Fluorescence from Soluble Polythiophenes in Uniaxially Stretched Polymers

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ABSTRACT: Fluorescence behavior of poly(3-alkylthiophenes)(P3ATs) in poly(methyl methacrylate)(PMMA) films was studied under tensile loadings. The elastic deformation of the matrix induced by small strains up to 0.2% had a greater influence on time-resolved fluorescence rather than the steady-state one from P3ATs. The decay time of fluorescence decreased linearly as the applied stress was increased, and reached a minimum. We maintained that the attractive phenomenon for the time-resolved fluorescence under the tensile loadings was associated with distortion or deformation of the π-conjugated structure in P3AT chains having large molecular weight. When the applied strain exceeded the elastic limit of the matrix, the time-resolved or steady-state fluorescence behavior was unchanged. However, large elongation over 10% led to the red-shift of the steady-state fluorescence maximum and an increase in the decay time. These fluorescence properties, indicating the growth of the π-conjugation, were mainly governed by strain. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 259–266, 1998

Key words: steady-state fluorescence; time-resolved fluorescence; poly(3-alkylthiophene); tensile loadings; π-conjugation

INTRODUCTION

Luminescence techniques have been extensively used in polymer science and processing.[1–4] In such investigations, a fluorescent dye is usually incorporated within the matrix at low concentration levels as a probe. The choice of the probe or luminescence approach depends on the nature of the information required. Wang and Wu have monitored the cure of epoxy resins using fluorescence recovery of photobleachable molecule.[5] The curing process has also been investigated by measuring fluorescence intensity of reactive fluorophores.[6] Soutar et al. have synthesized a poly(methyl methacrylate)(PMMA) labeled with vinylnaphthalene as a probe, and have measured time-re-

solved luminescence anisotropy of the probe to study molecular relaxation of the PMMA chains in dichloromethane.[7] Steady-state fluorescence anisotropy measurement using a polybutadiene tagged with anthracene has been utilized to examine shear-induced orientation in a matrix polymer melt.[8] Thus, the luminescence techniques have attracted much attention from the fundamental and technological viewpoints. This article relates a new luminescence technique for detecting residual stresses in polymer materials.

Poly(3-alkylthiophene)(P3AT) is a typical soluble conducting polymer consisting of a thiophene backbone and long alkyl groups.[9,10] P3AT luminescences because the quasi-one-dimensional nature of the delocalized π-system renders the polymer backbone relatively stiff.[11,12] The photoluminescence derived from the π-conjugation may be affected by regioregularity of polymer chain,[13,14] temperature,[15] and application of hydrostatic pressure.[15] Mechanical stretching also influences

photoluminescence.[16] When stretched unidirectionally, a soluble conjugated polymer dispersed in a polymer matrix shows spectral changes in absorption and steady-state emission that occur as a result of improved structural order induced by alignment of conjugated macromolecules.[17] In this article we report on the effect of mechanical stretching on steady-state and time-resolved fluorescence behavior from P3ATs in polymer films. In particular, we focus on time-resolved fluorescence from P3AT in the elastically deformed matrix. The results obtained suggest a possibility of P3AT as a molecular sensor for monitoring residual stresses in polymer materials.

EXPERIMENTAL

Preparation

The specimens in this work were solvent cast films of PMMA (Aldrich, Milwaukee, WI, M_w = 120,000) containing a small amount of P3ATs. The P3ATs used were poly(3-butylthiophene) (P3BT), poly(3-hexylthiophene)(P3HT), poly(3-octylthiophene)(P3OT), and poly(3-dodecylthiophene)(P3DDT). They were prepared by oxidative coupling of their monomer with $FeCl_3$ in chloroform.[18] The monomers were available from Tokyo Kasei and used as received. The P3ATs obtained were washed repeatedly by 2 N HCl at 70°C. The washed P3ATs were dissolved again in chloroform. After filtration of insoluble P3ATs, cast films of soluble P3ATs as fluorescence labels were prepared at room temperature. The residuals of Fe in the soluble P3ATs were between 0.22 and 0.34 wt % on inductively coupled plasma atomic emission spectrometry (Shimadzu Ltd, ICP-2000). P3HT was synthesized also by electrochemical polymerization of 3-hexylthiophene with $(C_4H_9)_4NBF_4$ in nitrobenzene.[19] The undoping of BF_4^- was achieved by exposing the prepared polymer to a reversed electric field in fresh nitrobenzene. Values of molecular weight of the P3AT labels, which were calibrated against polystyrene standards, are listed in Table I. The fluorescent probe of P3OT (no. 4 in Table I) was fractionated into several octylthiophene-based compounds by gel permeation chromatography (GPC) to study the effect of molecular weight on time-resolved fluorescence from P3OT. The octylthiophene-based compounds in Table II are expressed using the range of the molecular weight of the GPC used.

The solvent cast films as specimens were obtained from a solution of P3AT and PMMA in chloroform. The content of P3AT in the specimens was 0.05 wt %. The cast films were annealed for 5 h at 70°C. The thickness of the specimens was 280 μm.

TEM Observation

TEM micrographs were obtained with a JEOL 2000EX transmission electron microscope (using ×20000 magnification in Fig. 1). The samples in this study were PMMA cast films containing P3HT (no. 2) of 0.1 wt % and 1.0 wt %. The content of P3HT in Figure 1 was 0.1 wt %. As shown in Figure 1, P3HT has been found to be phase-separated in the PMMA matrix. The P3HT domains become small as the content of P3HT is decreased. It is suggested that the diameter of the P3AT domains in the specimens of this paper may be ~100 nm.

Measurements of Fluorescence Behavior

UV-vis absorption spectra of the soluble P3ATs in chloroform and in the PMMA film were measured by a highly sensitive spectrophotometer (Ohtsuka Dennshi, SM-410). Steady-state fluorescence spectra of them were recorded by a spectrofluorometer (Japan Spectroscopic Co. FP-777). Time-resolved fluorescence measurements were performed on a picosecond time-resolving photoluminescence spectrometer with a streak camera (Hamamatsu Photonics, C4780). These measurements were made at room temperature. The spectroscopic properties of the P3ATs in chloroform and in the PMMA film are listed in Tables I and II. $\lambda_{max,ab}$ and $\lambda_{max,em}$ represent wavelength maxima of absorption and of steady-state fluorescence in the absence of a tensile loading, respectively. τ indicates decay time of time-resolved fluorescence. The subscripts "sol" and "film" show the chloroform solution and the PMMA film, respectively.

Time-resolved fluorescence under tensile loadings was measured as follows. One end of the specimen (50 mm length, 10 mm width) was connected to a load cell (Kyowa Electric Instruments, LTS-1KA) and then the other end was elongated by small strains up to 2% at room temperature. Large strains of 5% to 100% were applied to the specimen at 80°C. Tensile stress acting on the specimen was monitored using the load cell.

For excitation we used a dye laser with an average power of 150 μJ and a frequency of 15 Hz. The

Table I Spectroscopic Properties of Poly(3-alkylthiophenes)

No.	P3AT	M_w	M_w/M_n	$\lambda_{max,ab}$[b] sol.	film	$\lambda_{max,em}$[b] sol.	film	τ[c] (ps)
1	P3BT	14,300	4.01	384	392	532	514	378
2	P3HT	24,000	2.83	414	423	562	518	478
3	P3HT[a]	54,200	2.64	423	430	560	523	477
4	P3OT	27,200	2.87	428	441	563	525	491
5	P3DDT	19,900	5.32	422	436	548	503	624

[a] Prepared by electrochemical polymerization.
[b] Wavelength maxima of absorption and emission (nm).
[c] Decay time of P3AT in PMMA films.

excitation wavelength was 420 nm with a pulse duration of 300 ps. The dye laser output was focused onto a spot size of 1.0 mm diameter. The excitation and detection of fluorescence were carried out using a measurement probe.

The decay curve of the fluorescence intensity between 480 nm and 575 nm was analyzed by the sum of exponential functions [eq. (1)]. The fitting was carried out using an analysis program (Hamamatsu Photonics, U4790).

$$I = \sum A \exp(-t/\tau) \qquad (1)$$

where I is the fluorescence intensity, A the constant, t the time, and τ the decay time.

The steady-state fluorescence measurements were carried out using the same tensile jig for the time-resolved fluorescence measurements.

Measurements of Mechanical Properties

Tensile tests of the soluble P3AT films in Table I were carried out using a viscoelastic spectrometer (Iwamoto Seisakusho, VES-F) at room temperature. A stress–strain curve of the PMMA film containing P3ATs was obtained by an Instron tensile tester. The tensile speed of both tests was 10 mm/min. Viscoelastic measurements of the soluble P3AT films were performed on the Iwamoto VES-F spectrometer.

RESULTS

Fluorescence Behavior Under Tensile Loadings

When small strains up to 2% were applied to the specimen, the steady-state fluorescence spectrum of the specimen was unchanged. The time-resolved fluorescence, however, was affected by the action of the loadings. Although all specimens revealed two exponential decays with decay times of ~500 ps (fraction 95%) and of ~2.5 ns (5%), the decay time of the main component varied under tensile loadings. Figure 2(a) shows the relationship between fluorescence decay time of the specimen containing P3HT (no. 2) and tensile strain applied. The decay time τ is 475 ps in the absence of a loading. τ decreases linearly as the applied strain ε is increased, and reaches a minu-

Table II Spectroscopic Properties of Octylthiophene-Based Compounds

No.	Molecular Weight[a]	$\lambda_{max,ab}$[b] sol.	film	$\lambda_{max,em}$[b] sol.	film	τ (ps)
6	500–900	370	382	526	509	422
7	900–1,600	401	408	540	520	413
8	1,600–2,800	425	434	553	519	468
9	5,300–10,500	430	455	560	518	554
10	10,500–23,000	428	451	563	516	572

[a] Determined by polystyrene standards.
[b] Wavelength maxima of absorption and emission (nm).

Figure 1 TEM micrograph of poly(3-hexylthiophene) P3HT in a poly(methyl methacrylate) film. The content of P3HT (no. 2) was 0.1 wt %.

mum of 420 ps at $\varepsilon = 0.053\%$. When $\varepsilon > 0.053\%$, τ reversely increases with ε and attains a constant ($\tau = 470$ ps, at $\varepsilon > 0.2\%$). A stress–strain curve of the specimen is also presented in Figure 2(a). Because the PMMA matrix shows an elastic deformation in the strain range of 0% to 0.2%, the drastic change in the decay time has been found to occur in the elastic deformation of the PMMA matrix. The plastically deformed PMMA matrix shows no change in the decay time. In Figure 2(b), the decay time is plotted as a function of tensile stress acting on the specimen. A similar aspect to the $\tau - \varepsilon$ curve is observed. There is a minimum of the decay time at 0.6 MPa. A diminution in the decay time due to the tensile stress is $\Delta \tau = 55$ ps.

The PMMA matrix deforms plastically under large strains up to 100%. Figure 3 indicates steady-state fluorescence spectra of the specimen containing the label (no. 2) under large strains. The fluorescence maximum is red-shifted as the applied strain ε is increased. The intensity of the fluorescence decreases with ε. These results say

that the elongation enhances the π-conjugation length. Figure 4(a) shows the effect of the large elongation on the decay time of fluorescence. Because the sample at $\varepsilon = 0\%$ was annealed at 80°C, τ diminished by 30 ps compared with that of unannealed specimen. The decay time is found to be proportional to the applied strain. After the specimens were cooled down from 80°C to 23°C, the fluorescence measurements under tensile loadings were made. The cooling process yields the specimen shrinking (or tensile) force. In Figure 4(b) is displayed the dependence of the tensile force on the decay time. The decay time is independent of the tensile force. Comparing with Figures 2(b) and 4(b), the time-resolved fluorescence behavior depends on the type of deformation of the matrix.
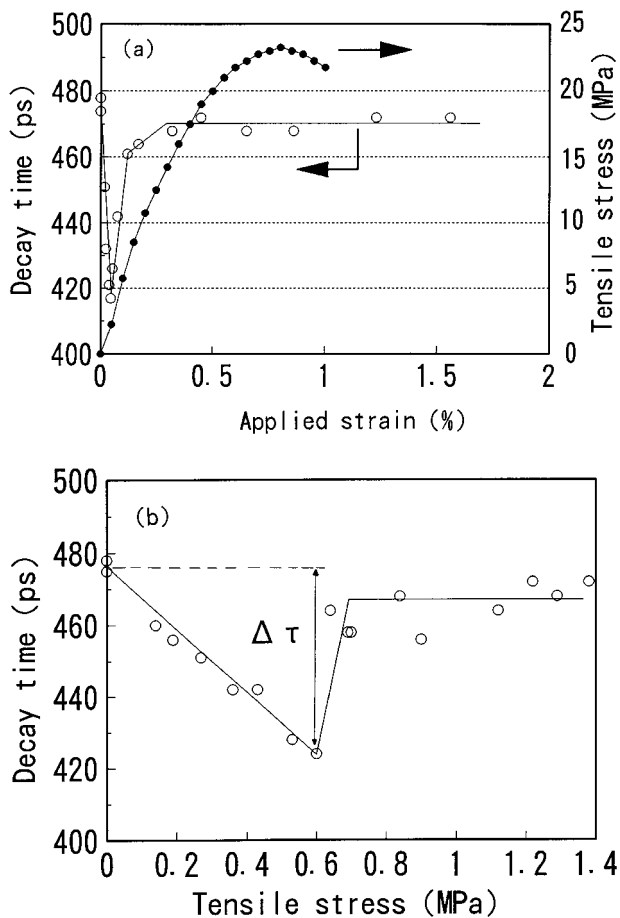

Figure 2 (a) Strain, and (b) stress dependences of decay time of P3HT (no. 2) in uniaxially stretched PMMA films. The solid symbol in Figure 2(a) represents a tensile stress–strain curve of the PMMA film. In Figure 2(b), $\Delta \tau$ shows a maximum diminution of the decay time induced by the tensile loading.
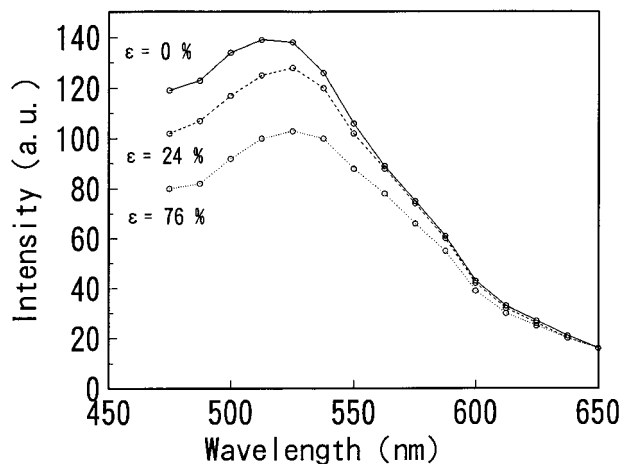
Figure 3 Fluorescence spectra of the specimen containing the label (no. 2) under large tensile strains. The strains of 24% and 76% were applied at 80°C.

Time-Resolved Fluorescence on Stress Relaxation

In the following sections we especially focus on time-resolved fluorescence in the elastic deformation of the specimen. The influence of stress relaxation of the matrix on the decay time of fluorescence from P3OT (no. 4) has first been examined. When a fixed strain which gave a tensile stress of 0.37 MPa was applied, τ immediately decreased from 478 ps to 442 ps. It gradually decreased with time during the stress relaxation. When the applied stress was removed at time $t = 17$ h, the decay time returned the starting value in the absence of a loading. Figure 5 shows the decay time in a varying tensile stress. Although a hysteresis has appeared, the decay time reverses the starting value after the removal of the tensile stress. These results suggest that the change in the decay time is governed by stress rather than strain. They also describe a possibility of stress monitoring of the order of 1 MPa utilizing the decay time.

Influence of Crystallinity

According to our previous article,[20] the oxidative coupling and electrochemical methods give crystalline and amorphous P3HTs, respectively. We have investigated the influence of crystallinity of P3HT on the time-resolved fluorescence under tensile loadings. The similar diminition of τ under tensile loadings as observed in crystalline P3HT (no. 2) was detected also in the amorphous P3HT (no. 3). The unique behavior of τ induced by external tensile stresses is, therefore, not affected by the crystallinity of the fluorophore.

Effect of Alkylchain Length

The fluorescence from P3AT is mainly based upon the π-conjugated structure of P3AT chains. Since it has many side chains, the π-conjugated structure is susceptible to be changeable in external stresses. It is to be expected that the length of the subchains influences the time-resolved fluorescence behavior under tensile loadings. The time-resolved fluorescence properties of four kinds of P3ATs (P3BT, P3HT, P3OT, P3DDT) have been investigated. The decrease in the decay time associated with tensile loadings has been observed in all the specimens. The order of the tensile stress was 1 MPa. The magnitude of dropping the decay time due to the tensile loadings $\Delta\tau$ [see Fig. 2(b)] was in proportion to the alkylchain length. P3DDT had $\Delta\tau$ three times as large as that of P3BT. Since $\Delta\tau$ reflects an interaction between the PMMA matrix and the alkyl subchains, the
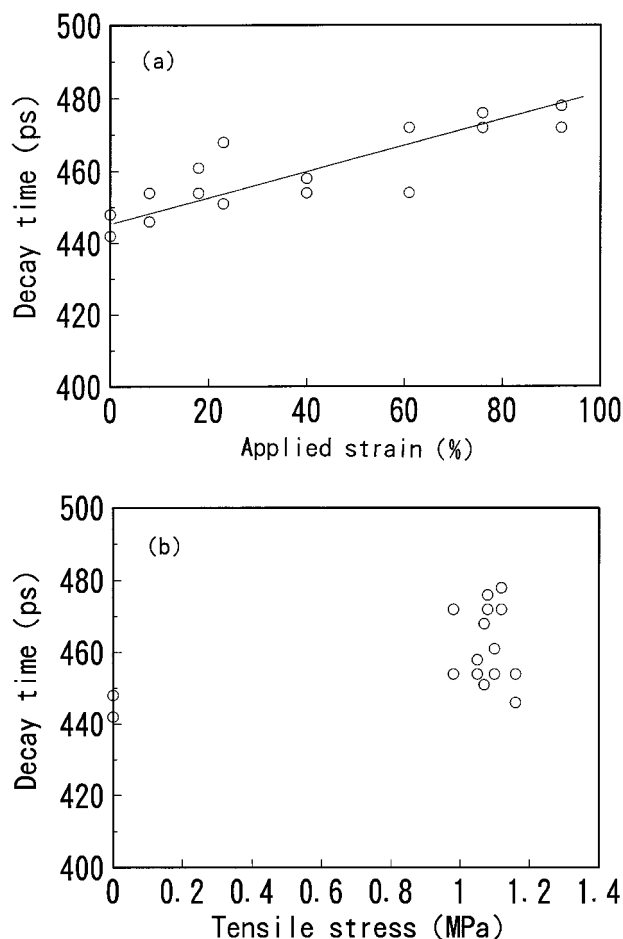

Figure 4 (a) Strain, and (b) stress dependences of decay time in plastically deformed matrix. The specimen used was the PMMA film containing the label (no. 2).
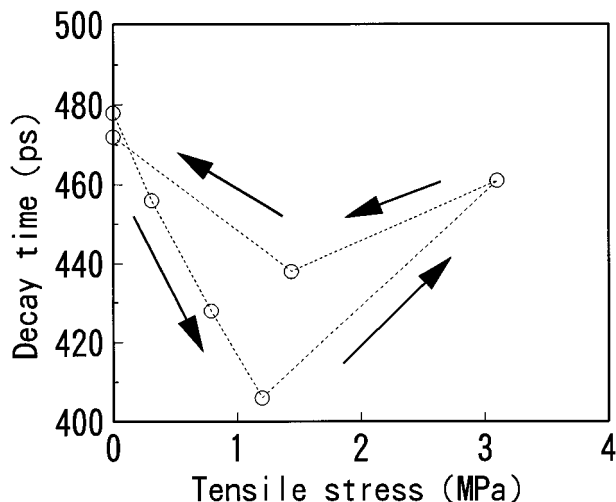
Figure 5 Decay time of the specimen in a varying tensile stress. The fluorescent probe used was no. 4.

dodecyl groups may strongly interact with the matrix.

Effect of Molecular Weight

The P3ATs have their broad distribution of molecular weight. In this section, we discuss the effect of molecular weight on the fluorescence behavior of P3AT under tensile loadings. To this end, we have fractionated the sample (no. 4) into several octylthiophene-based compounds using gel permeation chromatography (see Table II) and have measured the decay time of various octylthiophene-based compounds dispersed in the PMMA matrix under tensile loadings. In the absence of a loading, the absorption maximum of the octylthiophene-based compound $\lambda_{max,ab}$ is red-shifted with increasing molecular weight. When the molecular weight fractionated is more than $M > 5300$, $\lambda_{max,ab}$ remains constant. On the other hand, the fluorescence maximum $\lambda_{max,em}$ is not affected by the molecular weight (Table II).

Figure 6 indicates the relationships between the decay time and the applied stress for the octylthiophene-based compounds. The fluorescence label no. 6 is a compound composed of three or four thiophene rings. The label no. 7 has about seven sequence lengths. The decay time of the both compounds is independent of the applied tensile stress because the π-conjugation may not be grown adequately in these compounds. The label no. 8 with a large molecular weight shows a small decrease in τ by action of tensile loadings. The labels of nos. 9 and 10 are more sensitive to the

applied stress. A decrease in τ of ~100 ps is observed under a tensile stress of 1 MPa.

From the results in Figure 6 and Table II, it is concluded that the drastic change in the decay time under tensile loadings in Figure 2(b) is associated with a long π-conjugated structure of thiophene rings. Since the decay time in the absence of a tensile loading decreases with increasing the molecular weight, it is suggested that the decrease in τ under tensile loadings may be caused by distortion or deformation of the π-conjugated structure.

DISCUSSION

As shown in Figure 1, P3HT as a fluorescence label in the PMMA matrix is phase-separated and forms spherical domains of the order of 100 nm. In this section we discuss forces working at the interface between the PMMA matrix and the P3HT domains. The PMMA matrix takes a glassy state having a Young's modulus of 2.2 GPa at room temperature, while P3HT shows a rubbery-like property. Therefore, we now consider a glassy matrix containing a rubbery inclusion for a two-dimensional system under a uniform tension, σ_0. When we take a spherical coordinate system (r, θ) with its origin at the center of the spherical inclusion and its polar axis parallel to the applied σ_0, the stress components σ_r and σ_θ are given by Goodier.[21]

$$\sigma_r = 2G_1[-A/r^2 + (3B/r^4 - 2C/r^2)\cos 2\theta] \quad (2)$$
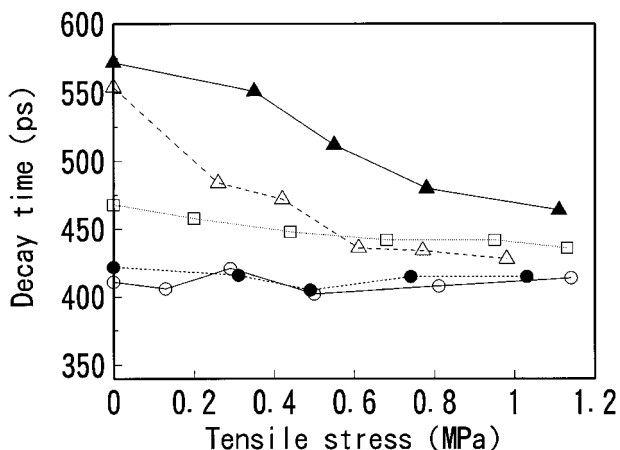

Figure 6 Effect of molecular weight on time-resolved fluorescence under tensile loadings. The probes used were no. 6 (●), no. 7 (○), no. 8 (□), no. 9 (△), and no. 10 (▲).
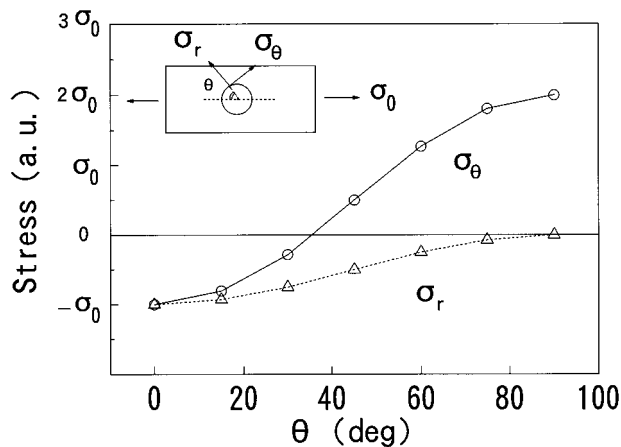
Figure 7 Forces acting on a spherical P3HT domain. The stresses of σ_r and σ_θ were calculated using Goodier's equation in ref. 21 with $G_1 = 2.2$ GPa, $G_2 = 10$ MPa, $\nu_1 = 0.35$ and $\nu_2 = 0.48$ at the interface between the P3HT inclusion and the PMMA matrix $r = a$.

$$\sigma_\theta = 2G_1(A/r^2 - 3B \cos 2\theta/r^4) \qquad (3)$$

where G is the elastic modulus, and A, B, and C, the constants. Subscripts 1 and 2 represent the matrix and the inclusion, respectively. At the inclusion–matrix interface ($r = a$), the three constants may be written as follows.

$$A/a^2 = (\sigma_0/4G_1) \cdot \frac{(1 - 2v_2)G_1 - (1 - 2v_1)G_2}{(1 - 2v_2)G_1 + G_2} \quad (4)$$

$$B/a^4 = (\sigma_0/4G_1) \cdot \frac{G_1 - G_2}{G_1 + (3 - 4v_1)G_2} \qquad (5)$$

$$C/a^4 = (\sigma_0/2G_1) \cdot \frac{G_1 - G_2}{G_1 + (3 - 4\nu_1)G_2} \qquad (6)$$

where v is Poisson's ratio and a the radius of the inclusion.

Figure 7 shows calculated results of σ_r and σ_θ using eqs. (2)–(6) with $G_1 = 2.2$ GPa, $G_2 = 10$ MPa, $v_1 = 0.35$, and $v_2 = 0.48$. Compressive forces act at $\theta = 0°$ while a tensile force of $2\sigma_0$ works at $\theta = 90°$. The stresses at the interface between the P3HT domain and the PMMA matrix are relatively equal to the applied uniform tension. When a uniform tension is 1 MPa, the tensile and compressive forces of 1 MPa are working on the interface. Because G_1 is much larger than G_2, both forces act mainly on the PMMA matrix. As the uniform tension gives the matrix a tensile strain of $\varepsilon = 0.045\%$ ($=\sigma_0/G_1$), a small force of the order of 10 kPa ($\sigma = \varepsilon G_2 = 4.5$ kPa) is applied to the

P3HT inclusion. When the inclusion is P3OT (no. 4), the tensile and compressive forces of ~1 kPa operate the P3OT domains.

We have next investigated mechanical behavior of soluble P3AT films. Figure 8 indicates tensile stress–strain curves of the P3HT and P3OT films at room temperature. In the strain range of 0 to 1%, the P3HT and P3OT films show their elastic deformation. From the results in Figures 7 and 8, it is maintained that the elastic deformation of P3AT inclusion relates the drastic change in decay time of P3AT under tensile loadings.

CONCLUSIONS

In summary, we have investigated the steady-state and time-resolved fluorescence behavior from P3ATs in uniaxially stretched polymer films. The results are obtained as follows: (1) the decay time of fluorescence from P3ATs in elastically deformed PMMA matrices diminishes with the applied stress or strain; (2) the unique phenomenon may be based upon distortion or deformation of the π-conjugated structure of large P3AT molecules; (3) when it exceeded the elastic limit of the matrix, the applied small strains up to 2% had no influence in the steady-state and time-resolved fluorescence properties of P3ATs; and (4) large elongation over 10% led to the growth of the π-conjugation length of P3AT, and as the consequence, the fluorescence maximum was red-shifted and the decay time was increased.
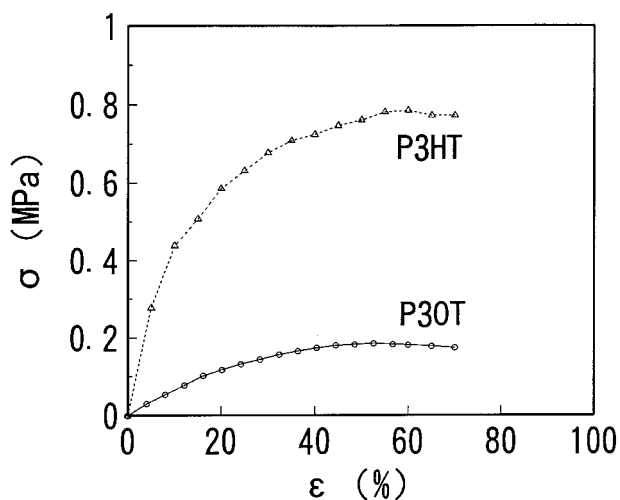
Residual stresses are important in understand-

Figure 8 Tensile stress–strain curves of soluble P3HT and P3OT films.

ing fractures and reliability of resigns, composites, and coatings. A variety of methods, including X-ray diffraction,[22] laser Raman spectroscopy,[23] and the photelastic method,[24] have been proposed. This article suggests a possibility of P3AT as a molecular sensor for nondestructive detection of residual stresses in polymer materials. Since it is performed on a system with a measurement probe having optical fibers, the measurement of the decay time is a useful method in practical applications. Although it is not analyzed perfectly, it is suggested that the variation in the decay time under tensile loadings may be caused by distortion or deformation of the π-conjugated structure.

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