Iridescence of 2-Hydroxyethyl Methacrylate/Aromatic Allyl Ester Reaction Mixtures

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ABSTRACT: Reaction of 2-hydroxyethyl methacrylate and diallyl phthalate or vinyl 4-*tert*-butylbenzoate has been found to give an iridescent reaction mixture. Transmittance spectra of the reaction mixture depended on the temperature in the range of 0 to 60°C. The temperature-transmittance curves showed a discrete stepwise change near the room temperature. Polymerization reaction of 2-hydroxyethyl methacrylate (PHEMA) in a nonreactive monomer substitute, dipropyl phthalate, showed a temperature dependence as was seen for the iridescent reaction mixture, but was not iridescent. PHEMA suspension in several aromatic solvents also showed iridescence, and some of them were temperature dependent. The mechanism of temperature-dependent iridescence of the copolymerization reaction mixtures is discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 125–131, 1999

Key words: iridescence; poly(2-hydroxyethylmethacrylate); heat-induced phase separation

INTRODUCTION

Iridescent material has a potential on application not only for decoration but also for display systems. An advantage of using iridescent material to display a system is its stability against light because the color is not caused by electronic absorption but by scattering of light. Many iridescent systems were found and studied, and their mechanism was explained by either specific light scattering or specific light diffraction (Bragg diffraction). Both liquid crystal and colloid solutions with lamellar structure have periodical structure, and show iridescence that is caused by specific light-diffraction. Color of this type of iridescence depends on the period of the structure. When colloid particles are relatively large compared with the wavelength of visible light, a specific light scattering is observed. Here, color of the iridescence depends on the size of colloid particles and on the difference of refractive indices between a colloid particle and the solvent.[1–9] Although many iridescence systems have been reported, their colors were not tunable. This is a disadvantage of iridescent materials compared with other display material that is either thermochromic or photochromic.

Recently, temperature-dependent iridescent systems have been reported to exist in lamellar liquid-crystalline phases and in polymer network gel systems.[10,11] The color-change mechanism of the former system was explained by the heat-induced change of the ordered structure [Fig. 1(a)]. The latter system was explained by the heat-induced association of highly refractive domains [Fig. 1(b)]. As far as the authors know, these are only two artificial systems reported, although a tunable iridescent system would be expected as a new display material.

Figure 1 Iridescence of ordered system and nonordered system: (a) Ordered system. Interference of scattered light depends on the distance, d, between layers of materials. (b) Nonordered system. Interferences of scattered light take place when highly refractive domains associate and become large scatterers: D, destructive interference; C, constructive interference. The interference depends on the associated domain size.

We have found new temperature-dependent iridescent systems during copolymerization of 2-hydroxyethyl methacrylate (HEMA) and several aromatic allyl esters (AAE). In this article, the mechanism of temperature-dependent iridescence phenomena of AAE/HEMA systems is discussed.

EXPERIMENTAL

Materials

2-Hydroxyethyl methacrylate, methyl methacrylate (MMA), vinyl 4-*tert*-butylbenzoate (VBBA),

diallyl phthalate (DAPA), and styrene was distilled from hydroquinone under reduced pressure. Azo-bis-isobutyronitrile (AIBN) was recrystallized from chloroform and dried under reduced pressure. Benzoyl peroxide (BPO) was precipitated from chloroform by adding methanol, and was dried under reduced pressure. Hydroquinone was used as received. 8-Anilino-1-naphtalenesulfonic acid magnesium salt (ANS-Mg) was obtained from Tokyo Kasei Kogyo Co. Ltd. (Tokyo, Japan), and used as received.

Acetonitrile, anisole, benzonitrile, methyl benzoate, and toluene were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and

Scheme 1

used as received. Dipropyl phthalate (DPPA) was purified by distillation. Structures are shown in Scheme 1.

Preparation of Reaction Mixtures

In a 12-mm diameter test tube, 3.3 g (25 mmol) of HEMA and 5.1 g (25 mol) of VBBA were placed. BPO or AIBN was used for a polymerization initiator. The amount of BPO was 20 mg for the experiment. For fluorescent probe experiments, AIBN was used instead of BPO. Amount of AIBN to the 10 g of monomer mixture was 7 mg. Absorbance of ANS-Mg in monomer mixture was prepared to 0.1 at 350 nm. The solution was deoxygenated by repeated freeze-pump-thaw cycles, and the test tube was flame-sealed. The test tube was heated in 80°C water bath for 10 min, and then cooled in ice water to terminate reactions. AIBN-contained samples were photo-irradiated by a 450 W high-pressure mercury lamp at 30°C, and cooled in ice water after 1 h.

Preparation of PHEMA and PHEMA Suspensions

HEMA was polymerized by the same method as the reaction mixtures. DPPA was used instead of comonomers. The mixture was heated at 80°C. After this treatment, white precipitate was filtrated, and the precipitate was dried under reduced pressure. PHEMA suspensions were prepared in a test tube. About 50 mg of PHEMA powder was added to 4 ml of a solvent. The mixture was sonicated for several minutes by 60 W ultrasonic cleaner.

Apparatus

Transmittance spectra were measured by Shimazu MPS-2000 multipurpose spectrophotometer. Fluorescence spectra were measured by Hitachi F-4000 spectrofluorimeter. Transmittance dependence on temperature was observed by intensity of a He-Ne laser passed through the sample. The temperature at the sample was controlled by circulating thermostated water (Haake F3-K Digital).

RESULTS

Reaction Mixtures

Mixture of DAPA and HEMA was a clear solution in any composition. The monomer mixture in a flame-sealed test tube became translucent gel after 10 min heat at 80°C. This gel became transparent and bluish after cooling in ice water. When the sample was warmed to 40°C, the color of gel became yellowish; more than 60°C, the mixture became translucent again. This heat-induced transparency change was reproducible for several times. Repeating this heat–cool treatment finally gave opaque solid. Neither monomer mixture nor completely polymerized products showed any temperature-dependent color change. In the presence of AIBN, irradiation of ultraviolet (UV) light to the monomer mixture gave a transparent bluish gel. Temperature-dependent behavior of this gel was almost the same as the thermally prepared sample. VBBA/HEMA gave almost the same results that were observed in DAPA/HEMA, although styrene/HEMA or MMA/HEMA did not.

Transmittance at 633 nm was measured for VBBA/HEMA and DAPA/HEMA in the range of 0 to 60°C. The results are plotted in Figure 2. A stepwise change is observed on each plot. Onset temperatures of transmittance versus tempera-

Figure 2 Transparency of reaction mixtures at 633 nm: (●) DAPA/HEMA; (○) VBBA/HEMA.

ture curves were determined from Figure 2; 3°C for VBBA/HEMA and 18°C for DAPA/HEMA, respectively.

Transmittance spectra of DAPA/HEMA and VBBA/HEMA are shown in Figure 3. These spectra have a peak maximum in UV-visible region. The transmittance maximum of DAPA/HEMA is at a shorter wavelength than that of VBBA/HEMA at the same temperature. The transmittance at UV region and near-infrared (NIR) region changed to the opposite directions. By heating the system, transmittance at UV increased, and at NIR decreased.

Fluorescence spectra of ANS-Mg in VBBA/HEMA were measured at 21°C and 48°C. By heating the reaction mixture, the spectral peak maxima red shifted from 460 nm to 475 nm and the intensity decreased to 68% of the initial intensity at the maximum wavelength.

PHEMA Suspension in Organic Solvents

A mixture of HEMA and DPPA gave white precipitate after heating at 80°C in the presence of

BPO. Although this reaction mixture was colorless, the transmittance was changed by temperature in the range of UV to NIR range. The mixture was filtrated, and the precipitate, PHEMA, was corrected. This product was used for preparation of PHEMA suspension.

PHEMA powder was immersed in various organic solvents, and the color was observed under the room light. The suspensions in benzonitrile, methyl benzoate, anisole, and toluene showed colors. Temperature-dependent color change was observed in PHEMA suspending in anisole, benzonitrile, and in methyl benzoate. The results are summarized in Table I together with properties of the solvent.

Transmittance spectra of PHEMA suspension in methyl benzoate are shown in Figure 4. These spectra have a peak, and the temperature-dependent behaviors at UV and NIR are the same as the reaction mixtures. PHEMA suspension in DPPA does not have any characteristic peak on

Figure 3 Transmittance spectra of reaction mixtures (a) VBBA/HEMA and (b) DAPA/HEMA at different temperatures.

Table I   Iridescence of PHEMA Suspension and Physical Properties of Their Solvents

Solvent	Iridescence[a]		n_D^{20b}	δ^c	H Bonding
	20°C	50°C			
Benzonitrile	Blue	Purple	1.525	17.2	Poor
Methylbenzoate	Blue	Yellow	1.516	21.5	Moderate
Anisole	Purple	Yellow	1.515	19.8[d]	Moderate
Toluene	Yellow	Yellow	1.497	18.2	Poor
Dipropyl phthalate	Colorless	Yellow	—	19.8	Moderate

[a] Observed in the lateral direction to the incident light.
[b] Refractive index at 20°C.[13]
[c] Solubility parameter in $[J \cdot m^{-3}]^{1/2} \times 10^{-3}$.[12]
[d] Calculated.[12]

its transmittance spectra; however, the intensity was decreased by heating.

DISCUSSION

Usually, iridescence is explained either as the specific light diffraction or as the specific light scattering. The color of the reaction mixture in

Figure 4   Transmittance spectra of PHEMA suspension in methyl benzoate at different temperatures.

this study would be due to a specific scattering of light, because these systems have displayed nearly complementary colors when observed toward the incident light direction and in the lateral direction. Then, what kind of substance plays as the scatterer in the presented systems? Iridescent systems in this study contain hydrophilic monomer, hydrophobic monomer, and their polymers. First, comonomers would be ruled out as the candidate because the monomer mixtures are completely transparent; monomer molecules are too small to scatter visible light. Then polymers in the reaction mixture have been estimated to be responsible for the light scattering. The polymers would be either homo polymer and/or copolymer. Monomer reactivity ratios have been estimated to assume the copolymer composition produced in the reaction mixture. Monomer reactivity ratios, r_1 and r_2, are 32.8 and 0.057 for styrene-DAPA, 0.57 and 0.65 for styrene-HEMA, respectively.[12] Then, r_1 and r_2 can be 32.8 and 0.65 for DAPA-HEMA. This means that composition of the polymers in the DAPA-HEMA would have long HEMA sequences. Composition of polymers produced in polymerization of VBBA and HEMA is also expected to have long HEMA sequences by the same consideration. PHEMA suspension in several organic solvents displayed iridescent colors. Therefore, PHEMA blocks are assumed to be responsible for the light scattering in the reaction mixture.

Presented monomer/monomer reaction mixtures gave white precipitates by elevating the temperature. The same phenomenon was observed in several aqueous solution systems that contain hydrophilic polymers, and the mechanism was explained as the collapse of individually solvated polymer coils followed by the formation of

the desolvated globules.[14,15] Behavior of the iridescent reaction mixture in this study would be attributed to the coil-globules transition of PHEMA blocks. ANS-Mg is known as a fluorescence probe of polarity and viscosity.[16,17] In the iridescent reaction mixtures, ANS fluorescence peak red shifted by elevating the temperature. This suggests the increase of polarity or decrease of viscosity around the probe. Because ANS is an anion, this probe would be near the hydroxyl groups of PHEMA chains. The change on the spectra by heating can be explained as the increase of hydroxy groups around the fluorescent molecule. This is when the PHEMA coils change to the globules. A discrete stepwise change observed on the transmittance vs. temperature curves in Figure 2 should correspond to this transition.

Figure 3 shows transmittance spectra of reaction mixtures at different temperature; by elevating the temperature, transmittance at UV regions is increased and transmittance at NIR regions is decreased. The color of the iridescence changed to red or yellow by heating. According to Mie's light-scattering theory, the longer wavelength light is scattered by the larger particle. Change of transparency at UV and NIR would correspond to the change of size distribution of scatterers by heating. Temperature dependence of the transmittance spectra would correspond to change of optical cross section of the light scattering material. This change can be attributed to optical heterogeneity of the system that depends on solvation of polymers in the reaction mixture. Figure 5 summarizes the mechanism of temperature dependence of iridescent reaction mixtures. Change of the refractive index that accompanies the coil-globule transition of the polymer is expected inside the broken line circle. In the iridescent reaction mixtures, short wavelength light would be scattered by polymer coils and long wavelength light would be scattered by the globules. Opposite temperature dependence of transmittance at short wavelength and long wavelength supports this mechanism because the increase of globule decreases the amount of polymer coil in the system.

Table I shows that PHEMA suspension is iridescent when a refractive index of the solvent is larger than 1.5 and the solvent has some ability of H bonding. Overall, iridescence has been observed in a system where difference of refractive indices between scatterer and solvent is large. The number 1.5 may be the borderline of refrac-

Figure 5 Mechanism of temperature-dependent iridescence of AAE/PHEMA. Circles represent comonomer molecules AAE and the thick line represents PHEMA chain.

tive index value to select a solvent for iridescent PHEMA suspension. We could expect the same situation in iridescent reaction mixtures.

In Figure 2, onset temperature of DAPA/HEMA is lower than VBBA/HEMA. In Figure 3, transmittance peaks of VBBA/HEMA are in shorter wavelengths than that of DAPA/HEMA at the same temperature. The higher transition temperature of DAPA/HEMA suggests that affinity of DAPA to PHEMA may be higher than that of VBBA. Because the peak position depends on the distribution of coil and globule, population of the polymer globule in VBBA/HEMA is expected to be higher than DAPA/HEMA at the same temperature. The major difference between DAPA and VBBA is the number of ester groups. Because an ester group has a capability of H bondings, solvation of PHEMA in reaction mixture would be as-

sociated with this functional group. Different color and transition temperatures of DAPA/HEMA and VBBA/HEMA may depend on the number of ester groups on the comonomer.

CONCLUSION

The mechanism of iridescence in the AAE/HEMA reaction mixture is explained by the specific scattering of light. The scatterer in the reaction mixture is the polymer that has long HEMA sequences in the composition. Iridescence of the reaction mixture depends on solvation of this polymer. Temperature dependence of iridescence of AAE/HEMA is explained by changes of optical homogeneity of the system that accompanies coil-globule transition of the polymer.

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