Thermochromism of Poly(Pentacosa-di-ynoic Acid) Formed on Zinc Oxide

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Keywords: UV illumination, pentacosa-di-ynoic acid, reversible thermochromism, zinc oxide

1. Introduction

In our previous study [1] on photo- and radiation-polymerization of pentacosa-di-ynoic acid (PDA) to develop a radiation sensitive coloration label to detect low level radiation, we found that by the presence of zinc oxide, poly (PDA) showed reversible change of color from blue to red and vice versa under heating and cooling cycles, otherwise, no color change was observed from red to blue during cooling process. Since we believe this phenomenon has not been reported according to a literature survey for past ten years, we wish to describe briefly our finding on reversible thermochromism of poly (PDA) with the presence of ZnO.

2. Method

2.1. Preparation of the samples

For preliminary tests, PDA-microcrystallite and ZnO dispersed in poly(acrylates) films supported on quartz plate were prepared by the method described previously [1]. PDA containing films without ZnO or with other inorganic substances such as ZrO_2 or TiO_2 were also prepared for reference purpose.

For visible spectral survey, more transparent and uniform PDA-ZnO films were prepared by the following method. Solution of zinc acetate in mixed solvent containing 2-methoxyethanol, diethanolamine and acetylacetone was spin-coated on a quartz plate (60mmX40mm, 1mm thick) and then the plate was heated to 600 °C. This procedure was repeated four

times to form 3.5 mg ZnO on the quartz plate. On this film, 1 ml of THF solution of PDA (0.07mol/l) was delivered, and PDA remained on ZnO film adsorbed after the solvent was evaporated at 72°C. During this procedure, electric current through the film (parallel to the surface) was found to decrease, indicating that PDA adsorbed may result some disorder in the ZnO structure.

2.2. UV illumination

When the PDA films with or without solid were illuminated by UV light (0.038mW/cm²) at 23°C, the film turned blue showing the PDA polymerized. The PDA film with ZnO showed higher sensitivity toward visible light than the other types of the films.

2.3. Observation of thermochromism

For the preliminary tests, the films dispersed with solid (poly (PDA) with or without a solid inorganic additive) were heated on a hot plate at a rate of 1°C/min and then cooled down (1°C/min) to room temperature. During heating and cooling cycle, phase change from blue phase to red, or vice versa was visually examined and the temperature at which the phase change occurred was recorded.

Electronic spectra were recorded on a Perkin-Elmer UV/Visible spectrophotometer Lambda 11 equipped with a cell housing that enables the sample to be kept at a required temperature between 23 and 100°C during spectrum acquisition.

3. Results and Discussions

In table 1, the temperature at which the color change was observed are listed for samples with the comment whether the change was reversible or irreversible.

Table 1 Phase change temperatures and reversibility in heat-cool cycles

Additives	B to R(C)	A
none	64	Irrev
ZrO ₂	110	Irrev
TiO ₂	B	Irrev
ZnO	95/135	rev/irrev
ZnO film	98/ b	Rev/irrev

a: reversibility of the phase change

b: not measured

As shown in the table, without solid additives and with ZrO₂, irreversible thermochromism from blue to red was observed at 64°C and 110°C, respectively. With the presence of ZnO, reversible thermochromism was observed at 95-98°C, but, after heating above 135°C, red to blue change was no more observed by the cooling process. The reason of the reversible thermochromism with the presence of ZnO is not clear at present, but a kind of loosening of the crystal structure of poly (PDA) may explain the observed reverse change from the red form to the blue during cooling process. This tentative explanation may not contradict to the results that the phase change occurs at different temperatures depending on whether or not a solid is present, or on the type of the solid in case it exists.

The reversible change between blue and red phases is more quantitatively confirmed by the visible spectra obtained for samples using ZnO coated quartz plates at different temperatures as shown in Fig. 1. No absorption was observed between 400nm and 700nm (spectra a through c) before the UV illumination.

On illumination of UV light, an absorption with several broad peaks appeared (spectra d and e). The spectrum turned to the spectrum with two main peaks (620nm, blue phase and 540nm, red phase) each with a satellite when the sample was heated to 60.7 – 67°C (spectrum f). On heating to about 86°C, the absorption at 620nm decreased (spectrum g).

When the sample was cooled down to 46°C, the absorption at 630nm appeared again (spectra h and i). The same spectral change was observed for another heating and cooling cycle (spectra j, k and l). The spectra

(d and e) that observed immediately after the illumination did not appear after heating, and therefore, the spectra (d and e) may be of poly (PDA) of transient and stable state.

Fig. 1. Electronic spectra of poly (PDA) adsorbed on ZnO coated quartz film recorded at different temperatures during two heating and cooling cycles.

4. Conclusion

Blue form of poly (PDA) without ZnO turned red when it was heated above 64°C, and did not turn blue when it was cooled below this temperature. It was found that the blue form of poly (PDA) adsorbed on ZnO turned red when it was heated above 95-98°C, but it turned blue when the film was cooled down to room temperature. The mechanism of this reversible thermochromism on heating and cooling cycles is not elucidated at present, but may be related to some loosening of the crystal structure of poly (PDA) on ZnO.

Acknowledgment

The authors wish to thank Dr. T. Tsumura for his kind assistance for preparing ZnO films.

References

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