

Excimer Formation in Uniaxially Stretched Polymer Films

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ABSTRACT: The steady-state fluorescence properties of naphthalene-labeled polymers dispersed in poly(methyl methacrylate) (PMMA) cast films were studied under tensile loadings at 80°C. The labeled polymers were composed of methyl methacrylate (MMA) and 1-naphthylmethyl methacrylate (NMMA). Three of the copolymers were used in this work, and the contents of NMMA were 0.59 mol % (CP1), 22.0 mol % (CP2), and 56.7 mol % (CP3), respectively. The fluorescence spectra of the films containing CP1 and CP2 were unchanged during elongation. For the film containing CP3, the excited monomer emission of naphthyl groups at around 337 nm decreased with increasing applied tensile strain. The strain enhanced the emission ascribed to the excimer of the naphthyl groups in the region of 390–420 nm. The ratio of fluorescence intensities at 400 nm and 337 nm, I_{400}/I_{337} , increased with the applied strain, which indicates that CP3 is a sensitive probe for detecting the structural changes of polymer matrices. The obtained results mean that the excimer-forming sites in the PMMA films during elongation depend both on the applied strain and the concentration of naphthyl groups in the dispersed polymer probes. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2347–2351, 2001

Key words: poly(methyl methacrylate); excimer fluorescence; elongation

INTRODUCTION

An excimer is an excited molecular complex formed between two identical aromatic rings, one of which is in a singlet excited state.¹ In polymers incorporating aromatic chromophores in the repeat unit, their fluorescence spectra are often characterized by excimer emission. The excimer sites may form: (1) through intermolecular interactions between aromatic rings on different chains, (2) from intramolecular interactions between rings on nonadjacent chain segments, or (3) between aromatic rings on adjacent segments. The number of excimer sites is proportional to the

ratio of excimer intensity (I_E) to emission intensity of the isolated “monomer” (I_M).

Excimer formation in polymer solutions is widely considered to be a diffusion-controlled process.² The influences of various factors such as solvent, microstructure, and conformation of polymers have been studied extensively by many research groups.^{3–5} Recently, Li et al.⁶ studied the concentration dependence of excimer formation in pyrenyl-labeled polystyrene solution. Two critical concentration points, C^+ and C_m , were observed. In the region $C^+ < C < C_m$, an abrupt increase of I_e/I_m was revealed because of intermolecular interaction. At $C > C_m$ the sharp decrease of I_e/I_m was ascribed to entanglements of polymer chains. The entanglements control the motion of segments, and the pyrenyl groups attached to polymer chains have difficulty in approaching each

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other to form intramolecular and intermolecular excimer.

In polymer films the conformation of the chains is frozen. Excimer formed is referred to as static excimer. In this case the intermolecular excimer sites arising from clustering of polymer chains are sensitive to aggregation of aromatic rings. This effect was employed to study the compatibility of polymer blends.⁷ In addition, static excimer was shown to be sensitive to variations in the spatial distribution and alignment of molecules in the local environment.⁸ It is to be expected, therefore, that mechanical stretching also strongly influences the fluorescence of chromophore-labeled polymer films. Ikawa et al.⁹ studied fluorescence from poly(*N*-vinylcarbazole) (PVCz) in uniaxially stretched PS films. The results they obtained suggest that PVCz is an effective molecular sensor for detecting residual strains in polymer matrices. In this article we report on steady-state fluorescence from naphthalene-labeled copolymers dispersed in PMMA films under tensile loadings. The results indicate that the concentration of naphthyl groups in the polymer probes influences the sensitivity of excimer formation to the applied strains.

EXPERIMENTAL

The polymer probes, naphthalene-labeled PMMAs, were copolymers of methyl methacrylate (MMA) and 1-naphthylmethyl methacrylate (NMMA), which were kindly supplied by Professor Chen Liusheng. The synthesis and characterization of the copolymers have been described elsewhere.¹⁰ Three labeled copolymers were used in this work. The content of NMMA in the copolymers was 0.59 mol % (CP1), 22.0 mol % (CP2), and 56.7 mol % (CP3), respectively. The weight-averaged molecular weight (M_w) was 1.07×10^5 , 1.16×10^5 , and 1.39×10^5 , respectively. Their dispersion indices were less than 2.0. The matrix of the purified PMMA had a M_w of 5.2×10^5 and a dispersion index of 3.2.

Solid films of the blends of a PMMA and the copolymers were prepared by casting THF solution on glass plates. The concentration of each copolymer in the PMMA matrix was less than 1.0 wt %, ensuring that the probe molecules were isolated from each other, no intermolecular interaction was involved, and there was good compatibility. THF was distilled and ensured to be free from fluorescent moieties prior to use. All films

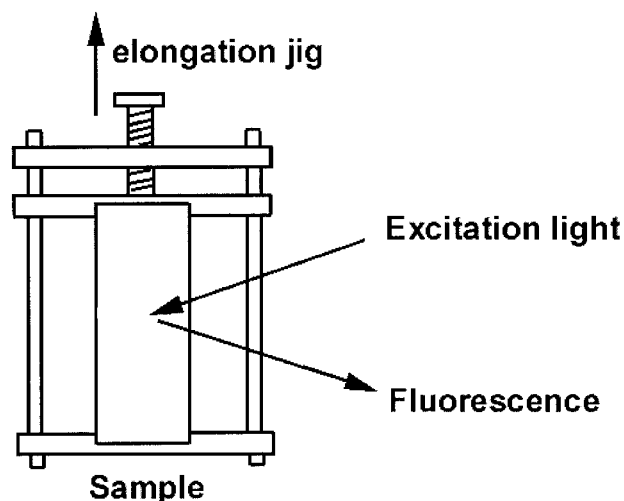


Figure 1 A schematic illustration of the test apparatus for fluorescence measurement during uniaxial elongation.

were dried in a vacuum oven at room temperature for a week. The final film thickness was about 30 μm .

The uniaxial drawing was carried out on a microtension device at 80°C. A schematic illustration of the fluorescence measurement under tensile loadings is displayed in Figure 1. A handmade jig was used for the uniaxial elongation of the sample. The strain rate was about 0.03 s^{-1} . Dumbbell-shaped strips 50 mm in total length were cut out from the casting films. The narrow midsection of the test strips was 4 mm in width and 20 mm in length. The applied strain was calculated from the crosshead displacement. Figure 2 gives the stress–strain curves of PMMA films obtained on an Instron tensile tester at different temperatures and strain rates. Here our work focused on the dependence of the fluorescence spectrum on the applied strain in the deformation region after yielding below the glass-transition temperature of PMMA. So, elongation of the PMMA films at 80°C is suitable for large deformation, as shown in Figure 2.

The fluorescence spectra were taken on the 22.5° front-face mode of a spectrofluorometer system, SPEX FL-212, at 80°C. The excitation wavelength was 280 nm.

RESULTS AND DISCUSSION

Figure 3 shows the typical emission spectra of the PMMA films containing a small amount of the

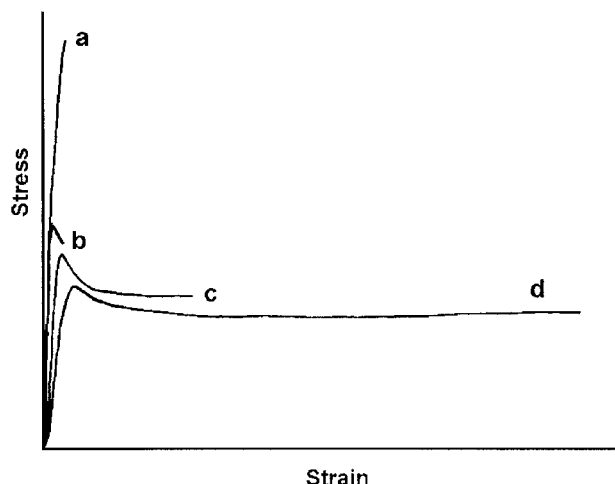


Figure 2 Stress-strain curves of PMMA films at different temperatures and strain rates: (a) room temperature, 5mm/min; (b) 80°C, 50mm/min; (c) 80°C, 20mm/min; (d) 80°C, 5mm/min.

naphthalene-labeled PMMA molecules without elongation. The spectra were normalized at 350 nm. From the spectrum of the CP1 film only the monomer emission bands of naphthyl groups with a maximum at 337 nm can be observed. This is in agreement with the measurement of the emission spectra of CP1 in solutions. The lower content of the naphthyl groups in the CP1 chains (0.59 mol %)

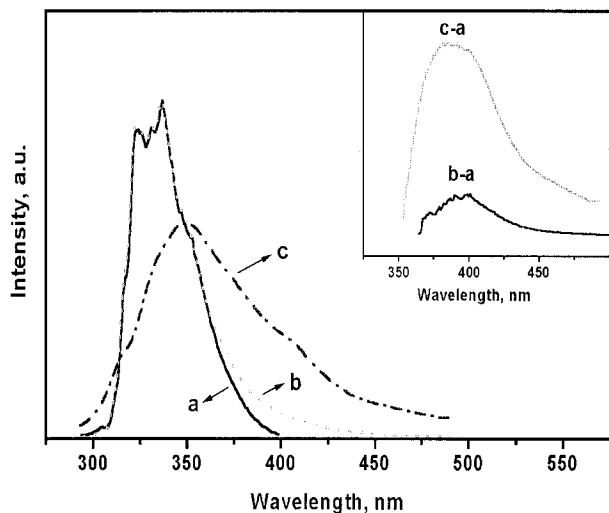


Figure 3 Typical emission spectra of naphthalene-labeled PMMA dispersed in PMMA films without elongation: (a) PMMA film with CP1; (b) PMMA film with CP2; and (c) PMMA film with CP3. The spectra were normalized at 350 nm.

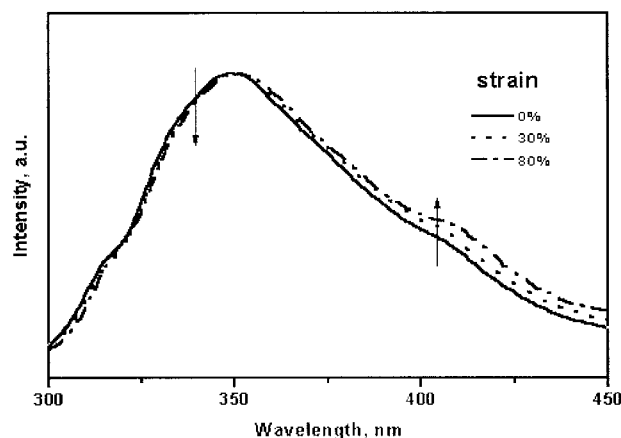


Figure 4 Fluorescence spectra of CP3 film under tensile elongation. Spectra were normalized at 350 nm.

each other, and no interaction occurs. Hence, the spectrum is narrow, and the fine structure can be observed. From the spectrum of the CP2 film a tail can be seen relative to the spectrum of the CP1 film. The slowly decaying tail is a result of the excimer emission of naphthyl groups, which overlapped with the monomer emission. By subtracting the monomer emission spectrum of CP1 film from the normalized emission spectrum of CP2 film, the excimer emission bands of naphthyl groups in CP2 film were obtained, as shown in the inserted graph of Figure 3(a,b). The excimer emission appears structureless and centered at about 400 nm. For the CP3 film sample, the spectrum was broadened and structureless, with a peak red-shifted to 350 nm. The monomer emission was depressed. The structure-lost emission of naphthyl monomers in this sample is attributed to the self-adsorption, which can be clearly seen by normalizing the emission spectra at 350 nm. By subtracting the monomer emission, the excimer emission in CP3 film can be obtained, as shown in the inset (c-a) in Figure 3. In addition, a featureless excimer emission spectrum can be observed.

Figure 4 shows the emission spectra of the CP3 film under tensile loadings. The spectra were normalized at 350 nm. Emission around 337 nm decreases as the strain is increased, while emission in the 390–420 nm region increases. The results indicate that the relative intensity of the excited monomer emission decreases under elongation while that of the excimer emission increases. The spectra of the films containing CP1 and CP2, respectively, were unchanged by the action of an external strain.

Figure 5 gives the plots of the excimer-to-monomer intensity ratio versus the applied tensile strain for the CP2 and CP3 films. The intensities of excimer and monomer were taken at 400 nm and 337 nm, respectively. It can be seen that the I_E/I_M value increases with the applied strain for CP3 film, which indicates that the excimer sites increased with stretching in the CP3 film. For CP2 film the I_E/I_M value keeps constant with the strain, indicating the number of excimer sites was unchanged by the applied strain.

In polymer films the conformation of the chains is frozen. An excited aromatic ring attached to the chain can only interact with the nearest ring of the ground state to form an excimer site. The distance between the two aromatic rings for excimer formation is supposed to be on the order of 0.4 nm.¹¹ It is known that upon drawing, the polymer chains will respond to the imposed strain via orientation of the chain segments toward the stretching direction.¹² The orientation makes the chains expand, which is expected to disrupt some of the preformed excimer sites in solid film. On the other hand, the orientation leads to highly dense packing of the macromolecules, which facilitates the aromatic rings approaching each other to form new excimer sites. Hence, it can be seen that excimer formation and dissociation in a polymer film during elongation is a competitive process, as shown in Figure 6.

In this work CP3 was shown to be a sensitive probe of the structure changes in the elongated PMMA film. The I_E/I_M value exhibited an increase with applied strain from 0% to 80%. This means that in the process of stretching, the newly

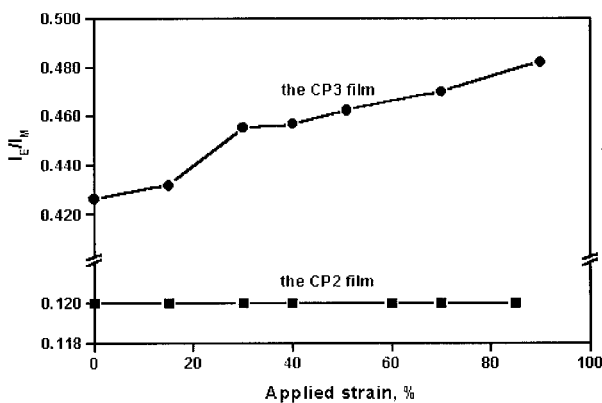


Figure 5 Plots of the ratio of the fluorescence intensities at 400 nm and 337 nm, I_E/I_M , versus applied tensile strain for the CP2 film and CP3 film, respectively.

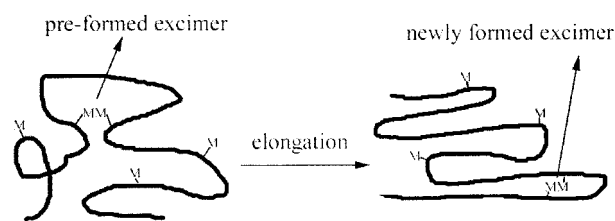


Figure 6 Proposed mechanism of excimer formation and dissociation during elongation in a chromophore labeled polymer film.

formed excimer sites increase more than the disrupted ones in the CP3 film, while the CP2 is not as sensitive a probe to the applied strain as the CP3. The I_E/I_M value remains constant with increasing the strain. This might be attributed to the equilibrium between the excimer formation and dissociation in the CP2 film under elongation at 80°C. In the film containing CP1, neither excimer formation nor dissociation occurred and only isolated naphthyl monomers existed in elongation. Ikawa et al.⁹ concluded that PVCz is a useful photoluminescent probe to detect tensile strains acting on polymer matrices. In their work the polymer probe, PVCz, was a homopolymer, but for copolymers containing pendant aromatic rings, as in our work, the content of the attached chromophores should be taken into account. In addition, the fluorescence behavior of the NMMA homopolymer was investigated. Only excimer emission was observed. When this homopolymer was dispersed in PMMA matrix, its fluorescence behavior showed no changes during elongation.

CONCLUSIONS

Three copolymers of methyl methacrylate (MMA) and 1-naphthylmethyl methacrylate (NMMA) were employed as polymer probes dispersed in PMMA film. The content of the NMMA component in the copolymers was 0.59 mol % (CP1), 22.0 mol % (CP2), and 56.7 mol % (CP3), respectively. Their fluorescence spectra were measured 80°C during uniaxial elongation of the PMMA films at. The spectra of the films containing CP2 and CP3 showed a composition of monomer and excimer emissions from naphthyl groups, respectively. Only monomer emission was observed in the spectrum of the film containing CP1. During elongation the excimer emission of around 400 nm was increased, and the monomer emission of about 337 nm was decreased in CP3 film. The intensity

ratio of excimer to monomer, I_E/I_M , increased with applied strain. In contrast, I_E/I_M remained constant with increasing strain in the CP2 film. No excimer emission was observed in CP1 film before and after elongation. These results indicate that CP3 is a sensitive probe for monitoring structural changes in an elongated PMMA film.

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