Preparation and Properties of Luminous Network Aliphatic Polyester Film via Thermally Reactive Processing

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Received December 3, 2004; Revised Manuscript Received February 15, 2005

ABSTRACT: For the past half-century, a number of polyesters have been used for application in textile and film manufacturing. Currently, the polyester R&D effort directed toward advanced materials involves further progress in the synthesis given by a wide range of potential monomer combinations, new blending technology, and the use of advanced functional additives. As one such effort, we developed a facile modulation method to afford unique photophysical properties to an aliphatic polyester film. For this purpose, a free-standing film based on a network aliphatic polyester consisting of malonate moiety was successfully prepared. The UV−vis, IR, and photoluminescence studies revealed that the prepolymer underwent a Knoevenagel-type self-condensation in situ in the solid film via thermally reactive processing, leading to formation of certain conjugating structures in the polymer chain: The film showed an apparent change from colorless to pale yellow by thermal treatment at 240 °C and then emitted a very intense greenish-blue light when excited at wavelengths longer than 325 nm. The characteristic IR absorption peak at 1654 cm^{-1}, due to the carbon−carbon double bond, appeared and gradually increased with increasing the heating time, whereas the absorptions due to the methylene and carbonyl groups slowly decreased. The thermally treated film was completely homogeneous at the micrometer level without such defects as decomposition and aggregation. The film showed excellent mechanical properties, relatively high density, and thermal stability. In addition, the prepolymer had excellent processability, due to the high adhesiveness, to afford pinholes and thin-line films with several micrometer features.

Introduction

Since two British chemists, Whinfield and Dickson, discovered poly(ethylene terephthalate) (PET) in 1941 after advancing the early research of Carothers, who opened a new field of synthetic condensation polymers, polyesters have been one of the most important polymers commercially today.[1−3] On the other hand, it has already been recognized as a certain problem among polymer processing engineers that some aromatic polyesters discolor relatively easily and exhibit a weak photoluminescence if exposed to high temperature and/or prolonged UV light. Although this problem has been solved practically by adding whitening agents, the elucidation of discoloration has been ignored for a long time because the reaction mechanism has been thought to be too complicated to generalize.[4−7] Noteworthily, Allen et al. have reported in recent years that luminescent impurities such as hydroxylated terephthalate species may contribute to the yellowing of PET on degradation.[8−12] Polyesters have been believed to intrinsically exhibit neither visible absorption nor fluorescence due to the forbidden transition of the carbonyl group. From the viewpoint of photophysical application, however, such thermo- and/or photoinduced discoloration of conventional polyesters is a very interesting and unique phenomenon, although it is ascribed to polymer decomposition and the mechanism is unclear.

Recently, we reported the synthesis of an aliphatic polyester containing a malonate moiety as a basic frame of the main chain.[13] Because of the strong acidity of the malonate moiety, the polymer readily underwent a Knoevenagel-type self-condensation in the presence of such a weak organic base as triethylamine at room temperature to produce certain conjugated forms in the polymer backbone. This approach indeed led to such unusual photophysical properties as a visible absorption and a very intense blue/greenish-blue photoluminescence. This polymer unusually appeared to be a gummy dye in dark orange, unlike the colorless conventional polyesters. Furthermore, the organic base-induced changes in photophysical properties were recognized by the naked eye and extremely evident compared to the thermo- and photoinduced changes of conventional polyesters. No decomposition effect on the photophysical properties of the aliphatic polymeric system needs to be considered because it cannot produce such luminescent impurities as hydroxylated terephthalate species even though an oxidation degradation occurs. This means that the photoluminescence is mainly due to inter- and/or intramolecular Knoevenagel reactions of the malonate moiety rather than degradation. The starting materials, such as diols, dicarboxylic acids, and diesters, are available commercially and are very cheap. Therefore, the aliphatic polymers might be regarded as potentially useful advanced materials applicable to photonic device materials and optical sensors, with the added benefit of low-cost production.

The film/fiber manufacturing of polyesters and the in situ solid-state modification of the photophysical property are important practically. However, the malonate-based synthetic aliphatic polyesters had poor film/fiber forming abilities due to the low molecular weight and the oily gummy feature. It has been reported previously that network aliphatic polyester gels show enhanced physical, chemical, and mechanical properties.[14−16] In this work, we thus prepared a film based on a network aliphatic polyester consisting of a malonate moiety in the main chain and investigated the in situ solid-state

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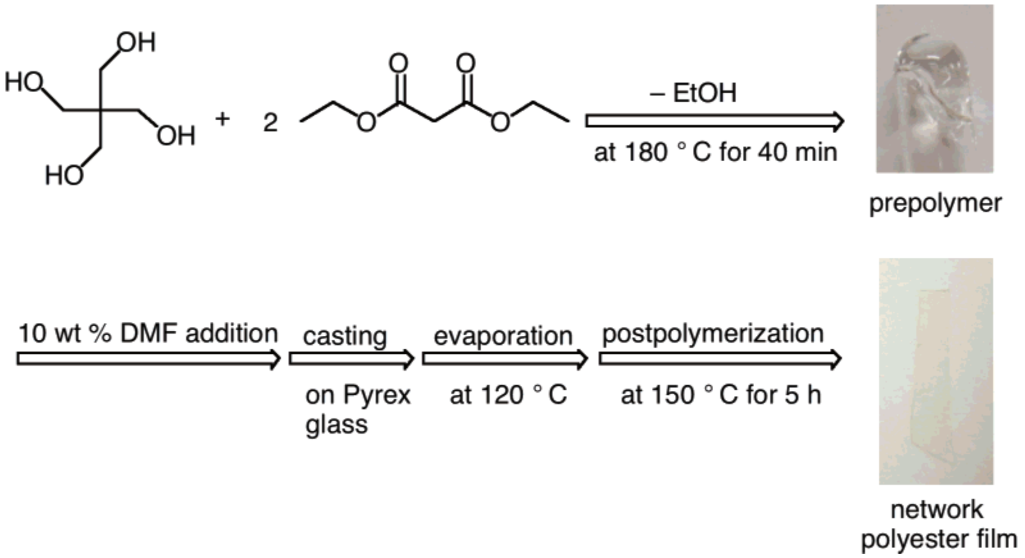
10.1021/ma047506c CCC: $30.25

Scheme 1. Preparation Procedure of the Network Polyester Film



thermal modification of the photophysical property. The malonate moiety readily underwent Knoevenagel-type self-condensation through an appropriate thermal treatment even in the solid state, leading to the formation of certain conjugated structures in the polymer chain. The thermally treated film emitted a very intense greenish-blue light, whereas the original film showed little fluorescence.

Experimental Section

Monomers. Diethyl malonate (TCI), pentaerylthritol (Wako), and diethyl isopropylidenemalonate (Aldrich) were used as received.

Preparation of Prepolymer. Prepolymer was prepared by bulk polymerization. A Pyrex glass tube was equipped with a condensate collector and flushed with dry nitrogen. After pentaerylthritol (2.0 g, 14.7 mmol) and diethyl malonate (4.7 g, 29.4 mmol) were put into the glass tube, the reaction mixture was slowly heated to 180 °C in a silicon oil bath, and then the system was kept for 40 min. Further heating caused the gelation of the prepolymer. After the glass tube was taken from the oil bath, it was cooled to room temperature. The appearance was a colorless gum. ^{1}H NMR (DMSO-d_6, δ): 4.07 (b, $\mathrm{OC}H_2\mathrm{C(CH_2O)_3}$), 4.02 (b, $\mathrm{CH_3OC}H_2\mathrm{OCO}$), 3.55 (b, $\mathrm{HOC}H_2\mathrm{C(CH_2O)_3}$), 3.49 (b, $\mathrm{C}H_2\mathrm{(COO)_2}$), 1.18 ppm (b, $\mathrm{(C}H_3\mathrm{)CH_2O}$).

Film Preparation and Postpolymerization. The prepolymer obtained was cast on Pyrex glass plate from a 10 wt % anhydrous dimethylformamide solution. After evaporation of the solvent at 120 °C in air for 1 h, the cast film was heated at 150 °C for 5 h, during which the temperature was controlled on a hot plate (Heidolph MR 3003). After the cast film was removed from the glass plate, it was washed with water and methanol in turn several times and dried under reduced pressure. The film obtained was free-standing, colorless, and flexible.

Thermal Treatment. The obtained film was heated on the hot plate fixed at 240 °C in air during a desired time. A change from colorless to pale yellow was clearly seen by the naked eye.

Measurements. IR, UV−vis, and photoluminescence spectra were measured on Horiba FT-730, JASCO UV-550, and JASCO FP-6500 spectrophotometers, respectively. The SEM image was recorded on a Hitachi S-3500N scanning electron microscope using an accelerating voltage of 20 kV. Elemental analysis was determined using a Horiba EX-400 energy-dispersive X-ray (EDX) spectrometer attached to the microscope. Differential scanning calorimetry (DSC) analysis was performed in a stream of nitrogen gas at a heating rate of 10 °C/min from −50 to 200 °C using a Seiko EXSTRA6000/DSC6200 apparatus. The polymer was also characterized by thermogravimetric differential thermal analysis (TG-DTA-2000s, MAC-Science, Japan) in air between 30 and 900 °C, with a heating rate of 10 °C/min, using a 7.5 mg sample in a platinum crucible. Film tensile strength and percentage elongation at break were determined with an Instron Universal Testing Machine (model 5566, Instron Engineering Corp., Canton, MA). The CCD image was recorded on a Nikon Eclipse E400 fluorescence microscope equipped with a Nikon DL-5M digital camera. The refractive indices of the film and the Pyrex glass were determined from a variable angle spectroscopic ellipsometer (Unisel, Horiba Jobin Yvon, Japan) using the wavelength range of 300−800 nm in air at room temperature. The density of each sample was determined using a Mettler Toledo AX205 analytic balance coupled with Mettler Toledo density determination kit at room temperature. The density determinations were performed by Archimedes' principle, and methanol was used as auxiliary liquid.

Results and Discussion

Scheme 1 outlines the preparation procedure of the network polyester film. The bulk condensation of pentaerythritol with 2 equiv of diethyl malonate at 180 °C for 40 min gave a prepolymer as a colorless oily gum. The prepolymer provided a transparent, flexible, and free-standing film by postpolymerization at 150 °C for 5 h. This indicates formation of certain network structure in the polymer. The IR spectrum of the film exhibited the absorption due to the terminal hydroxyl group at 3500 cm^{-1} as well as two strong absorptions due to the carbonyl (1750 cm^{-1}) and methylene (2900 cm^{-1}) groups.

Figure 1 shows the changes in the UV−vis spectra of the film with the heating time at 240 °C in air. Similar to the conventional aliphatic polyesters, the film hardly showed a visible absorption before heating. On the other hand, the absorption band in the range 300−450 nm significantly increased with an increase in the heating time up to 4 h. In accordance with the spectral change, the color of the film changed from colorless to pale yellow (see the inserted pictures). This means that certain conjugated structures were actually formed in the network polymer matrix. As mentioned above, the discoloration of PET has been thought to be due to formation of luminescent impurities by oxidation. As for the present polymer, however, the yellowing of the film was also shown even after the thermal treatment in

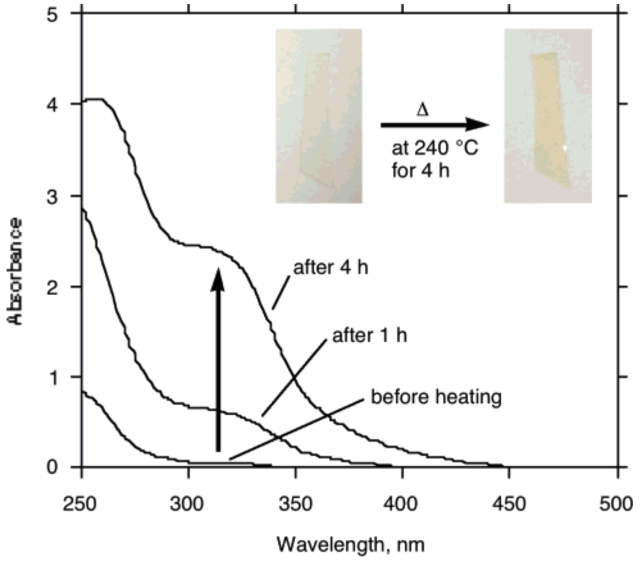


Figure 1. Changes in UV−vis absorption of the film (85 μm in thickness) with heating time at 240 °C in air.

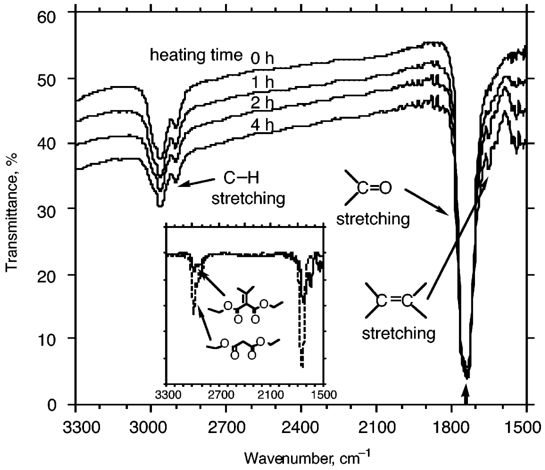


Figure 2. Changes in IR spectra of the film (85 μm in thickness) with heating time at 240 °C in air.

nitrogen gas or under vacuum. Moreover, such luminescent species were not detected in solvent extraction experiments. Even after keeping the thermally treated film in methanol for 24 h, the UV−vis and luminescence spectra of the highly concentrated extract showed neither absorption nor emission bands, indicating the complete incorporation of the conjugating structures into the polymer network.

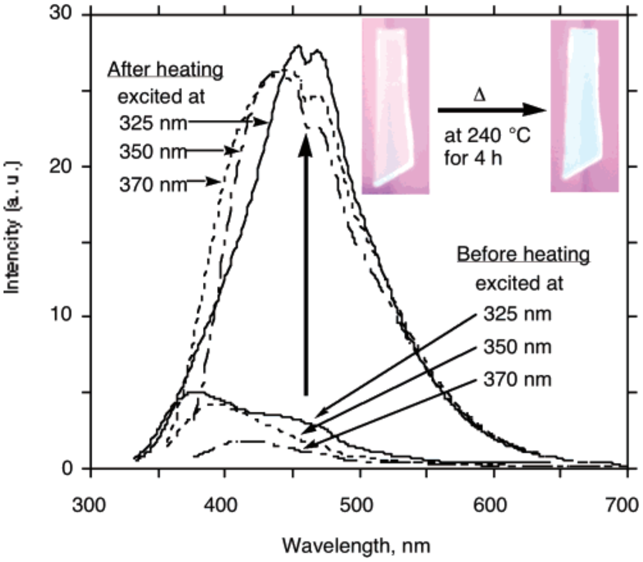
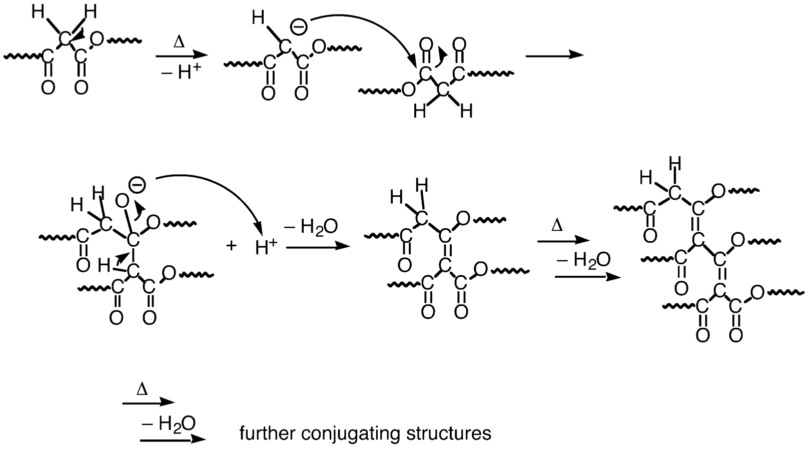


Figure 3. Photoluminescence spectra of the film (85 μm in thickness) before and after heating at 240 °C in air for 4 h.

The heat of deprotonation (ΔH_D) of acidic methylene within malonate is as low as $\Delta H_D = -31$ kcal/mol in DMSO at 25 °C for diethyl malonate.[17] Also, in the Knoevenagel reaction, a base-induced carbanion of acidic methylene has been believed to attack a carbonyl carbon to form a carbon−carbon double bond.[18,19] These led to the idea that the acidic methylenes in the present polymer may readily form carbanions even in the solid film at the relatively high temperature, and presumably, the thermoinduced nucleophilic carbanions subsequently attack carbonyl carbons to newly form certain conjugated structures in the polymer chain. To gain more concrete evidence for the formation of conjugated structures, we measured changes in the IR spectra of the film with heating time. As shown in Figure 2, a characteristic absorption peak at 1654 cm^{-1}, due to the carbon−carbon double bond, appeared and gradually increased, whereas the absorptions due to the methylene and carbonyl groups slowly decreased. This was further confirmed by the fact that the model compound, diethyl isopropylidenemalonate with a carbon−carbon double bond, clearly showed a strong absorption peak around 1650 cm^{-1}, while the diethyl malonate did not. On the basis of these results, we propose an in situ thermoreaction mechanism as shown in Scheme 2.

Figure 3 shows the photoluminescence spectra of the film before and after thermal treatment at 240 °C in

Scheme 2. Proposed Mechanism of the Thermal Treatment



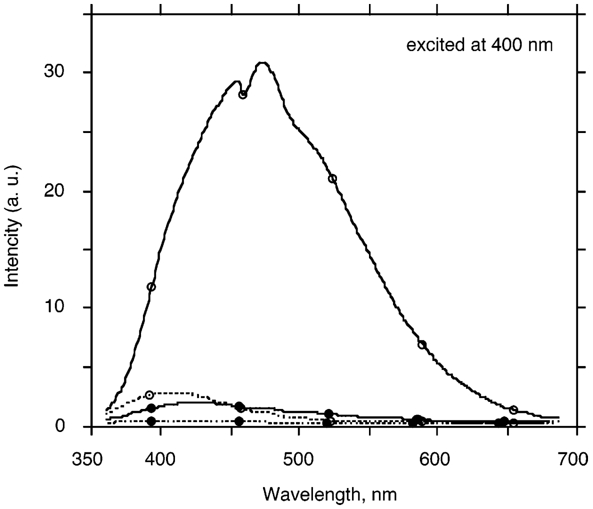


Figure 4. Photoluminescence spectra of the film from the network polyester consisting of succinate moiety (●, 102.5 μm in thickness) compared to the malonate-based polymer film (○, 93.2 μm in thickness) before (- - -) and after (—) heating at 240 °C in air for 4 h.

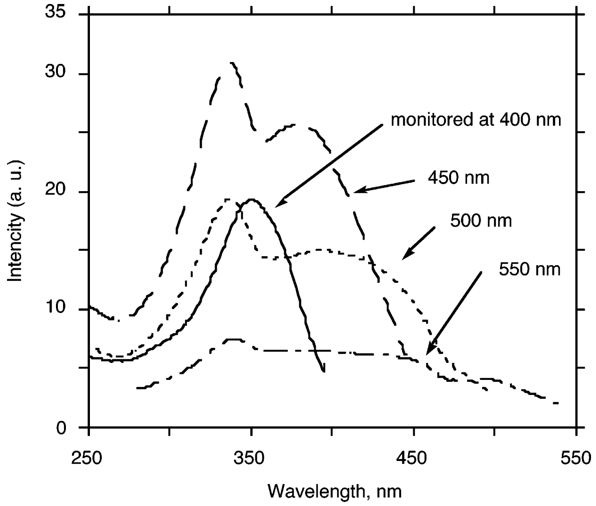


Figure 5. Excitation spectra of the thermally treated film (85 μm in thickness).

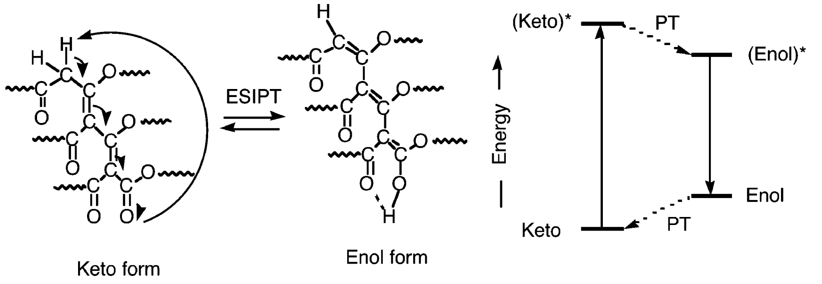
air for 4 h. The thermally treated film emitted a quite strong greenish-blue light when excited at wavelengths longer than 325 nm, whereas the original film showed little emission (see the inserted pictures). In accordance with the greenish-blue emission, the emission spectra exhibited significantly broad bands with the maxima around 450 nm upon irradiation of UV light in the range 325−370 nm. Thus, we assumed that the luminescence of the thermally treated film is associated with the newly formed conjugating structures in the chain. As shown in Figure 4, this was further confirmed by the fact that the corresponding network polyester, consisting of succinate moiety as the model of aliphatic polyester with no malonate moiety, showed little spectral change in luminescence although the film was thermally treated at the same condition. In certain compounds and polymers having both a proton donor and an acceptor (e.g., 3-hydroxychromones, 2-(2′-hydroxyphenyl)benzothiazole, and salicylideneaniline), an excited-state intramolecular proton transfer (ESIPT) causes photoluminescence with a large Stokes shift.[20−25] ESIPT should also occur in the present polymer chain because it has both acidic methylene and dicarbonyl groups capable of acting as a proton donor and an acceptor, respectively. However, the ESIPT within the malonate moiety cannot cause photoluminescence because the keto−enol tautomerization of dialkyl malonates is adjusted to the nonradiative process. Thus, the luminescence of the film is presumably due to the ESIPT between the acidic methylene group adjacent to the conjugated form and the carbonyl group within the conjugated form, as shown in Scheme 3.

Figure 5 shows the excitation spectra of the thermally treated film at 240 °C in air for 4 h. When the monitor wavelength was changed in a wide range from 400 to 550 nm, the excitation bands were significantly different from each other. This means that the luminescence comes from plural photoexcited species in the course of ESIPT. This is probably because different degrees of conjugating structures were randomly formed in the network film by the thermal treatment. The markedly broad emission band in the range 350−700 nm also supports this idea.

Several experiments on controlling the conjugation length were attempted by changing the heating temperature and the treatment time. As a result, the absorbance and the fluorescence were found to increase continuously with reaction time at 240 °C while the red shifts of the absorption and emission bands were not recognized. However, the fluorescence intensity began to decrease on the boundary of the treatment time of 4 h. This decrease in fluorescence intensity is explained by the idea that ESIPT cannot occur any more because the most of acidic methylene protons are consumed along with the reaction time. Although it is expected that the absorbance rapidly increases at a more elevated treatment temperature, the reaction at a higher temperature than 240 °C was not examined in this study because the polymer began to significantly degrade at 350 °C. This led to the conclusion that the thermal treatment of the film at 240 °C for 4 h was the best condition for affording the intense luminous polyester film without degradation.

Figure 6a−c shows the scanning electron microscope (SEM) image (a), the energy-dispersive X-ray spectrum (EDX) (b), and its elemental maps of the surface of the

Scheme 3. Proposed Radiative Keto ↔ Enol Tautomerization and Schematic Representation of Energy States in the Conjugated Form; PT Denotes a Proton Transfer Transition



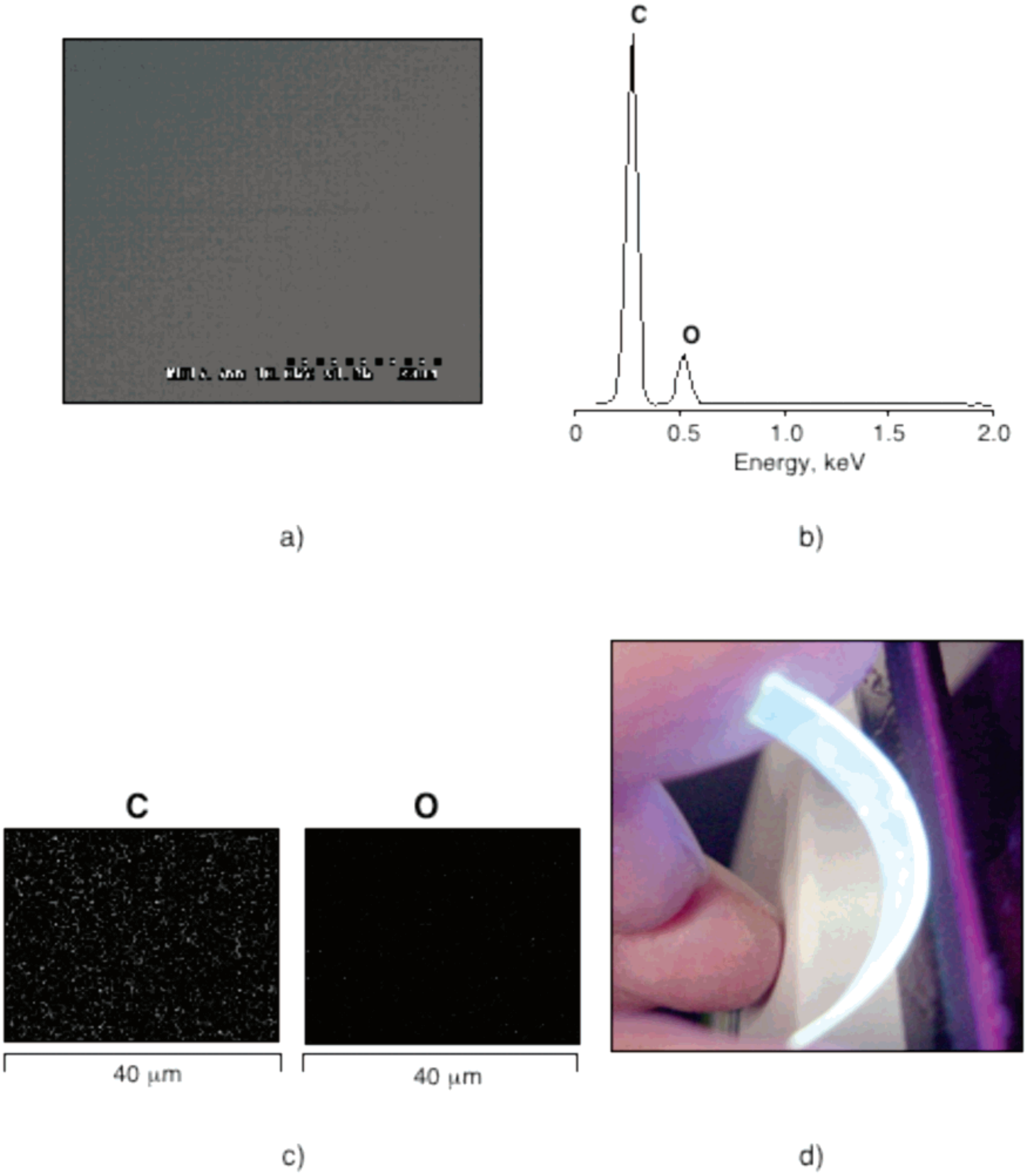


Figure 6. (a) SEM image, (b) EDX spectra, and (c) X-ray elemental maps of the thermally treated film. (d) Photograph of the bent film (irradiated by UV light).

Table 1. Tensile Properties, Density, and Refractive Index of the Original and Thermally Treated Films

film	tensile strength (MPa)	elongation (%)	Young's modulus (MPa)	density (d, g/cm^3)[a]	refractive index (n)[b]
original one	8.20	69.1	335.0	1.39	1.45
thermally treated one[c]	31.5	11.2	550.0	1.43	1.52

[a] At 25 °C. [b] Determined at 400 nm. [c] Treated at 240 °C for 4 h.

thermally treated film (c). The SEM image appeared to be a homogeneous matrix at the micrometer level. Furthermore, the EDX analysis revealed that the film consists only of carbon and oxygen atoms, whose average contents were determined to be 79 and 21 wt %, respectively. Also, the highly uniform distribution of each atom was seen from the X-ray elemental maps. This suggests that the thermally treated film has no significant defects, such as decomposition and aggregation. Actually, in the differential scanning calorimetry (DSC) of the thermally treated film, no significant endothermic and exothermic peaks, due to the glass transition temperature (T_g) and melting point (T_m), were seen in the range from −50 to 200 °C. The thermogravimetric differential thermal analysis (TG-DTA) demonstrated a fairly good thermal stability of the film in air: extensive degradation began near 350 °C, and the exothermic peak due to decomposition was around 375 °C. These results indicate the excellent thermal stability due to the network structure.

Table 1 gives the density (d) and refractive index (n) of the thermally treated film in addition to the mechanical properties, as compared to those of the original film. As the bent film tells us (see the photograph in Figure

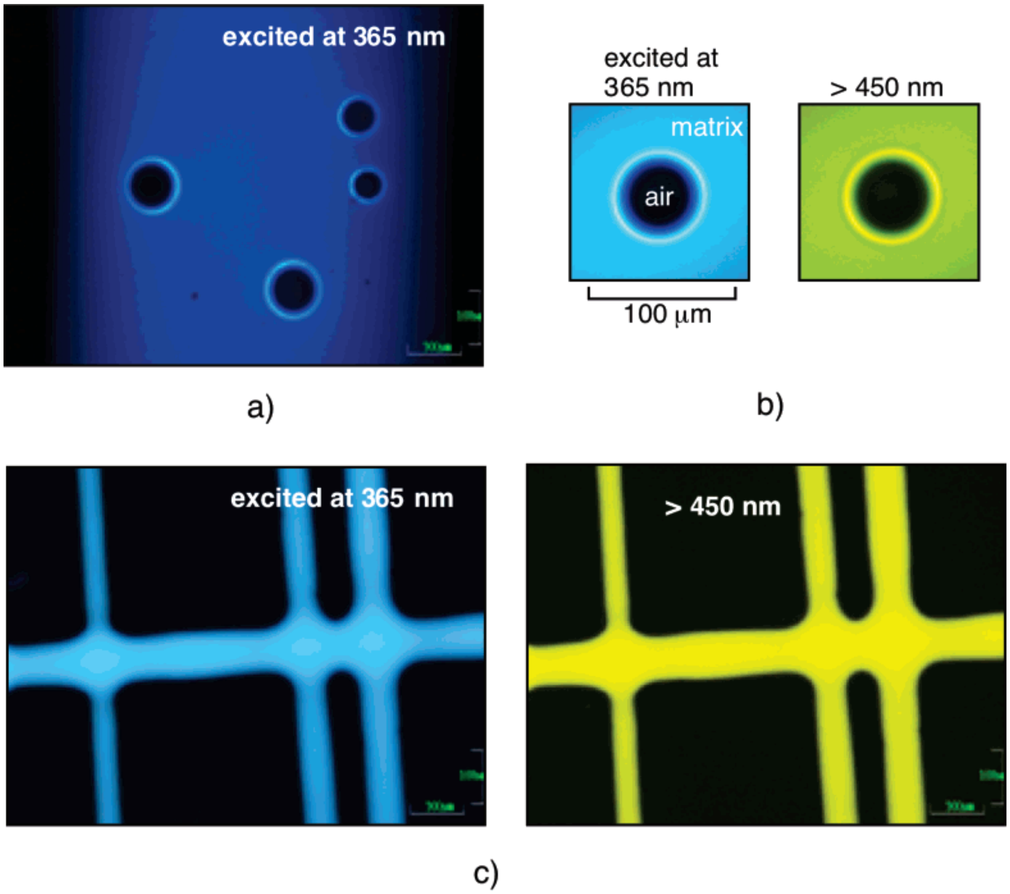


Figure 7. (a) CCD image of pinholes in the thermally treated film. (b) The refractive indices of the film, surrounding media (air) and the Pyrex glass. (c) CCD image of the patterned thin-line film.

6d), the thermally treated film showed an excellent mechanical property: the tensile strength and Young's modulus were 32 (elongation 11%) and 550 MPa, respectively, which were much higher than those of the original film with 8.2 (69%) and 335 MPa. Furthermore, the d value of the thermally treated film was as high as 1.43 g/cm^3, compared to that of the original film with 1.39 g/cm^3, indicating the high molecular compactness due to the network structure. In accordance with the increase in density, the n value increased to 1.52 compared to the original film with 1.45. The remarkably enhanced mechanical properties, compared to the corresponding linear oily gummy polymer, may be due to the network structure of the polymer.

The prepolymer showed excellent processability in film manufacturing due to the high adhesiveness. In the process of the thermal treatment of the film, pinholes whose diameter are 10−200 μm were readily formed by directly postpolymerizing the prepolymer at 240 °C, although the pinholes are randomly formed and the size was widely dispersed (Figure 7a). This is probably due to a kinetically rapid evaporation of such byproducts as ethanol and water. The rim outside of a pinhole appeared, to the naked eye, strongly fluorescent as compared to the surface of the film. However, the shape and intensity of the photoluminescence spectrum in the rim outside of a pinhole were almost the same as those on the surface of the film. This means that the emitting light on the rim was significantly scattered in the pinhole. The present system may be regarded as an optical waveguide consisting of a cylindrical cavity (air, $n \sim 1.00$), the polymer matrix ($n \sim 1.52$), and a Pyrex glass ($n \sim 1.47$) substrate, as shown in Figure 7b. Thus, this could be responsible for the extremely scattered light on the rim. Moreover, we succeeded in obtaining a micrometer-width-sized thin-line film with a length more than several centimeters simply by drawing the gummy prepolymer without using any special apparatus (Figure 7c).

Conclusion

We demonstrated that the yellowing and photoluminescence in a malonate-based network aliphatic polyester film can be thermally induced by Knoevenagel-type self-condensation in situ in the solid film, which is different from those of PET due to oxidation degradation. The present facile modulation method of the photophysical property of the aliphatic polyester film may be available for new development of photonic device materials and optical sensors, with a benefit being their low-cost production.

Acknowledgment. This work is dedicated by G.K. with best wishes to Prof. Toshio Masuda on the occasion of his 60th birthday. We thank Profs. Masao Tanihara and Chikara Ohtsuki at Nara Institute of Science and Technology for permission to use the tensile testing and TG-DTA instruments, and we are also grateful to Prof. Keiji Sasaki and Dr. Hideki Fujiwara at Hokkaido University for the fruitful discussions. We also thank Drs. Doo-Jin Byun, Sung-Young Kim, Jeonghan Kim, Shin-Ichi Ogata, and Masanobu Kamitakahara for their helpful discussions and Tomohiro Uchino and Masaaki Ishikawa for technical assistance. This research was supported by a Grant-in-Aid for Scientific Research

(Exploratory Research, No. 16655081) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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MA047506C