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Photodegradation mechanisms in poly(2,6-butylenenaphthalate-*co*-tetramethyleneglycol) (PBN–PTMG), Part III: Photodegradation induced by the carbonyl group in n, π^* excited states

Yasutaka Nagai [a,*], Daisuke Miyagishi [a], Tomoko Akagawa [a], Fujio Ohishi [a], Hitoshi Ueno [b], Koji Kobayashi [b], Katsuhisa Yamashita [b], Junji Watanabe [c]

[a] *Department of Materials Science, Faculty of Science, Kanagawa University, 2946 Tsuchiya, Hiratsuka city, Kanagawa 259-1293, Japan*
[b] *TOYOBO Co., Ltd. Research Center, 2-1-1 Katata, Ohtsu city, Shiga 520-0292, Japan*
[c] *Graduate School of Technology, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan*

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Abstract

In order to identify the initiation step in the photodegradation of poly(2,6-butylenenaphthalate)-*block*-poly(tetramethyleneglycol) (PBN–PTMG), we undertook its photolysis with monochromatic irradiation. We discuss the initiation reaction on the basis of the analytical results for the PBN–PTMG in the presence or absence of 2,2′-dihydroxy-4-methoxybenzophenone as a UV absorber, 2-hydroxy-4-methoxybenzophenone as a UV absorber, β-carotene as a quencher of singlet oxygen or methylene blue as a photosensitiser, respectively.

The PBN–PTMG containing 2,2′-dihydroxy-4-methoxybenzophenone exhibits better resistance to the incident light of *ca.* 370 nm corresponding to the absorption of the n, π^* transition of the carbonyl group in the PBN block than the PBN–PTMG containing 2-hydroxy-4-methoxybenzophenone. The PBN–PTMG containing β-carotene shows similar photodegradation tendencies as that of the PBN–PTMG without β-carotene. In contrast, the PBN–PTMG with methylene blue is not degraded by monochromatic radiation in the range $\lambda = 600$–690 nm. These facts indicate that singlet oxygen does not participate in the initiation reaction of the photodegradation of the PBN–PTMG. Therefore, we concluded that the photodegradation of the PBN–PTMG is induced through the hydrogen abstraction by carbonyl groups in n, π^* excited states.

Keywords: Poly(2,6-butylenenaphthalate)-*block*-poly(tetramethyleneglycol); Thermoplastic polyester elastomer; Photodegradation mechanisms; Carbonyl group; n, π^* Excited state

1. Introduction

In recent years, a thermoplastic polyester elastomer composed of poly(2,6-butylenenaphthalate)-*block*-poly(tetramethyleneglycol) (PBN–PTMG) which has improved resistance to heat, chemicals, oil and water, compared to PBT–PTMG (poly(butyleneterephthalate)-*block*-poly(tetramethyleneglycol)) has been developed.

So far, we have investigated the photodegradation mechanisms of the PBN–PTMG and its wavelength dependence. In our previous papers [1,2], we reported on the photodegradation of the PBN–PTMG resulting from irradiation by polychromatic light or monochromatic light. In those studies, it became clear that ester bonds are formed on the soft-segment and that formate, propyl, aldehyde and hydroxyl groups result from the main chain scission. It also became clear that the threshold wavelength for the photodegradation of the PBN–PTMG is *ca.* 380 nm. In the previous paper [2], we reported that the most effective wavelength for the photodegradation of the PBN–PTMG is from 370 to 380 nm. Those wavelengths correspond to the n, π^* absorption band of the

* Corresponding author.
E-mail address: yasutaka@kanagawa-u.ac.jp (Y. Nagai).

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carbonyl group. In that article, we proposed the photodegradation mechanisms of the PBN–PTMG as shown in Fig. 1. Therefore, we anticipate the following pathways in the initiation process in the photodegradation mechanisms of the PBN–PTMG on the basis of the analytical results. The first pathway is the reaction via the hydrogen abstraction by the carbonyl group in the n, π^* excited states. A second pathway is the reaction of the PTMG block with $^1O_2$ generated by the energy transfer from the PBN block in an excited state. A third pathway is the oxidative reaction of the PTMG block which is excited by the energy transfer process from the PBN block in an excited state. In addition, a reaction via the formation of a charge transfer complex between the PTMG block and oxygen may also take place. Oxidative reaction of diethyl ether through the formation of the charge transfer complex has been reported [3]. In that paper, the authors showed that wavelength responsible for photochemical reaction of diethyl ether with oxygen lies between 218 and 278 nm. When the oxidative reaction of the elastomer takes place through the formation of the charge transfer complex, the wavelength of the light required to cause the photodegradation to the PBN–PTMG should correspond to the wavelength reported in that paper [3]. However, the most effective wavelength for the photodegradation of the PBN–PTMG lies around 370 nm. Therefore, the charge transfer complex should not be formed in this elastomer. So far, studies on the photodegradation reaction through the formation of the charge transfer complex between a polyether and oxygen has not been reported except for poly(2,6-dimethyl-1,4-phenylene ether) [4].

In this paper, we report on the initiation reaction in the photodegradation of the PBN–PTMG on the basis of the analytical results obtained in monochromatic irradiation experiments.

2. Experimental

2.1. Preparation of test samples

PBN–PTMG sheets which have 50% PTMG content by weight were supplied by TOYOBO Co., Ltd. Research Center. The sample films (*ca.* 100 μm in thickness) were prepared by casting from the chloroform solution onto flat Petri dishes and dried under reduced pressure at room temperature for *ca.* 24 h. The sample films without light stabilizers and the sample films containing 2,2′-dihydroxy-4-methoxybenzophenone (2,2′DH4MBP) with *ca.* 0.3%, 2-hydroxy-4-methoxybenzophenone (2H4MBP) with *ca.* 0.3%, β-carotene (BC) with *ca.* 1% or methylene blue (MB) with *ca.* 1% in weight, respectively, were also prepared. Fig. 2 shows the chemical structure of 2,2′DH4MBP, 2H4MBP, BC and MB.

2.2. Photo-irradiation experiments

The monochromatic light irradiation of the samples was carried out with the OLS [5] at the National Institute for Basic Biology (NIBB). Irradiations of the samples containing 2,2′DH4MBP, 2H4MBP or BC were carried out at intervals of 10 nm from 280 nm to 400 nm at 23 °C in air. Irradiations of the samples containing MB were carried out at wavelengths of 600, 610, 620, 630, 640, 650, 660, 670, 680, and 690 nm in air at 23 °C. The photon flux density of the light was measured with a RAYON IND. Co., Ltd., model RMS-101 photon flux density meter. Radiant exposure at each position of samples was adjusted to 2.0 MJ/m^2.

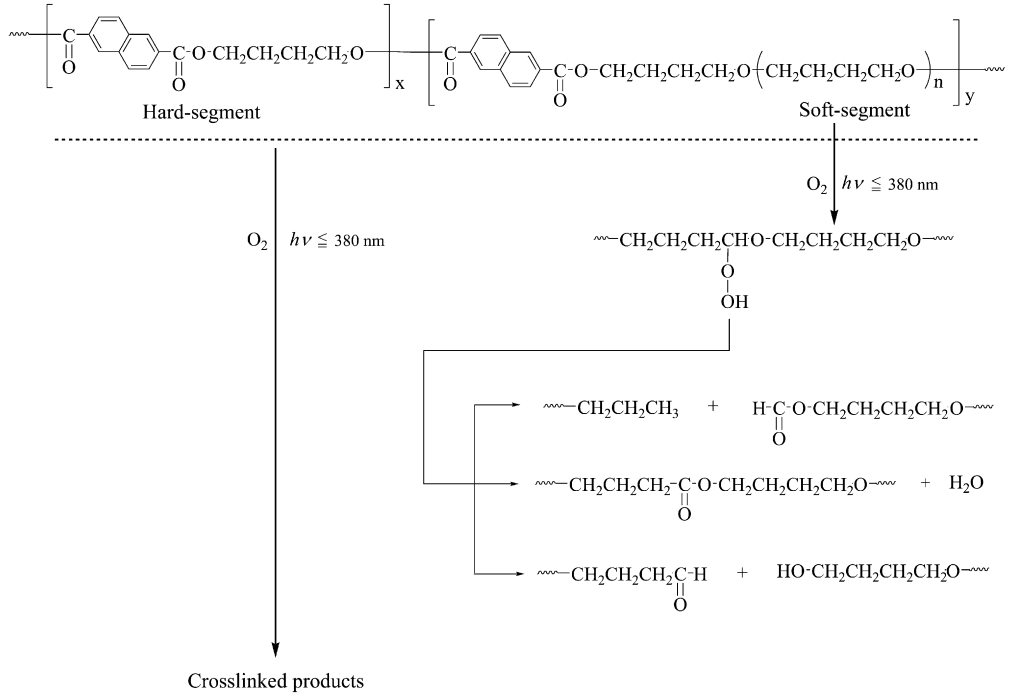

Fig. 1. Photodegradation mechanisms of the PBN–PTMG thermoplastic polyester elastomer.