

Analysis of Photodegradation of Cyclic Olefin Polymers

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In order to make clear the photodegradation mechanisms of the cyclic olefin polymers, hydrogenated poly (cyclohexadiene-*ran*-butadiene) (H-CHB) and hydrogenated polystyrene (H-PS), photo-irradiation experiment and analysis of the photodegradation products have been taken place. Under our experimental conditions, we concluded that the polymer degradation occurs similar to the degradation of general polyolefin. Photo-irradiation generates ester bonds, ether bonds, ketones, alcohols and end groups such as carbon-carbon double bonds, aldehydes and chain-end methyl. The photo-irradiation on these cyclic olefin polymers forms the gel mainly.

Key words: cyclic olefin polymer, photodegradation, polyolefin, transparent plastic, cross-linking products

1. INTRODUCTION

Recently, inorganic glasses have been replaced by transparent plastics. Cyclic olefin polymer (COP), which is a kind of the transparent plastics, is expected for optical uses. The electronic transition absorption of COP is small because it has only single bonds in the polymer unit. Moreover, COP has little crystallinity. Therefore, it is expected that COP has high transparency and photo-resistance. So far, however, few studies on the photo-resistance of COP have been reported. In this study, we analyze the photodegradation products of two types of COP. Hydrogenated poly (cyclohexadiene-*ran*-butadiene) (H-CHB) and hydrogenated polystyrene (H-PS) included cyclohexane in main-chain or side-chain, respectively, were selected to examine the difference of photodegradation products.

2. EXPERIMENTAL

2.1 Sample preparation

In order to remove the low molecular weight compounds and impurities, hydrogenated poly (cyclohexadiene-*ran*-butadiene) (H-CHB) and hydrogenated polystyrene (H-PS) were precipitated in methanol (Fig. 1). Samples for photo-irradiation experiments were casted from each carbon tetrachloride (CCl₄) solution onto a flat petri dish and dried under reduced pressure for 12 hours at room temperature.

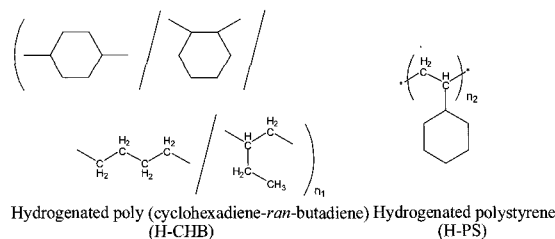


Fig. 1 Chemical structure of samples.

2.2 Photo-irradiation

The sample films with 85-90 μm thickness on a flat petri dish were photo-irradiated using an Atlas SUNTEST CPS+ at 63 $^{\circ}\text{C}$ (no water spray) with

continuous radiation from a 1500-watt xenon arc lamp through a series of reflective silicon bromide filter and UV glass filters that cut off ultraviolet rays shorter than 290 nm. Each sample was irradiated for 50, 100, 200 and 300 hours.

2.3 Analytical methods

All samples before and after irradiation were separated into the portion soluble in CCl₄ or insoluble in CCl₄, respectively. Samples before irradiation dissolved in CCl₄ completely. Each portion insoluble in CCl₄ was hardly soluble in several solvents, such as chloroform, cyclohexane, iso-octane, tetrahydrofuran, dimethylformamide and dimethylsulfoxide, but each insoluble portion was dissolved slightly in dichloromethane (CH₂Cl₂). Therefore, each sample after irradiation was separated into the portion soluble in CCl₄, soluble in CH₂Cl₂ or insoluble in solvents (gel).

Number-average molecular weight of each soluble portion in CCl₄ of H-CHB or H-PS was measured by a TOSHO GPC system (Degasser: Model SD-8000, Pump: Model CCPS, Column oven: Model CO-8020, Detector: RI-8020) with a chloroform solution. In every case, the molecular weight of the samples represented in this paper as the relative value after conversion to the molecular weight of the standard polystyrene. The flow rate of the chloroform mobile phase was 0.7 ml/min. UV/vis spectra of each soluble portion in CCl₄ of H-CHB or H-PS were measured with a JASCO Corporation Model V-560. The infrared absorption spectra were measured as KBr tablets using JASCO Corporation Model FT-IR 420. ¹H NMR spectra of the portion soluble in CCl₄ were recorded on a JEOL Model JNM-ECP500 at room temperature. The chemical shifts were determined in solution (mixed CDCl₃ and CCl₄ solvent in a volume ratio of 1 to 1) using tetramethylsilane as internal standard. Furthermore, each soluble portion in CCl₄ was separated by thin layer chromatography with chloroform into the photodegradation products and the nondegraded component. UV/vis spectrum (in CH₂Cl₂ solution), IR spectrum (as KBr tablet) and NMR spectrum (in CD₂Cl₂ solution) of each soluble portion in CH₂Cl₂ were

measured similar to the portion soluble in CCl_4 . Each gel was analyzed by UV/vis spectroscopy, IR spectroscopy, NMR spectroscopy and X-ray photo-electron spectroscopy. Diffuse reflection UV/vis spectrum of the gel was measured using a JASCO Corporation Model V-560 equipped with a integration sphere attachment Model ISV-469. IR spectra of the gel were measured as KBr tablets using JASCO Corporation Model FT-IR 420. Solid state ^{13}C CPMAS spectrum of the gel was recorded on a JEOL Model JNM-ECP300. Solid state ^{13}C CPMAS spectrum was referenced to the chemical shift of methyl group carbons of solid hexamethylbenzene at 17.4 ppm. XPS measurements were carried out with a JEOL Model JPS-9010MC using a Mg $K\alpha$ X-ray source. The X-ray source has been working at 100W, 10 mA and 10 kV. The electron takeoff angle with respect to the sample surface was 90° . In order to analyze the chemical structure of each gel, the gel was hydrolyzed in methanol solution of 0.2 mol dm^{-3} potassium hydroxide at 50°C for 48 hours.

3. RESULTS AND DISCUSSION

3.1 Amount of the insoluble portion in CCl_4

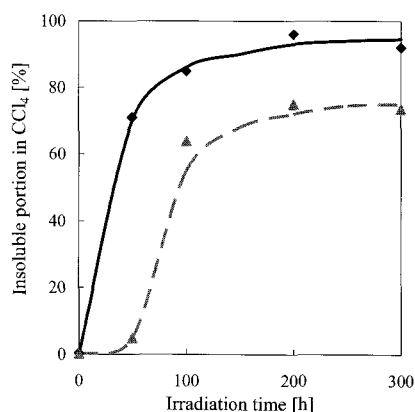


Fig. 2 Changes in the amount of the insoluble portion in CCl_4 with irradiation time.

—●— : H-CHB, —▲— : H-PS

For two samples, the amount of the insoluble portion in CCl_4 increased with increase in irradiation time (Fig. 2). The amount of the insoluble portion in CCl_4 of H-CHB and H-PS reached over 90 % or 70 % after irradiation for 200 hours, respectively. The portion insoluble in CCl_4 of each sample was dissolved little in several solvents (see section 2.3) except for CH_2Cl_2 . The amount of soluble portion in CH_2Cl_2 in the insoluble portion in CCl_4 of the each sample was *ca.* 10 %.

3.2 Analysis of the portion soluble in CCl_4

Change in the normalized number-average molecular weight of each sample is shown in Fig. 3. The number-average molecular weights of each soluble portion in CCl_4 decreased with increase in irradiation time. This finding indicates that main-chain scission occurs during photo-irradiation. Finally the number-average molecular weight decreased one-fifth of that measured prior to irradiation.

UV/vis spectra of each sample are shown in Fig. 4. UV/vis absorptions of the portion soluble in CCl_4 of the each sample after irradiation appeared in the wavelength region shorter than 450 nm.

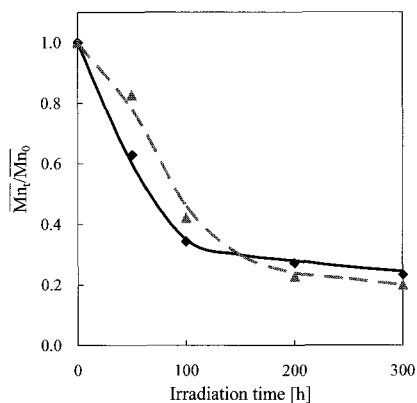


Fig. 3 Changes in the normalized number-average molecular weight of the portion soluble in CCl_4 with irradiation time.

—●— : H-CHB, —▲— : H-PS

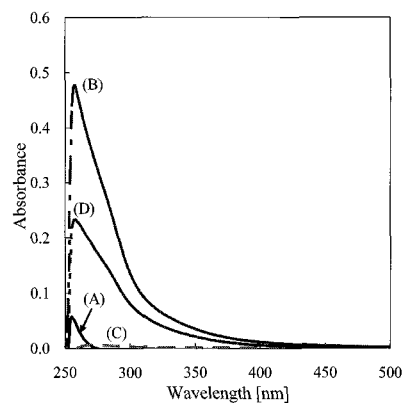


Fig. 4 UV/vis spectra of samples before irradiation and the portion soluble in CCl_4 after 300-hour irradiation.

(A) — : H-CHB before irradiation (B) - - - : H-CHB after 300-hour irradiation
(C) — : H-PS before irradiation (D) - - - : H-PS after 300-hour irradiation

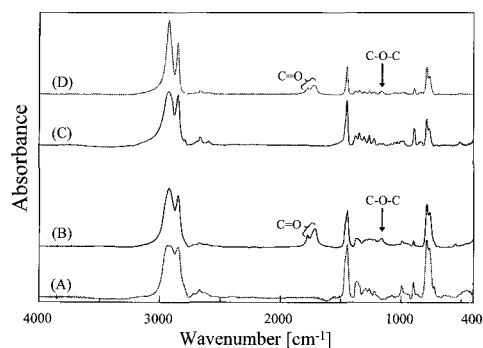


Fig. 5 FTIR spectra of samples before irradiation and the portion soluble in CCl_4 after 300-hour irradiation.

(A) H-CHB before irradiation (B) H-CHB after 300-hour irradiation
(C) H-PS before irradiation (D) H-PS after 300-hour irradiation

IR spectra of each sample are shown in Fig. 5. The peaks at 1710 cm^{-1} and 1780 cm^{-1} assigned to stretching vibrations of carbonyl group, and peaks at 1160 cm^{-1} assigned to asymmetric stretching vibration (C-O-C) were appeared by photo-irradiation. Whereas, the peaks at 1395 cm^{-1} to 1180 cm^{-1} , 785 cm^{-1} and 760 cm^{-1} which are assigned to C-H stretching vibration and the peak at 990 cm^{-1} assigned to skeletal vibration of cyclohexane were decreased with increase in irradiation time.

It is well known that the photodegradation of polyolefin progresses via auto-oxidation¹⁾. Auto-oxidation is initiated by the formation of hydroperoxide. So far, detailed studies on the photodegradation mechanisms of polypropylene were reported^{2),3)}. The analysis of the photodegradation of polyethylene⁴⁾ and polynorbornene⁵⁾ were also reported. In the case of our samples, it is expected that auto-oxidation takes place. The analytical results suggested that the cross-linking, chain scission arise from photolysis of hydroperoxide. The cross-linking products are constituted with carbon-carbon single bonds, ether bonds and ester bonds. Therefore, the appearance of C-O-C bond and C=O bond indicated that the possibility of the formation of cross-linking. It is indicated that the main-chain scission and ring-opening of cyclohexane and/or elimination of cyclohexane result in the decrease of the IR absorbance caused by stretching vibration of C-H and skeletal vibration of cyclohexane.

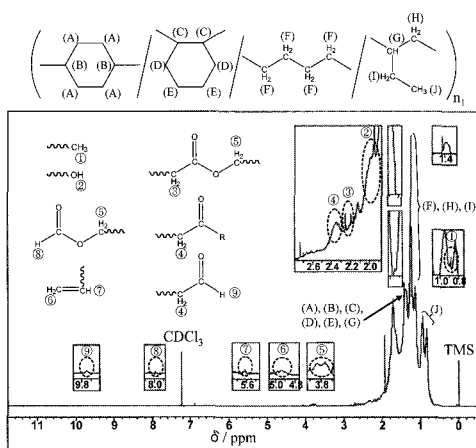


Fig. 6 ^1H NMR spectrum of the portion soluble in CCl_4 of H-CHB after 300-hour irradiation.

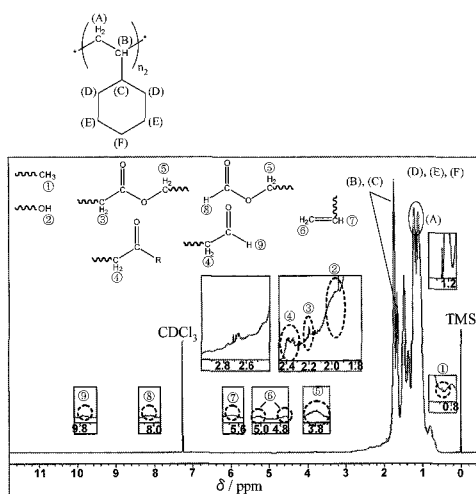


Fig. 7 ^1H NMR spectrum of the portion soluble in CCl_4 of H-PS after 300-hour irradiation.

^1H NMR spectrum of the portion soluble in CCl_4 of H-CHB or H-PS after irradiation for 300 hours is shown in Fig. 6 and Fig. 7, respectively. A capital letter with the parenthesis and a number with circle in those figures

are corresponding to the protons of the products inserted in the figures. The peaks at 0.9 ppm, 8.0 ppm and 9.7 ppm appeared after irradiation for 300 hours of each sample are assigned to the protons of methyl, formic ester and aldehyde end groups, respectively. The peaks at 2.0 ppm, 2.3 ppm, 3.8 ppm and 5.6 ppm are assigned to the protons of hydroxyl, ketone, ester and alkene groups, respectively. Chain scission and photolysis of hydroperoxide resulted in the formation of alcohols, alkenes, aldehydes and esters.

The peaks of degradation products partly overlapped with peaks of the nondegraded components of the sample so that we tried to separate those products and components by using thin layer chromatograph (TLC) techniques. However ^1H NMR spectrum of each sample separated by TLC technique was not so clear.

3.3 Analysis of the portion soluble in CH_2Cl_2

From the analytical results except for the results of IR analysis, most of the photodegradation products of the soluble portion in CH_2Cl_2 were similar to the products which were identified to the portion soluble in CCl_4 . Fig. 8 shows the IR spectra of the H-PS measured prior to irradiation, the portion soluble in CH_2Cl_2 of H-PS after irradiation for 300 hours and the portion soluble in CCl_4 of H-PS after irradiation for 300 hours.

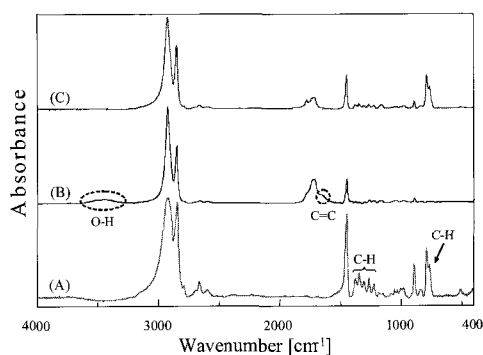


Fig. 8 FT/IR spectra of H-PS before irradiation and after 300-hour irradiation. (A) H-PS before irradiation (B) The portion soluble in CH_2Cl_2 of H-PS after 300-hour irradiation (C) The portion soluble in CCl_4 of H-PS after 300-hour irradiation

As shown in Fig. 8, the peaks at 3450 cm^{-1} assigned to stretching vibration of hydroxyl group and peaks at 1650 cm^{-1} assigned to stretching vibration of carbon-carbon double bond were appeared in the IR spectrum of the portion soluble in CH_2Cl_2 after irradiation for 300 hours. IR absorption peaks at 1395 cm^{-1} to 1180 cm^{-1} , 785 cm^{-1} and 760 cm^{-1} of the portion soluble in CCl_4 are absent in the IR spectrum of the portion soluble in CH_2Cl_2 .

From the results of the NMR analysis, it is made clear that the peak at 1.4 ppm and 3.4 ppm which assigned to the protons of the hydroxyl group of tertiary alcohol and of the methylene adjacent to the ether oxygen, respectively, appeared in the spectrum of the portion soluble in CH_2Cl_2 .

3.4 Analysis of the portion insoluble in solvents (gel)

DR UV/vis spectra of each sample prior to irradiation and the gel after irradiation for 300 hours are shown in Fig. 9. As shown in Fig. 9, DR UV/vis spectra of the gel after irradiation broadened in longer wavelength side

compared with the spectra measured prior to irradiation.

FT/IR spectra of each sample prior to irradiation and the gel after irradiation for 300 hours are shown in Fig. 10. The IR absorption band assigned to stretching vibration of hydroxyl group and that band assigned to stretching vibration of carbon-carbon double bond arose in the IR spectrum of the gel.

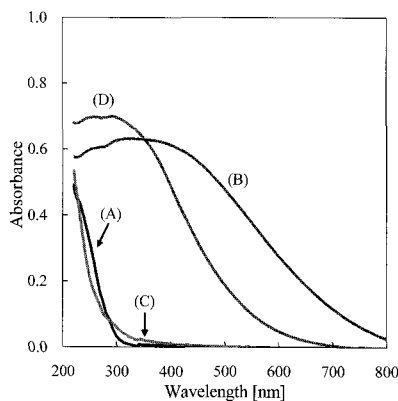


Fig. 9 DR UV/vis spectra of samples before irradiation and the portion insoluble in solvents after 300-hour irradiation.
(A) — : H-CHB before irradiation (B) - - - : H-CHB after 300-hour irradiation
(C) - - - : H-PS before irradiation (D) - - - - : H-PS after 300-hour irradiation

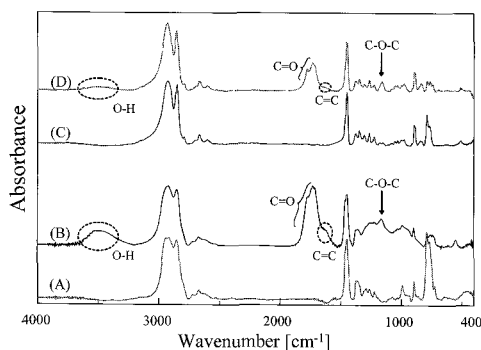


Fig. 10 FT/IR spectra of samples before irradiation and the portion insoluble in solvents after 300-hour irradiation.
(A) H-CHB before irradiation (B) H-CHB after 300-hour irradiation
(C) H-PS before irradiation (D) H-PS after 300-hour irradiation

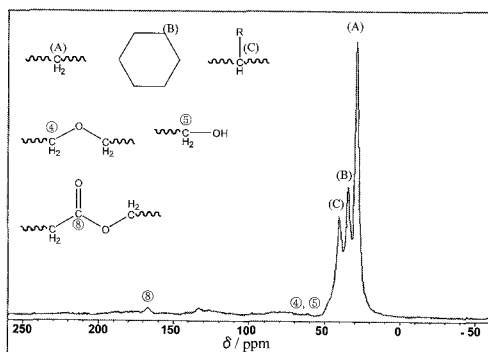


Fig. 11 ^{13}C CPMAS NMR spectrum of the portion insoluble in solvents of H-PS after 300-hour irradiation.

The peaks of alcohol, ether and ester appeared in the ^{13}C CPMAS spectrum of the gel of H-PS as shown in Fig. 11. It is suggested that the gel consisted of the component having C-C bonds, ether bonds and ester bonds like photo-degraded polyolefin.

In order to analyze the chemical structure of the gel,

the gel was hydrolyzed in methanol solution of potassium hydroxide. However, the gel was hardly hydrolyzed.

4. CONCLUSION

A systematic examination of two types of cyclic olefin polymers: hydrogenated poly(cyclohexadiene-*ran*-butadiene) (H-CHB) and hydrogenated polystyrene (H-PS) shows the auto-oxidation occurs, which are similar to the reaction of the photodegradation of general polyolefin. The reaction of cross-linking and main-chain scission results from the photolysis of the hydroperoxide. The photodegradation products of these cyclic olefin polymers are complicated by the ring-opening reaction of cyclohexane. Photodegradation products of these cyclic olefin polymers are constituted with the components having hydroxyl, ester, ether, ketone, carbon-carbon double bond and aldehyde groups. The main product of these cyclic olefin polymers is the gel.

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