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Photodegradation mechanisms in poly(2,6-butylenenaphthalate-*co*-tetramethyleneglycol) (PBN–PTMG). I: influence of the PTMG content

Yasutaka Nagai[a,*], Daisuke Nakamura[a], Tomoyuki Miyake[a], Hitoshi Ueno[b], Naomi Matsumoto[b], Atsushi Kaji[b], Fujio Ohishi[a]

[a]*Department of Materials Science, Faculty of Science, Kanagawa University, 2946 Tsuchiya, Hiratsuka city, Kanagawa 259-1293, Japan*
[b]*TOYOBO Research Center Co., Ltd., 2-2-1 Katata, Ohtsu city, Shiga 520-0292, Japan*

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Abstract

We have investigated the mechanisms of the photodegradation of poly(2,6-butylenenaphthalate-*co*-tetramethyleneglycol) (PBN–PTMG) using polychromatic radiation and have analyzed its photodegradation products. As PTMG contents increase, the degree of photodegradation rises. Under our experimental conditions, we concluded that the polymer degradation occurs mainly in the ether parts of the soft-segments, where photo-irradiation generates ester bonds, aldehyde, formate and propyl end groups, and, we believe, crosslinking as well.

Keywords: Poly(2,6-butylenenaphthalate-*co*-polytetramethyleneglycol); Thermoplastic polyester elastomer; Photodegradation; Soft-segment; Hard-segment; Gel

1. Introduction

A newly developed thermoplastic polyester elastomer, made of poly(2,6-butylenenaphthalate) and poly(tetramethyleneglycol) (PBN–PTMG) has a higher thermal performance than an earlier thermoplastic polyester elastomer made from poly(butyleneterephthalate) (PBT) and poly(tetramethyleneglycol) (PTMG) (PBT–PTMG). To this point, the literature contains studies on the weathering and thermal aging of PBT–PTMG [1–5], and on the photodegradation mechanism of PBN, which is a component of PBN–PTMG that plays the role of a hard-segment [6]. In the latter article, the authors reported that the photo-oxidation of PBN yields mainly carboxylic acid end groups and anhydrides; its photo-yellowing and gel formation are the results of the formation of structures with an extended conjugation involving the naphthalene group.

In order to extend the outdoor usage lifetime of PBN–PTMG, it is important to clarify the mechanisms of its photodegradation; however, are still unknown. In this study, we examine the mechanisms of and the effect of the PTMG content on the photodegradation of PBN–PTMG.

2. Experimental

2.1. Preparation of test samples

Copolymer materials supplied by TOYOBO Co. Ltd, consisting of poly(2,6-butylenenaphthalate)(PBN) and

* Corresponding author. Fax: +81 463 58 9684.
E-mail address: yasutaka@chem.kanagawa-u.ac.jp (Y. Nagai).

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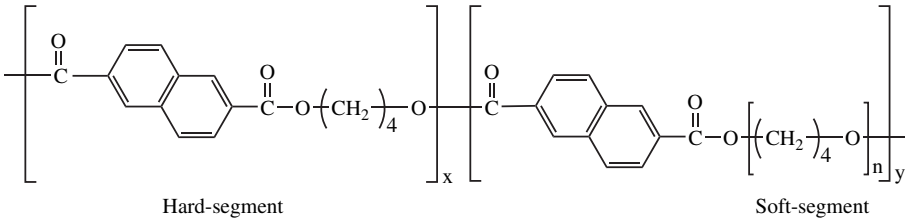

Fig. 1. Chemical structure of the PBN–PTMG.

poly(tetramethyleneglycol) (PTMG), with PTMG contents by weight of about 50%, 32% and 20% were injection molded into sheets 2 mm in thickness, 100 mm in length and 100 mm in width. Fig. 1 shows the chemical structure of the sample materials.

The PBN–PTMG sheets were dissolved in chloroform ($CHCl_3$) or a mixed solvent consisting of chloroform and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) in the volume ratio of 7 to 3; it was always used for the two samples that had a low PTMG content. The sample films (ca. 100 μm in thickness) were prepared by casting from the solution (chloroform or the mixed solvent) onto flat Petri dishes and dried under reduced pressure at room temperature for ca. 24 h. None of the samples contained light stabilizers.

2.2. Photo-irradiation experiment

The photo-irradiation was carried out at 63 °C using a Heraeus INDUSTRIETECHNIK Model SUNTEST CPS+. This apparatus is equipped with a 1500 W xenon lamp and a series of quartz glass and UV special glass filters that cuts off ultraviolet rays shorter than 290 nm.

2.3. Measurement of gel fraction

The insoluble portion was separated from the solution by filtration through a filter (10 μm pore size) and then dried under reduced pressure at ambient temperature for ca. 12 h. The gel fraction was calculated from the ratio of the weight of the insoluble part in $CHCl_3$, or the mixed solvent, to the initial weight of the sample.

2.4. Analysis of photodegradation by FT-IR, SEC and NMR

The infrared absorption spectra were measured as KBr tablets using a JASCO Corporation Model FT-IR 420. The molecular weight and molecular weight distributions were taken with a TOSOH gel-permeation chromatography (GPC) system (Degasser: Model SD-8000, Pump: Model CCPS, Column oven: Model CO-8020, Detector: Model UV-8020). In all cases, the molecular weights of samples are given relative to polystyrene standard. The flow rate of the chloroform (or the mixed solvent) mobile phase was 0.7 ml/min. The liquid state ^{1}H, ^{13}C, and $^{1}H-^{13}C$ correlation spectroscopy (COSY) NMR spectra of the samples were recorded on a JEOL Model JNM-ECP500 at room temperature. The chemical shifts were determined in solution ($CDCl_3$ or a mixed $CDCl_3$ and HFIP–d_2 solvent in a volume ratio of 7 to 5) relative to a tetramethylsilane (TMS) internal standard.

3. Results and discussion

3.1. Analysis of photodegradation products

The change in the gel fraction with increase in irradiation time is shown in Fig. 2. For the sample with 50% PTMG content, the gel fraction rose sharply up to the 20-h irradiation point; it then increased moderately up to 100 h of irradiation. It is apparent that the gel fraction of the samples with 32% PTMG content and 20% PTMG content increased gradually compared with that of the sample with 50% PTMG content. The gel fraction of the sample with 20% PTMG content at 100-h irradiation point was about one-half of that of the sample with 50% PTMG content at 100-h irradiation point. The portion insoluble in $CHCl_3$ was also

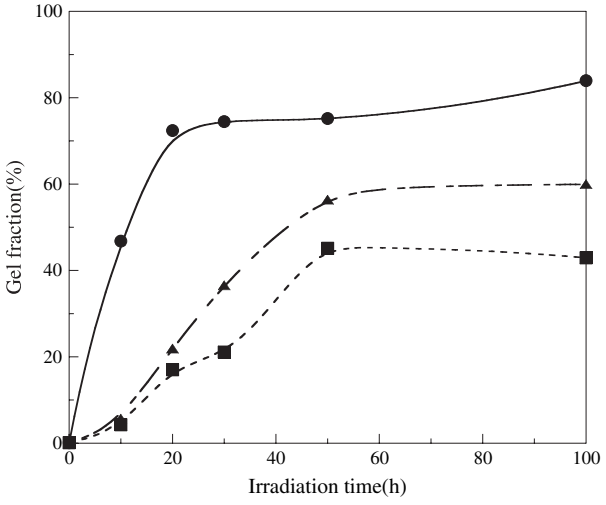

Fig. 2. Change in the gel fraction with irradiation time. ●, 50% PTMG content; ▲, 32% PTMG content; ■, 20% PTMG content.