

Morphological Studies of Elongated PMMA by Excimer Formation

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ABSTRACT: The technique of excimer fluorescence has been employed to study the orientational structure of poly (methyl methacrylate) (PMMA). The PMMA films used contain a small amount of naphthalene-labeled PMMA, and were uniaxially stretched to various elongation at 80°C. The results show that the fluorescence intensity ratio of excimer to monomer, I_E/I_M , increases with the elongation ratio. The increase of excimer forming sites in the system after drawing is attributed to the orientation of both the chain segments and side groups along the drawing direction. The orientation leads to highly dense packing of the PMMA molecules. The conclusion drawn from excimer fluorescence is in agreement with those from other techniques. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1869–1872, 2000

Key words: poly (methyl methacrylate); excimer fluorescence; uniaxial drawing; orientational structure

INTRODUCTION

Uniaxial drawing of the amorphous polymers, such as PS, PMMA and PET, frequently leads to the anisotropy in structure. Although the general effect of drawing is to produce some degree of molecule alignment parallel to the drawing direction, the morphological changes are complex.¹ Only orientation can be observed when PS or PMMA is drawn, whereas crystallization occurs when amorphous PET is drawn. The structural changes have strong effects on the mechanical properties of the final products. Hence, a number of techniques have been used to investigate the

structural changes of amorphous polymers during drawing process. These include WAXD,^{2,3} electron microscopy,^{4,5} etc.

The morphology of oriented PMMA has been extensively investigated. Grosskurth⁴ concluded that its morphology depends on the degree of molecule orientation but is independent of the method of orientation. Bezruk et al.⁵ pointed out that the morphological changes of PMMA films are similar to those of amorphous-crystal polymers during the uniaxial elongation.

In this report, the structural changes of uniaxially stretched PMMA films are studied by excimer fluorescence, which, to our knowledge, has not been reported.

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EXPERIMENTAL

Materials

The atactic PMMA used in this work was polydispersed with a weight average molecule weight of

5.2×10^5 . Before use, PMMA was purified by repeated dissolving and precipitation cycles using THF as solvent and methanol as precipitating agent. Naphthalene-labeled PMMA (PNMMA) was a copolymer of 1-naphthylmethyl methacrylate (NMMA) and methyl methacrylate (MMA). The synthesis and characterization of the copolymer have been described elsewhere.⁶ Two labeled copolymers were used in this work: one has a molecule weight (M_w) of 1.07×10^5 and a polydispersity index of 1.76; the other has an M_w of 1.39×10^5 and a polydispersity index of 2.10. The contents of NMMA in the copolymers were 0.59 mol % (PNMMA1) and 56.7 mol % (PNMMA2), respectively.

Sample Preparation

Solid films of the blends of PMMA and PNMMA were prepared by casting THF solution on glass plates. THF was distilled, and ensured to be free from fluorescent moieties prior to use. All films were dried in a vacuum oven at room temperature for a week. The final film thickness was about 30 μm .

Uniaxial Tension

The uniaxial drawing was carried out on a micro-tension device at 80°C. The strain rate was ca 0.03 s^{-1} . Dumbbell-shaped strips of 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 elongation ratio was calculated from the crosshead displacement. In the case of deorientation, the strips, without unloading on the device, were rapidly cooled to room temperature after drawing to certain elongation. From the PMMA relaxation tests (ref. 11), the strain-birefringence coefficient remained constant in the temperature range from 0 to 37°C, indicating the orientational structure was frozen at room temperature.

Fluorescence Measurements

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

RESULTS AND DISCUSSION

An excited aromatic molecule and a ground state molecule of the same species may form an exci-

mer.⁷ In polymer blends containing chromophore-labeled polymers, excimer sites may be formed: (1) through intermolecular interaction between aromatic rings on different chains, and (2) through intramolecular interaction between rings on nonadjacent or adjacent chain segments. At this stage of the study, it is difficult to distinguish the two kinds of excimer sites by their fluorescence spectra. And the excimer sites formed between rings on nonadjacent segments are considered as a subclass of the intermolecular case. The ratio of excimer emission intensity (I_E) to emission intensity of the isolated "monomer" (I_M) is proportional to the number of excimer sites.

The intermolecular excimer sites arising from the cluster of polymer chains are sensitive to the aggregation of aromatic rings, so the intermolecular interaction is important in the study of polymer miscibility.^{8,9} In contrast, the intramolecular excimer formation plays an important role in studying the conformation of polymer chains in dilute solution.

In this work, the excimer sites are regarded as arising from the intramolecular interaction. The reasons are as the follows: (a) the good miscibility between PNMMA and PMMA, as deduced from the high content of MMA component in PNMMA; (b) the low concentration of PNMMA in the blends; and (c) the difficulty for the separated PNMMA chains to aggregate in solid films below the glass transition temperature.

Figure 1 shows the typical uncorrected emission spectra of PNMMA/PMMA blends without deformation. From the fluorescence spectrum of the blend containing 1.0 wt % PNMMA1, only a monomer emission with a maximum at 340 nm is observed. When the concentration of naphthyl groups in PNMMA is 56.7 mol % (PNMMA2), the spectrum shows a broad band at about 400 nm, corresponding to the excimer emission. The structure-lost monomer emission of naphthyl groups in the PNMMA2/PMMA blend is attributed to the self-adsorption effect, which can be clearly seen by normalizing the emission spectra of the two samples at the peak of $\lambda = 350 \text{ nm}$.

Figure 2 shows the emission spectra of solid films of the blend containing 0.4 wt % PNMMA2. The inserted graph is the excimer emission bands of the naphthyl groups in the blend, which were obtained by subtracting the monomer emission spectrum of PNMMA1 (Fig. 1) from the normalized emission spectra of the elongated samples containing PNMMA2 (Fig. 2). The spectra of both the elongated films and the unelongated film

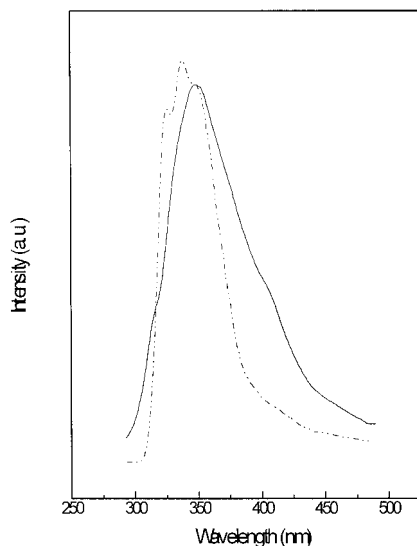


Figure 1 Fluorescence spectra of the solid films of PNMMA/PMMA blends without deformation. The spectra are normalized at 350 nm: (—) with 1.0 wt % PNMMA1; (—) with 0.4 wt % PNMMA2.

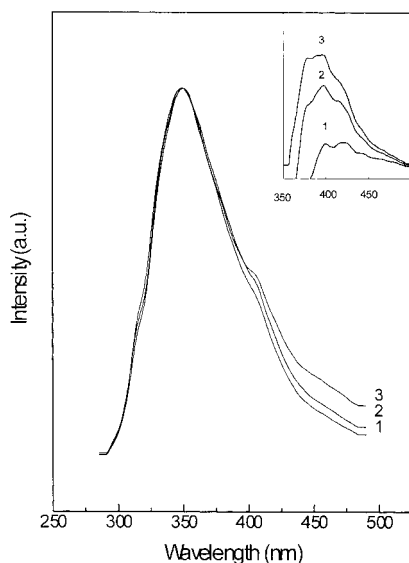


Figure 2 Fluorescence spectra of the solid films with 0.4 wt % PNMMA2 at various elongation ratios, (1) 0, (2) 51.0, (3) 90.0%. All spectra are normalized at 350 nm. The inserted graph is the excimer emission spectra of naphthyl groups in the blend. The spectrum of the solid film with 30.1% elongation ratio is omitted for clearness.

show the normal excimer emission at ca. 400 nm as well as the similar monomer emission. However, all the excimer emission bands are broadened to a longer wavelength, and a new band appears at ca. 425 nm. This suggests occurrence of multinaphthyl ring interaction, probably arising from the contract tendency of the PNMMA2

coils duo to the high content of naphthyl groups in the chains. The multiphenyl ring interaction has been systematically studied with styrene polymers.^{10–12} Moreover, the emission of the elongated samples also shows a high energy excimer peak at ca. 375 nm, indicating the naphthyl groups in the excimer are not fully eclipsed duo to the frozen unequilibrated chain conformation formed upon the sample drawing.

Figure 3 gives the plot of excimer to monomer intensity ratio vs. elongation ratio. The intensities of excimer and monomer are taken from Figure 2 at 400 and 340 nm, respectively. It can be seen that the fluorescence intensity ratio of excimer to monomer slightly increases with the elongation ratio, which indicates the excimer sites in the system increase with stretching. This result has been proven to be well reproducible.

The change of the number of the excimer sites indicates the structural changes in the system during elongation. 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. The resultant morphology of polymer chains will influence the intramolecular excimer formation between nonadjacent rings. As showed in Figure 4(a), the long-range orientation makes the polymer chains expand. Thus, it can be expected that the drawing of the samples will disrupt some of the excimer sites formed between the nonadjacent naphthyl groups. However, the observed overall effect is not consistent with this expectation. Instead, the fluorescence intensity ratio of excimer to monomer shows a slightly increase with elongation. This result should serve as an evidence for short-range orientation, as showed in Figure 4(b), and the local folding of the polymer chains must be involved and densely packed nematic structure may be formed, which facilitates the intramolecular interaction and leads to the increase of excimer sites. Milagin et al.¹³ investigated the change of the density of amorphous PMMA during orientational drawing. It was found that the drawing of PMMA increases the segmental density.

Nevertheless, the expected long-range orientation effect of disruption of the excimer forming sites duo to the nonadjacent naphthyl group interaction seems to be not predominant. This could be ascribed to the higher content of naphthyl groups in PNMMA2, and furthermore, that the extent of large-scale distortion of the polymer chains along orientation is relatively small.

Another contribution to the increase of excimer sites is the conformational change of the ester

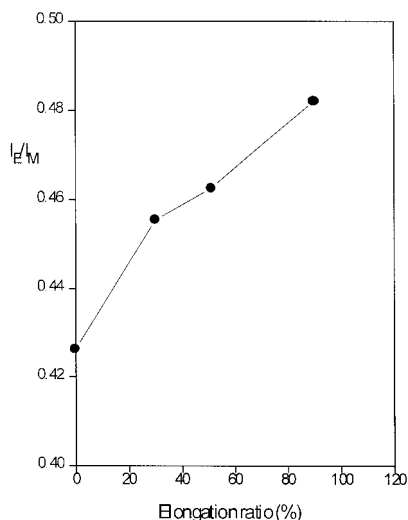


Figure 3 Excimer to monomer intensity ratio vs. elongation ratio of the solid films with 0.4 wt % PNMMA2.

groups. Su-Don Hong et al.¹⁴ studied the molecular deformation mechanisms in glass PMMA. They concluded that strain-induced distortion of the conformation of the COOCH₃ group might involve only rotation of the OCH₃ group around the C—O bond. The ester group tends to be distorted from its thermal equilibrium conformation upon deformation. And the alignment of the side groups in the drawing direction will favor the intramolecular interaction between the adjacent naphthyl rings attached to the side groups, which also leads to the increase of excimer sites in the PNMMA2/PMMA blend.

CONCLUSIONS

The excimer formation has been adopted to study the morphological changes of amorphous polymers



Figure 4 Orientational scheme of the PMMA chains in the elongated films: (a) long-range orientation; (b) short-range orientation and chain folding.

during the uniaxial orientation. The polymer probes labeled with the naphthyl groups were incorporated into the PMMA matrix. By analyzing the excimer formation in the blend, the bulk structural changes could be investigated on molecular level. The results show that the I_E/I_M values for the solid films of the blend with 0.4 wt % PNMMA2 increase with the elongation ratio. The increase of the excimer sites in the system can be explained in terms of intramolecular interactions arising from the local orientation of both the chain segments and side groups along the drawing direction.

Obviously, the content of the naphthyl groups in the labeled polymeric chains will affect the I_E/I_M value measured. However, as showed by the result, the excimer formation is a sensitive probe to study the structural changes of amorphous polymers during the uniaxial orientation. Further investigation is being carried out in our laboratory.

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