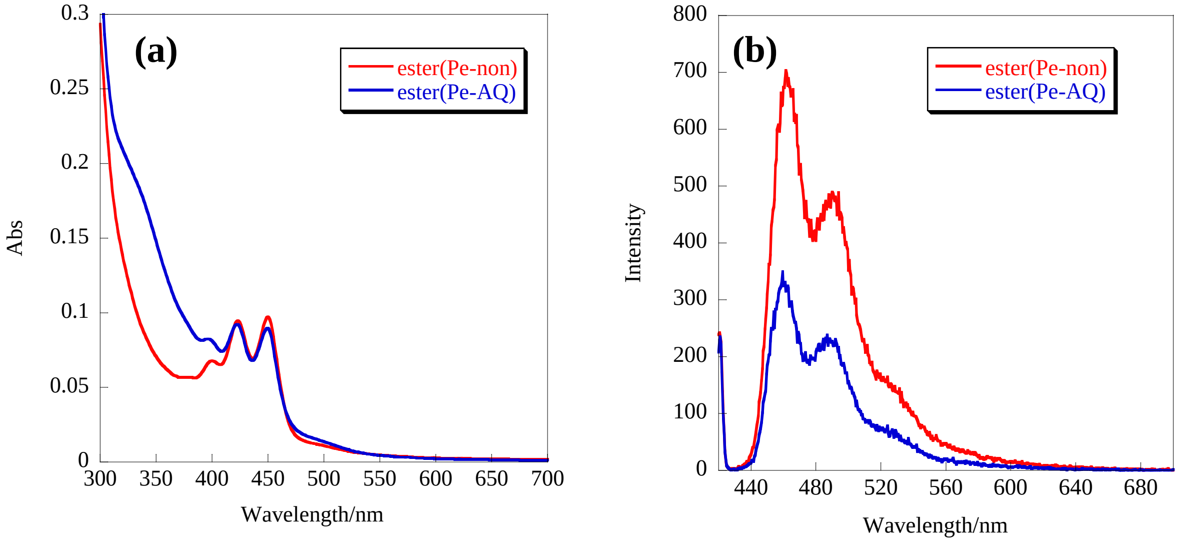


Figure 2-2-3-4. (a) Absorption and (b) fluorescence spectra of ester polymers dissolved in water with 0.1% triton X at 25 °C; abs (420 nm) = 0.01, (b) excited at 420 nm, cell length = 1 cm.

2-2-3-2. The properties of A, B-block type polymers having different energy levels:

Energy levels of polymers have been studied in **2-2-3-1**, we know the energy level of ester polymer is higher than the energy level of THB polymer. Both of the prepared polymers have different energy levels. Ester (Pe)-THB (AQ) means electron donor (Pe) in the ester part (high energy level part), and electron acceptor (AQ) in the THB part (low energy level part); e.g., Two sets reference polymers were prepared for this purpose: (1) ester (Pe)-THB (AQ)/ ester (Pe)-THB (non); (2) THB (Pe)-ester (AQ) / THB (Pe)-ester (non).

Steady-State Spectroscopy

Figures 2-2-3-5a and b show the absorption, and fluorescence spectra of ester (Pe)-THB (AQ) and ester (Pe)-THB (non), respectively. In the absorption spectra, the absorption bands of AQ unit appeared around 350 nm, while Pe unit bands appeared around 420 nm. In the fluorescence spectra (λ_{exc} = 420 nm), which were dominated by the Pe unit, the fluorescence intensity (λ_{exc} = 420 nm) of Pe in polymer ester (Pe)-THB (AQ) was quenched in comparison with polymer ester (Pe)-THB (non), which lacked the AQ acceptor. This result suggested that electron transfer from the electron donor (Pe) in the ester part (high energy level part) to the electron acceptor (AQ) in the THB part (low energy level part) had occurred via the A, B-block type polymers having different energy levels.

On the other hand, Figures 2-2-3-6a and b show the absorption, and fluorescence spectra of ester (AQ)-THB (Pe) and ester (non)-THB (Pe), respectively. In the fluorescence spectra (λ_{exc} = 420 nm), the fluorescence intensity (λ_{exc} = 420 nm) of Pe in polymer ester (AQ)-THB (Pe) was similar to that of ester (non)-THB (Pe). In the other words, there is no electron transfer in this A, B-block type polymer. Based on the dates of Steady-State spectroscopy, the structure of polymer was controlled which donor in high energy level part (A-block), and acceptor in low one (B-block), having the different energy levels (A, B-block polymer). It was suggested an electron transfer with a one-way direction (Figure 2-2-3-7). It can form a long live charge-separated state by using this polymer.

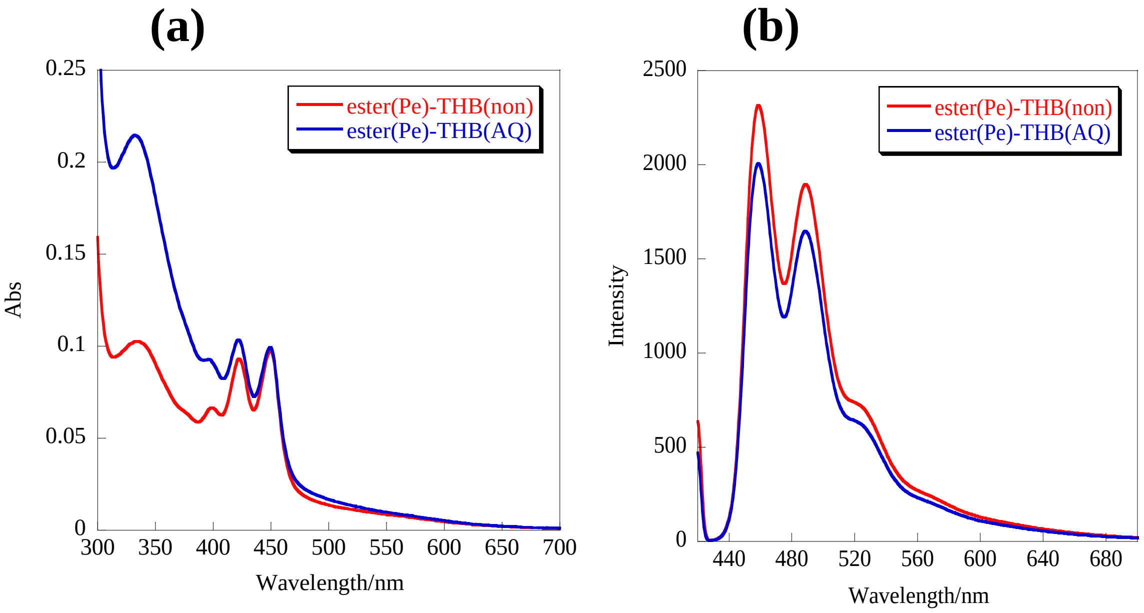


Figure 2-2-3-5. (a) Absorption and (b) fluorescence spectra of A, B-Block type polymers dissolved in water with 0.1% triton X at 25 °C; abs (420 nm) = 0.01, (b) excited at 420 nm, cell length = 1 cm.

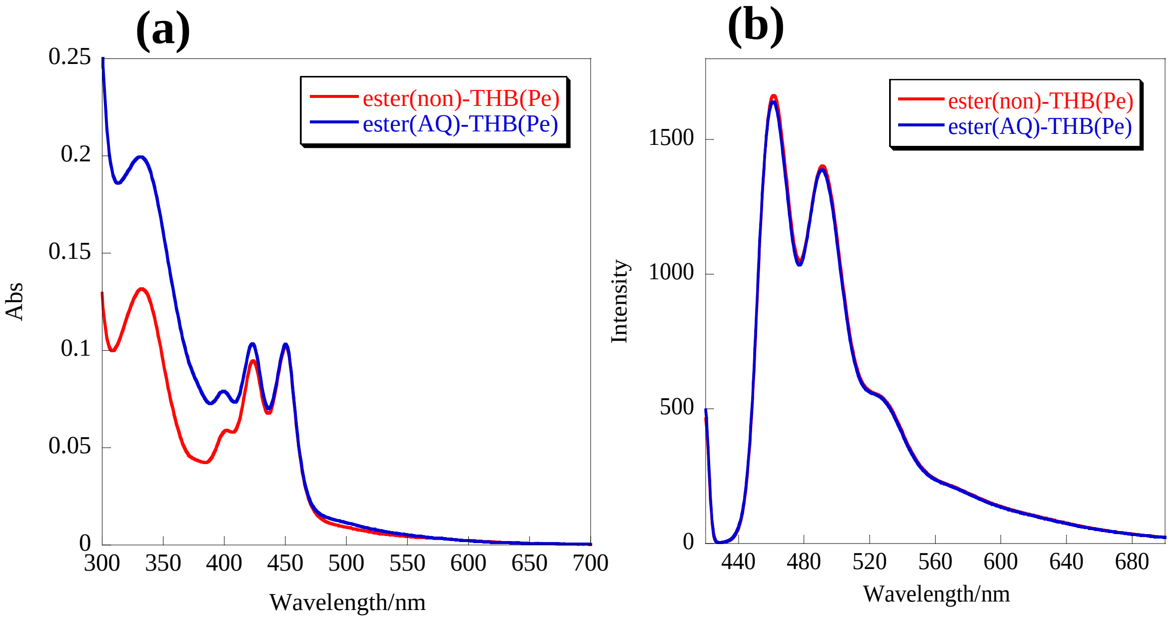


Figure 2-2-3-6. (a) Absorption and (b) fluorescence spectra of A, B-Block type polymers dissolved in water with 0.1% triton X at 25 °C; abs (420 nm) = 0.01, (b) excited at 420 nm, cell length = 1 cm.

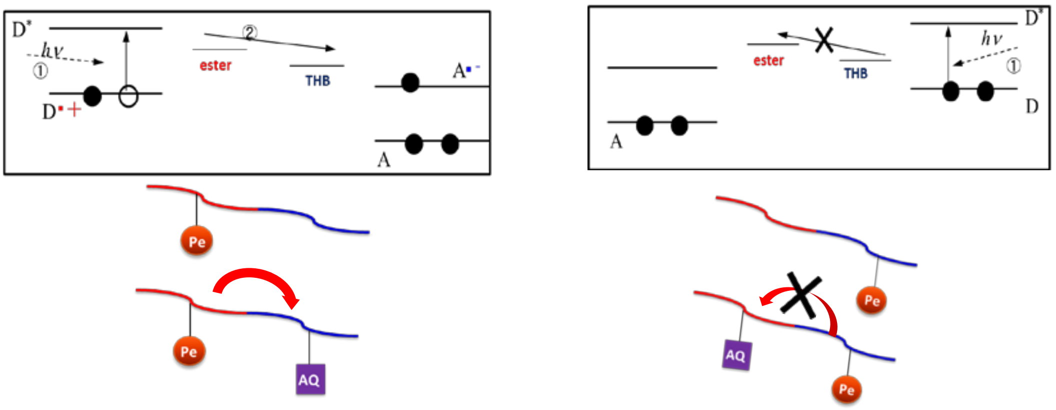


Figure 2-2-3-7. Photoinduced electron transfer mechanisms described in this section.

Laser Spectroscopy

To evaluate an electron transfer with a one-way direction via the A, B-block type polymers having different energy levels which electron donor (Pe) in the ester part (high energy level part) to the electron acceptor (AQ) in the THB part (low energy level part). Fluorescence decay and femtosecond transient absorption measurements were carried out.

Figure 2-2-3-8 shows the fluorescence decay profile of ester (Pe)-THB (non) and ester (Pe)-THB (AQ) in water with 0.1 % triton X at different time intervals using a 388 nm laser light with a 150 fs pulse width as excitation source. Comparing from the fluorescence decay profile of ester (Pe)-THB (non) and ester (Pe)-THB (AQ), the difference between the polymers has been found. The decays for ester (Pe)-THB (non) was slower than ester (Pe)-THB (AQ). The maximum difference appeared at 2 ps. This result suggested that electron transfer from Pe to AQ via macromolecular wire occurred at 2 ps. On the other hand, the fluorescence decay profile of ester (AQ)-THB (Pe) was similar to that of ester (non)-THB (Pe). In the other words, there is no electron transfer in this A, B-block type polymer.

In addition, the transient spectra at 2 ps of ester (Pe)-THB (AQ) and the mixture of THB (Pe) and THB (AQ) were shown in Figure 2-2-3-9. The difference between the polymers has been found. The reason of the difference should be the charge-separated state of $Pe^{\cdot +}$ and $AQ^{\cdot -}$ having been formed in ester (Pe)-THB (AQ). On the other hands, there is no change in the transient spectra at 2 ps of ester (AQ)-THB (Pe) and the mixture of THB (Pe) and THB (AQ) (Figure 2-2-3-10).

Based on the dates of laser spectroscopy, these suggested an electron transfer with a one-way direction occurred from electron donor (Pe) in the ester part (high energy level part) to electron acceptor (AQ) in the THB part (low energy level part) via the A, B-block type polymer. It can form a long live charge-separated state by using this polymer.

In future, we plan to measure the rate constants of energy and electron transfer, and explore the detailed mechanism in the polymer.

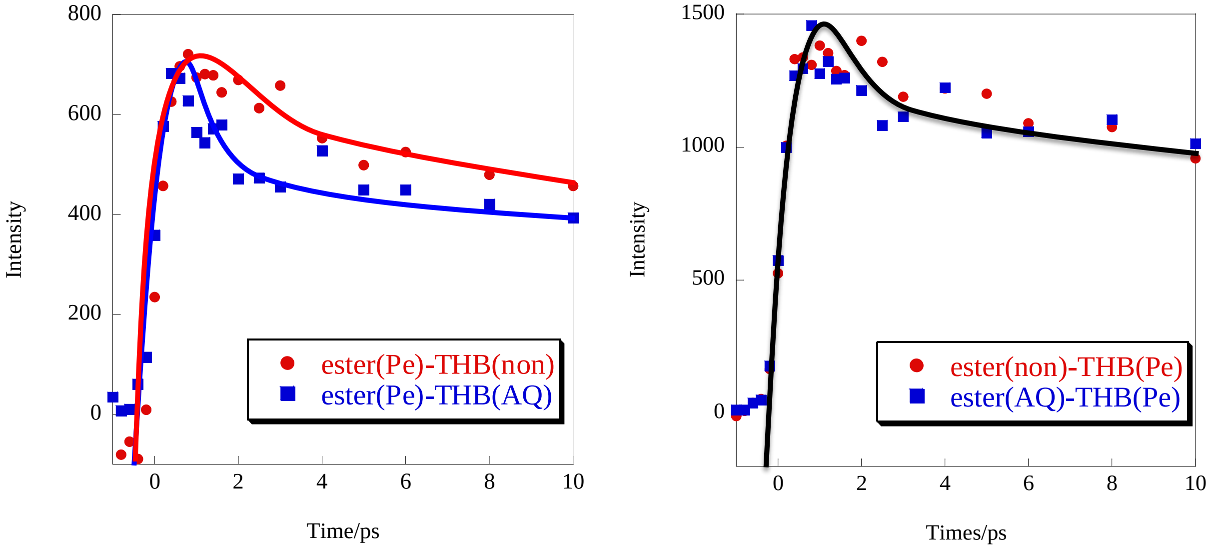


Figure 2-2-3-8. Fluorescence decay profile of A,B-block polymers containing Pe or Pe and AQ units, dissolved in water with 0.1 % triton X, excitation at 388nm; [polymer]=24g/l.

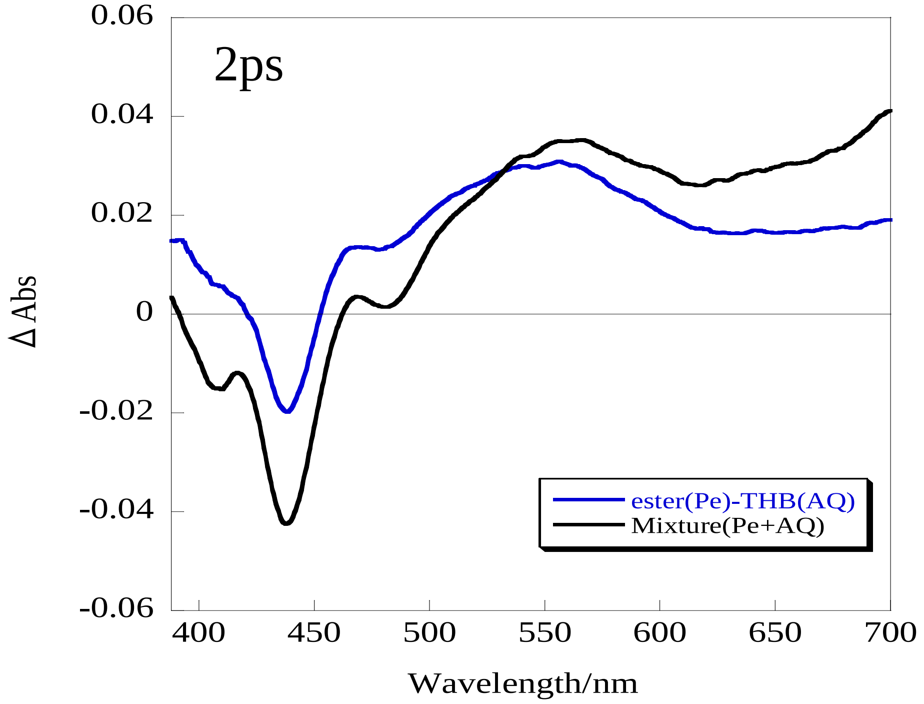


Figure 2-2-3-9. Transient Absorption spectra of THB polymers containing Pe and AQ, dissolved in water with 0.1% triton X, cell length=0.5mm, excited at 388nm ;[polymer]=24g/l, time=2ps.

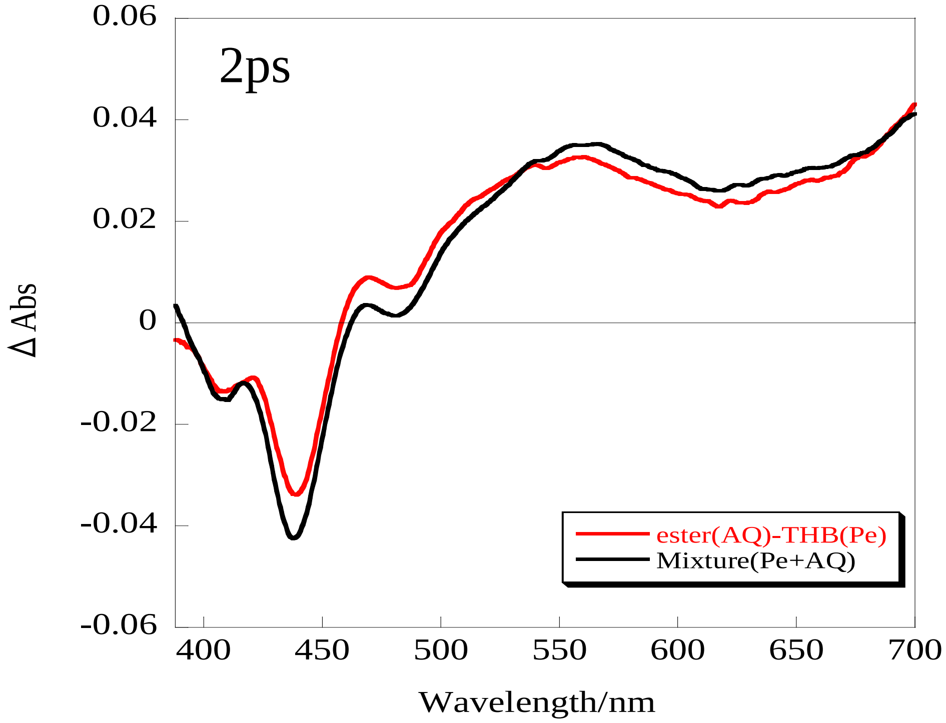


Figure 2-2-3-10. Transient Absorption spectra of THB polymers containing Pe and AQ, dissolved in water with 0.1% triton X, cell length=0.5mm, excited at 388nm ;[polymer]=24g/l, time=2ps.

2-2-4. Conclusions

In this section, the long-range photoinduced electron transfer was considered using step-π-conjugated polymers with two different energy level blocks. The structure was controlled that donor was in high energy level part (A-block), and acceptor was in low one (B-block). The macromolecular wire with the different energy levels (A, B-block polymer) was suggested an electron transfer with a one-way direction. It can form a long live charge-separated state by using this polymer.

2-2-5. References

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CONCLUDING REMARKS

In this study, syntheses of structure-controlled polymers and application to artificial photosynthesis are discussed. Each section is summarized below.

In **CHAPTER 1**, MePyr type structure-controlled polymers were prepared by pseudo-living addition-condensation polymerization and their application to study on subject for artificial photosynthesis are described.

Section 1-1

A new type of pseudo-living polymerization by continuous addition of monomers to the addition-condensation of 1-methylpyrrole and aldehydes is shown. The pseudo-living addition-condensation polymerization is able to control the polymer main structures. The conversions and molecular weights of the obtained polymers by pseudo-living addition-condensation polymerization are shown. The linear relationship of the Mw and the added amount of monomers means that this polymerization progresses like a living-polymerization.

Section 1-2

Many types of aldehydes can be used in pseudo-living polymerization. The controlled addition of certain aldehydes leads to structure-controlled polymers. An A, B-block amphiphilic polymer is prepared by the sequential addition of hydrophobic and hydrophilic aldehydes. A fluorescence quenching method was used to provide evidence that the prepared polymer exists at the heterophase boundary with the donor and acceptor groups positioned in the two different phases. This type of polymer showed an interphase photoinduced energy transfer in a micellar system.

Section 1-3

A branched polymer with high and low amounts of energy donors and acceptors was prepared by the pseudo-living addition-condensation polymerization. The polymer features a high amount of energy donors (Py) in branched parts and a low amount of energy acceptors (Pe) in centers. According to the fluorescence, and excitation spectra of the prepared polymers, the photoinduced energy transfer occurs from the multi donors to one acceptor. This indicates an efficient light-harvesting mechanism.

Section 1-4

Another branched polymer which integrates singlet-singlet energy transfer and photoinduced electron transfer was prepared by pseudo-living addition-condensation polymerization. The polymer, which features a high amount of energy donors (Py) in branched parts and a low amount of energy acceptors (Pe) in the centers, also bears Pe–AQ electron donor-acceptor units similar to those seen in natural photosynthetic antenna-reaction center complexes.

In **CHAPTER 2**, syntheses of benzene type polymers and their application to study on subject for artificial photosynthesis are described.

Section 2-1

We defined a step-π-conjugated polymer which alternately consists of a small π-conjugated molecule as like as a benzene unit and a sp^3-methine carbon. The benzene units have no coplanar each other. Therefore, no strong interaction exists between benzene units; however, superexchange and/or hopping of electrons occurs. The polymer can work as a molecular wire with high efficiency electron transfer.

Obtained results are described as follows:

1, Comparing from the steady-state fluorescence and transient spectra of the obtained polymers, those results suggest the electron transfer occurs from electron-donor (Pe) to electron-acceptor (AQ) via the polymer.

2, The electron transfer from Pe to AQ maybe proceed by the superexchange mechanism because of the LUMO-LUMO energy gap between Pe and THB polymer is > 1eV.

Section 2-2

The long-range photoinduced electron transfer was considered using step-π-conjugated polymers with two different energy level blocks. The structure was controlled that donor was in high energy level part (A-block), and acceptor was in low one (B-block). The macromolecular wire with the different energy levels (A, B-block polymer) was suggested an electron transfer with a one-way direction. It can form a long live charge-separated state by using this polymer.

Obtained results are described as follows:

1, The ionization potential measurement and absorption spectra results show the energy level of polymers. The energy level of ester polymer is higher than that of THB polymer. Therefore, the A,B- block polymers have different energy levels in a polymer chain.

2, According to the steady-state fluorescence, transient spectra, and fluorescence decay profile of the obtained polymers, those results suggest an electron transfer with a one-way direction via the polymer.

PUBLICATIONS LIST

CHAPTER 1

Section 1-1, 1-2, and 1-3.

Hao-xuan Guo, Keisuke Yoshida, and Hiroyuki Aota

“Structure-controlled polymers prepared by pseudo-living addition-condensation polymerization and their application to light harvesting”

Chemical Communications, **2016**, *52*, 11819-11822.

Section 1-4.

Hao-xuan Guo and Hiroyuki Aota

“Light-Harvesting and Electron Transfer in a Structure-Controlled Polymer for Artificial Photosynthetic Antenna-Reaction Centers”

Chemistry Letters, in press.

CHAPTER 2

Section 2-1.

Hao-xuan Guo, Yuichi Ishikawa, Chihiro Fujiwara, and Hiroyuki Aota

“Macromolecule-wire behaviour in step-π-conjugated polymer prepared from trihydroxybenzene and aldehydes”

To be published.

Section 2-2.

Hao-xuan Guo, Yuichi Ishikawa, Chihiro Fujiwara, and Hiroyuki Aota

“Electron transfer with a one-way direction via an A, B-block type macromolecule wire having different energy levels”

To be published.

ACKNOWLEGMENTS

Foremost, I gratefully acknowledge Professor Hiroyuki Aota, Department of Chemistry and Material Engineering, Faculty of Chemistry, Material and Bioengineering, Kansai University, for his thorough guidance and hearty encouragement for achievement of this work.

I wish to my sincere appreciation to Professor Fumio Sanda and Professor Hideya Kawasaki for their helpful suggestions in preparing this thesis.

This research has been carried out in Photo chemistry and polymer chemistry Laboratory in Kansai University. I wish to express my sincere gratitude to students of Kansai University for proceeding on experimental and discussing of this work. I also thank all other members of Photo chemistry and polymer chemistry Laboratory (2012-2016) for their helpful assistance and friendship. I am very grateful to Ministry of Education, Culture, Sports, Science and Technology-JAPAN for its scholarship.

Finally, I wish to my deepest gratitude to my mother, my father, my grandmother, my uncle, my friends and all the people who support me for giving me good advice, encouragement, mental and financial supports in accomplishment of this work.

October 2016

Hao-xuan Guo