A Consideration of Thermochromic Behavior in Poly(*p*-phenylene vinylene) Derivatives

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Keywords : conducting polymer, poly(*p*-phenylene vinylene) derivatives, thermochromism, photoluminescence, *trans-gauche* transition, solid-liquid phase transition

we report on the thermochromic behavior of ROPPVs and poly(2,5-dialkyl-*p*-phenylene vinylene), RPPVs. The variation of properties with side chain lengths is also mentioned. The results will be discussed in comparison to those of PATs.

The mechanism of thermochromism in a conducting polymer was proposed by Yoshino *et al.*⁽¹³⁾. With increasing temperature, the side chain changes its conformation due to the *trans-gauche* transition and becomes bulky. The steric hindrance between the bulky side chain and the polymer main chain forces the main chain to twist. Therefore, the π -electron systems in the main chain of the polymer tend to lose their planarity with increasing temperature, resulting in decreased effective π -conjugation length and increased bandgap energy.

The difference in the thermochromic behavior between ROPPV, RPPVs and PATs can be tentatively interpreted in terms of the main chain structure. The phenyl rings composing the PPV-type main chain can rotate freely with respect to the main chain without significant deformation of the main chain, as they are connected at *para*-position. Therefore, the planarity of π -electron systems can be gradually decreased with increasing temperature. On the other hand, the thiophene rings in PATs cannot rotate without causing significant deformation of the main chain, because the bonds connecting a thiophene ring and the main chain are not in a straightline. This indicates that the planarity of the π -electron systems in PATs change not in the solid state but in the liquid state. Therefore, the π -electron systems in PATs lose their planarity not gradually with increasing temperature at the solid state, but suddenly at the solid-liquid phase transition.

As the mechanism of the decrease of PL intensity of ROPPVs and RPPVs, we speculate the separation of the excited species due to the reduction of the distance between polymer main chains and the enhancement of the overlap of π -electrons with the twist of polymer main chain. The distance between polymer main chains is widened by the side chains. The side chains take *trans* conformation at lower temperature and *gauche* conformation near and above the melting point. The side chain is more bulky and shorter when it is in *gauche* than in *trans*. Therefore, with increasing temperature, the distance between polymer main chains becomes shorter. In this case, the dissociation probability of the excited species such as excitons and/or exciton polarons through interchain charge transfer increases and the probability of radiative recombination decreases.

On the other hand, the twist of polymer main chain would enhance the overlap of π -electrons, as schematically shown in Fig. 8. Assume that there is a pair of neighboring polymer main chains whose phenyl rings are perpendicular to each other and therefore the π -electrons do not overlap each other. In such a case, the interchain charge transfer does not occur. However, with

Fig. 1. π -electrons of polymer main chains and non-bonding electrons in oxygen atoms of alkoxy groups

increasing temperature, the polymer main chain starts to twist and the π -electron orbitals of the pair become more parallel to each other. Consequently, the dissociation probability of the excited species through the interchain charge transfer increases and the probability of radiative recombination decreases.

In the above discussion, we only concentrated on the change of interaction between polymer main chains. However, the interaction between the main chain and the oxygen atoms of alkoxy side chains would also play an important role, because the interaction essentially contributes to the electronic energy structure of ROPPV⁽¹⁵⁾. As shown in Fig. 1, because the oxygen atoms of alkoxy side chains have non-bonding electrons except bonding electrons, these non-bonding electrons and π -electrons of the polymer main chains interact. That is, in ROPPV, the non-bonding electrons of the oxygen atoms composing the alkoxy side chain mix with π -electrons of polymer main chain and the π -electron systems extends. Therefore, the effective π -conjugation length of ROPPV is longer than that of RPPV, which does not have the oxygen atoms in the side chains. Accordingly, the bandgap energy of ROPPV becomes smaller than that of RPPV.

On the other hand, the steric hindrance between polymer main chains occurs due to the conformation change of alkoxy groups of side chains with increasing temperature. As a result, not only bonding angle between the side chain and the main chain but also bonding angle between oxygen atoms of side chain and the main chain also change. Accordingly, the interaction between non-bonding electrons of side chain and π -electrons of main chain also becomes weak, resulting in effective π -conjugation length decreases. With increasing temperature, the bandgap energy of RPPV shows nearly constant values, but the bandgap energy of ROPPV increases gradually.

A Consideration of Thermochromic Behavior in Poly(*p*-phenylene vinylene) Derivatives

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The thermochromic behavior of poly(2,5-dialkoxy-*p*-phenylene vinylene)s (ROPPV)s and poly(2,5-alkyl-*p*-phenylene vinylene)s (RPPV)s have been studied. The temperature dependence of optical properties and the variation of properties with the side chain length have been compared with those of poly(3-alkylthiophene)s (PAT)s. The difference of bandgap energy between PPV derivatives and PATs can be tentatively interpreted in terms of the main chain structure. The photoluminescence intensity of ROPPVs and RPPVs decrease monotonically with increasing temperature. To explain this mechanism, we speculate on the separation of the excited species due to the reduction of distance between polymer main chains and the enhancement of the overlap of π -electrons with the twist of polymer main chain. Furthermore, the interaction between polymer main chain and the oxygen atoms of alkoxy side chain plays an important role for the optical properties of ROPPVs.

Keywords : conducting polymer, poly(*p*-phenylene vinylene) derivatives, thermochromism, photoluminescence, *trans-gauche* transition, solid-liquid phase transition

1. Introduction

The Nobel Prize for chemistry in the last 20th century has been awarded to Professors Hideki Shirakawa, Alan G. MacDiarmid and Alan J. Heeger for their pioneer works on discovery and development of conducting polymers. Many of these conducting polymers are generally difficult to be processed due to their insolubility and nonfusibility. This is a serious problem in the practical utilization of these compounds.

Recently, however, by the appropriate modification of the molecular structure of these polymers such as the introduction of long alkyl or alkoxy side chains, they have been found to be soluble in any solvents⁽¹⁾, and even to be fusible at relatively low temperature⁽³⁾⁽⁴⁾. This is a great advantage from the viewpoint of application to electronic devices.

Moreover, conducting polymers such as poly(3-alkylthiophene)s, PATs with a substituted long alkyl chain ($-\text{C}_n\text{H}_{2n+1}$) at the 3 position of the thiophene ring and poly(2,5-dialkoxy-*p*-phenylene vinylene), ROPPVs with a substituted long alkoxy chain ($-\text{OC}_n\text{H}_{2n+1}$) at the 2 and 5 positions of the phenyl ring have attracted great attention, because various interesting phenomena such as thermochromism⁽⁵⁾, mechanochromism⁽⁶⁾ and solvatochromism⁽⁷⁾ *etc.* were found in a relatively low temperature range. These findings are very important from both fundamental and practical points of view.

In this paper, we report on the thermochromic behavior of ROPPVs and poly(2,5-dialkyl-*p*-phenylene vinylene), RPPVs. The variation of properties with side chain lengths is also mentioned. The results will be discussed in comparison to those of PATs.

2. Experimental Details

Figure 1 (a), (b) and (c) show schematic diagrams of the synthetic route to PATn, ROPPVn and RPPVn, respectively, where

“n” indicates the number of carbon atoms in the alkyl and alkoxy chains. As shown in Fig. 1 (a), PATns were prepared from corresponding 3-alkylthiophene monomers using FeCl_3 as a catalyst. That is, 3-alkylthiophene monomer and FeCl_3 were dissolved in anhydrous chloroform at -10°C . After reaction the mixture was kept at this temperature for 12 h. The polymer was precipitated by pouring the whole reaction mixture into a large excess of methanol and isolated by filtration. The raw product was

Fig. 1. Schematic diagram of the synthetic route to (a) PATn, (b) ROPPVn and (c) RPPVn

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washed in a Soxhlet apparatus with methanol to remove FeCl_3 .

The PATn is soluble in conventional organic solvents such as chloroform, tetrahydrofuran, dichloromethane, *etc.* and red in color. Details of the preparation method, procedures and properties of PATn were already reported in our previous paper.

ROPPVns were prepared from 1,4-bis(chloromethyl)-2,5-dialkoxybenzene monomer using KOt-Bu (potassium *t*-butoxide) as a catalyst as shown in Fig. 1 (b). That is, 2,5-dialkoxybenzene was prepared through the use of the Williamson ether synthesis from hydroquinone and alkylbromide⁽⁸⁾. 1,4-bis(chloromethyl)-2,5-dialkoxybenzene mono-mer was obtained according to the procedure, which is an adaptation of the method described by Wood and Gibson⁽⁹⁾. A solution of KOt-Bu in *t*-butanol was quickly added at room temperature under N_2 atmosphere to a stirring solution of 1,4-bis(chloromethyl)-2,5-dialkoxybenzene in *p*-xylene/*t*-butanol. The reaction mixture was refluxed for 22 h. The red solution was concentrated and the polymer was precipitated by pouring the whole reaction mixture into a large excess of methanol and isolated by filtration⁽¹⁰⁾. The raw product was washed in a Soxhlet apparatus with methanol to remove KOt-Bu and dried under vacuum. The ROPPVn is soluble in conventional organic solvent such as chloroform, tetrahydrofuran, dichloromethane, *etc.*, and red in color.

On the other hand, RPPVns were prepared from 1,4-bis(chloromethyl)-2,5-dialkylbenzene monomer using KOt-Bu as a catalyst as shown in Fig. 1 (c). That is, 1,4-dialkylbenzene was prepared through the use of the Grignard reaction from 1,4-dichlorobenzene and alkylmagnesium bromide. 1,4-bis(chloromethyl)-2,5-dialkylbenzenemonomer was obtained according to the procedure, which is an adaptation of the method described by Sonoda *et al.*⁽¹¹⁾. RPPVns were prepared in much the same way as ROPPVns. The RPPVn also is soluble in conventional organic solvent and light yellow in color.

The side chain length dependence of melting points of ROPPVs, RPPVs and PATs is shown in Fig. 2. It is observed that the melting points of ROPPVs, RPPVs and PATs with longer side chains is lower. The spin-coated films and casted films of these conducting polymers were fabricated on the glass substrates from chloroform solution. The thickness of spin-coated film and casted film is about 200 nm and about 1 μm , respectively.

Fig. 2. Dependence of the melting point of ROPPVs, RPPVs and PATs on the side chain length

The optical absorption spectra of the spin-coated films were measured using a Hitachi U-3410 spectrophotometer. The bandgap energies of these conducting polymers were evaluated from the absorption edge of optical absorption spectrum by the $(\alpha h\nu)^2$ vs. $h\nu$ plot, in which α and $h\nu$ are the absorption coefficient and photon energy, respectively. The photoluminescence (PL) spectra of the casted films excited by a monochromated light from a Xe lamp were obtained using a photomultiplier tube combined with a monochromator (Koken Kogyo, SA-250). The ionization potential of these conducting polymers was evaluated with a low-energy photoelectron spectroscopy instrument (Rikenkeiki, AC-1). Monochromatic ultraviolet light in the energy range of 3.4–6.2 eV is irradiated onto the casted films in air. The photoelectrons emitted from the casted film surface stimulate the ionization of the atmospheric oxygen, and the number of ionized oxygen molecules is counted. These measurements ranging from room temperature to 200 °C.

For the measurements of the optical absorption spectra and the PL spectra, the surface of the polymers spin-coated or casted on a glass plate were covered with another glass plate in order to avoid oxidation during heating in air. Prior to carrying out the measurements, the polymers were heated at temperatures higher than their melting points to adhere them to the glass plate.

3. Results and Discussion

3.1 Temperature Dependence of the Optical Absorption Spectra Figure 3 (a), (b) and (c) show the optical absorption spectrum of ROPPV12, RPPV12 and PAT12 measured at various temperatures, respectively. In Fig. 3 (a), the absorption peak and the absorption edge of ROPPV12 shift slowly to higher energy with increasing temperature. As a result of this spectral change, the color of the sample varies from reddish orange to yellow, *i.e.*, thermochromism occurs. As shown in Fig. 3 (b), the absorption peak and the absorption edge of RPPV12 do not shift with increasing temperature. The sample is yellow in color as it is and the thermochromism of RPPV12 is not observed distinctly. On the other hand, the temperature dependence of the optical absorption spectra of ROPPV12 and RPPV12 is different from that of PAT12 shown in Fig. 3 (c), in particular, at the shift of the absorption edge. That is, with increasing temperature, though the behavior of the absorption peak of PAT12 is almost the same as that of ROPPV12, the absorption edge of PAT12 shift suddenly to higher energy. For example, the bandgap energy of PAT12 increases suddenly from about 2.0 eV to about 2.4 eV around the melting point of 160 °C. However, the bandgap energy of ROPPV12 increases gradually from about 2.1 eV at room temperature to about 2.2 eV with increasing temperature. This difference of bandgap energy shift is more clearly indicated in Fig. 4, which shows the temperature dependence of the bandgap energy of various ROPPVs, RPPVs and PATs. The side chain length dependence of the increase of bandgap energy is clear in PATs, but not in ROPPVs and RPPVs. In other words, the bandgap energies of PATs change suddenly at the melting point, which is lowered with longer alkyl side chains. This clearly shows a correlation between the thermochromism in PATs with the solid-liquid phase transition. On the other hand, the increase of bandgap energies of all ROPPVs shows a similar tendency and the bandgap energies of all RPPVs do not depend on temperature, and the side chain length dependence is not observed distinctly. ROPPVs and RPPVs are not correlated with the solid-liquid phase transition.

Fig. 3. Optical absorption spectra of (a) ROPPV12, (b) RPPV12 and (c) PAT12 measured at various temperatures

3.2 Temperature Dependence of the PL Spectra

Figure 5 (a) and (c) show the PL spectra of ROPPV12 and PAT12 measured at various temperature under irradiation of light with 450 nm, respectively. The PL peak of ROPPV12 shifts slowly to higher energy corresponding to the increase of bandgap energy with increasing temperature. However, the PL intensity of ROPPV12 decreases monotonically with increasing temperature. A similar unique temperature dependence of the PL was also observed in RPPV12 under irradiation of light with 350 nm shown in Fig. 5 (b). With increasing temperature, the PL intensity

Fig. 4. Temperature dependence of the bandgap energies of ROPPVs, RPPVs and PATs

decreases gradually, but the PL peak wavelength does not almost change. These results are opposite to the tendency of PAT12 shown in Fig. 5 (c), which indicates that the PL intensity of PAT12 increases with increasing temperature.

The origin of the increase of PL intensity of PATs with increasing temperature in the solid state is explained as follows⁽¹²⁾⁽¹³⁾. With increasing temperature, the polymer main chain twists and the effective π -conjugation length decreases, resulting in the enhancement of the confinement effect of the radiative-excited species such as exciton and/or exciton-polarons. Therefore, the probability of radiative recombination is increased and the PL intensity is enhanced. However, the decrease of PL intensities of ROPPVs and RPPVs with increasing temperature cannot be explained by this mechanism.

3.3 The Difference in the Thermochromic Behavior Between PPV Derivatives and PATs The mechanism of thermochromism in a conducting polymer was proposed by Yoshino *et al.*⁽¹³⁾. With increasing temperature, the side chain changes its conformation due to the *trans-gauche* transition and becomes bulky. The steric hindrance between the bulky side chain and the polymer main chain forces the main chain to twist. Therefore, the π -electron systems in the main chain of the polymer tend to lose their planarity with increasing temperature, resulting in decreased effective π -conjugation length and increased bandgap energy.

The difference in the thermochromic behavior between ROPPV, RPPVs and PATs can be tentatively interpreted in terms of the main chain structure which is schematically shown in Fig. 6⁽¹⁴⁾. The phenyl rings composing the PPV-type main chain can rotate freely with respect to the main chain without significant deformation of the main chain, as they are connected at *para*-position. Therefore, the planarity of π -electron systems can be gradually decreased with increasing temperature. On the other hand, the thiophene rings in PATs cannot rotate without causing significant deformation of the main chain, because the bonds connecting a thiophene ring and the main chain are not in a straightline. This indicates that the planarity of the π -electron systems in PATs change not in the solid state but in the liquid state. Therefore, the π -electron systems in PATs lose their planarity not gradually with increasing temperature at the solid state, but suddenly at the solid-liquid phase transition.

Fig. 5. Photoluminescence spectra of (a) ROPPV12, (b) RPPV12 and (c) PAT12 measured at various temperatures

3.4 The Origin of the Decrease of PL Intensity of ROPPVs and RPPVs

As the mechanism of the decrease of PL intensity of ROPPVs and RPPVs, we speculate the separation of the excited species due to the reduction of the distance between polymer main chains and the enhancement of the overlap of π -electrons with the twist of polymer main chain. As schematically shown in Fig. 7 (a), the distance between polymer main chains is widened by the side chains. The side chains take

Fig. 6. Relationship between polymer main chain structure and torsion

Fig. 7. Separation of the excited species due to the reduction of the distance between polymer main chains

trans conformation at lower temperature and *gauche* conformation near and above the melting point. The side chain is more bulky and shorter when it is in *gauche* than in *trans*. Therefore, with increasing temperature, the distance between polymer main chains becomes shorter as shown in Fig. 7 (b). In this case, the dissociation probability of the excited species such as excitons and/or exciton polarons through interchain charge transfer increases and the probability of radiative recombination decreases.

On the other hand, the twist of polymer main chain would enhance the overlap of π -electrons, as schematically shown in Fig. 8. Assume that there is a pair of neighboring polymer main chains whose phenyl rings are perpendicular to each other and therefore the π -electrons do not overlap each other, as shown in Fig. 8 (a). In such a case, the interchain charge transfer does not occur. However, with increasing temperature, the polymer main chain starts to twist and the π -electron orbitals of the pair become more parallel to each other, as shown in Fig. 8 (b). Consequently, the

Fig. 8. Enhancement of the overlap of π -electrons due to the torsion of polymer main chains

Fig. 9. π -electrons of polymer main chains and non-bonding electrons in oxygen atoms of alkoxy groups.

dissociation probability of the excited species through the interchain charge transfer increases and the probability of radiative recombination decreases.

3.5 The Difference in the Thermochromic Behavior Between ROPPVs and RPPVs

In the above discussion, we only concentrated on the change of interaction between polymer main chains. However, the interaction between the main chain and the oxygen atoms of alkoxy side chains would also play an important role, because the interaction essentially contributes to the electronic energy structure of ROPPV⁽¹⁵⁾. As shown in Fig. 9, because the oxygen atoms of alkoxy side chains have non-bonding electrons except bonding electrons, these non-bonding electrons and π -electrons of the polymer main chains interact. That is, in ROPPV, the non-bonding electrons of the oxygen atoms composing the alkoxy side chain mix with π -electrons of polymer main chain and the π -electron systems extends. Therefore, the effective π -conjugation length of ROPPV is longer than that of RPPV, which does not have the oxygen atoms in the side chains. Accordingly, the bandgap energy of ROPPV becomes smaller than that of RPPV.

Fig. 10. Temperature dependence of ionization potential of ROPPVs, RPPVs and PATs

On the other hand, the steric hindrance between polymer main chains occurs due to the conformation change of alkoxy groups of side chains with increasing temperature. As a result, not only bonding angle between the side chain and the main chain but also bonding angle between oxygen atoms of side chain and the main chain also change. Accordingly, the interaction between non-bonding electrons of side chain and π -electrons of main chain also becomes weak, resulting in effective π -conjugation length decreases. With increasing temperature, the bandgap energy of RPPV shows nearly constant values, but the bandgap energy of ROPPV increases gradually.

Figure 10 shows the temperature dependence of ionization potentials of ROPPVs, RPPVs and PATs with different side chain length. The ionization potentials of PATs change steeply from about 4.7 eV to about 5.4 eV, near the melting point. Thus, the electronic states of PATs change significantly with solid-liquid phase transition. However, in ROPPVs and RPPVs, the ionization potentials decrease slightly with increasing temperature and the degree of decrease becomes larger with longer alkoxy and alkyl chains. The origin of the temperature dependence of ionization potentials of ROPPVs and RPPVs is not clear at this stage, but we speculate as follows. The photoelectron emission from the polymer main chain is hindered, because the longer side chains become entangled in polymer main chains. That is, in case *trans* conformation at lower temperature, the photoelectron emission from the main chains can be detected easily, but the photoelectron emission is very difficult at higher temperature, because with increasing temperature, the side chains are combined with polymer main chains in a complicated way and become *gauche* conformation and contract.

From the results mentioned above, the schematic energy diagrams of ROPPV12, RPPV12 and PAT12 are estimated as shown in Fig. 11. The electronic state of PAT12 changes markedly at the melting point. That is, the bandgap energy increases from about 2.0 eV to about 2.4 eV, and the ionization potential increases from about 4.7 eV to about 5.4 eV. In ROPPV12 and RPPV12, the bandgap energy and the ionization potential do not change with increasing temperature very much.

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