PROMOTION OF PHOTODEGRADATION OF POLYMERS FOR PLASTIC WASTE TREATMENT

EIJI IKADA and MICHIO ASHIDA
Faculty of Engineering, Kobe University, Nada
Kobe 657 JAPAN

Mainchain photo-scission in a polymer chain often occurs via oxidation. The rate-determining step of the chain scission is abstraction of a hydrogen atom accompanied by hydroperoxide formation. Solvent and temperature effects in the photochemical chain scission were studied to promote the photodegradation for prevention of plastic waste pollution. Rate of the mainchain scission was dependent on the species of the organo-halogen solvents of the polymer solution for irradiation, but did not increase linearly with rising temperatures.

1. Introduction

Marked increase of the plastic (polymeric) waste in our environments is one of the most serious problems in the present world. Further, plastic waste is very stable as compared with iron waste. Therefore, plastic garbages are easily found everywhere, on the sea surface and on the streets.

Now consumers make protests against too much quantity of plastic packing materials. From these circumstances, polymer chemists and engineers now have to design some preventive methods of these plastic environmental pollution. Biodegradation and photodegradation are at present two methods available for such design. In the limited cases, bio- and photo-degradable polymers are...
possible to decrease environmental plastic pollution because micro-organisms and light energy can give rise to reaction leading to decompose these polymers into some other materials.

Union Carbide Co., for example, produces ethylene-carbon monoxide copolymers, which is degraded by light\(^2\). This photodegradable copolymer is highly expected because of its degradability. Unfortunately, it is difficult in the universities to prepare this copolymer. Yabumoto collected synthetic methods of such copolymers, vinyl acetate, vinyl chloride, ethyleneimine with carbon monoxide\(^3\).

The ethylene-carbon monoxide copolymer seems to be only one commercial photo-degradable polymer in the present Japanese market. Therefore, this material is considered to be used in future plastic package.

On the other hand, Professor Scott in University of Aston in Birmingham has studied photo-degradation of polymers through introduction of photosensitizers for a long time. The methods of degradation via addition of transition metal compounds such as metal acetyl acetonates are also successful in preparing the polymers having a time-controlled life\(^4,5\).

Anyhow, the Norrish-type mainchain scission in the photolysis of polymers is a very powerful and practical tool for a molecular architecture for photodegradable polymers at the present stage.

We studied accelerating methods of photodegradation from the above point of view. Several factors controlling the photodegradation are discussed. Solvent and temperature effects on mainchain scission with UV irradiation are studied.

2. Method

UV irradiation was done to a polymer solution. Fig. 1 shows the irradiation system.

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Determination of change of molecular weight after irradiation was measured with a conventional viscometer. Change of the molecular structure after irradiation was observed by IR and UV spectrometers. This change was also ascertained by elemental analysis.

UV irradiation was also done onto the polymer films directly.

3. Results

Effects of the solvents on photodegradation of polystyrene

UV irradiation was done to benzene, chloroform, and carbon tetrachloride solutions of polystyrene. Rate of decrease of the molecular weight of the different polystyrene solution was measured. Fig. 2 shows the solvent effects of the rate.

Fig. 2. The relationship between variation of the limiting viscosity number and the number of main-chain scission of degraded polystyrene in the three kinds of the solvents and irradiation time. O, benzene; o, chloroform; O, carbon tetrachloride.

The upper figure shows the decrease of molecular weight.

The lower figure shows variation of number of scission with irradiation time.

\[ S = \frac{M_0}{M_t} - 1 \]

: Number of scission

\[ M_0 \] : original molecular weight

\[ M_t \] : molecular weight at irradiation time t
As is seen in Fig. 2, it is clear that the solvent media affect chain scission of polystyrene. The rate-determining step of UV degradation of polystyrene is considered to be abstraction of hydrogen on the carbon atom to which the phenyl group is attached. Carbon tetrachloride contributes to this hydrogen abstraction most effectively, but in benzene solution the mainchain scission occurs scarcely even at 24 hours irradiation. Photo-stable benzene may be ineffective in this hydrogen abstraction. Another possible reason is "filter effect" of benzene solvent because this solvent absorbs UV light.

Fig. 3 shows another method of promotion of photodegradation. The photosensitizers parabenzoquinone and chloranil were added to this inactive benzene solution system. It was found that chloranil was effective for activation of mainchain scission of polystyrene as seen in this figure. Parabenzoquinone, however, was ineffective in chain scission of polystyrene.

The halogen-atom-containing solvents and chloranil can be used as photoactivator in plastic degradation.

Change of the molecular structure was observed by fluorescence spectroscopy. The fluorescence peak due to the excimer formation in a polystyrene...
chain decreased with increasing irradiation time as is shown in Fig. 4.
Irregular molecular structure of the degraded polystyrene resulted from substitution of hydrogen atoms by chlorine atoms leads to the decrease of the excimer formation. Introduction of chlorine atoms into the irradiated polystyrene chain in the halogen solvents was also observed by elemental analysis.

As conventional polymers such as polystyrene and polyethylene are essentially photo-stable, it is necessary for promotion of photodegradation of these polymers to design activators.

UV irradiation at high temperatures

Pyrolysis is also an important method for polymer decomposition. Therefore, the UV irradiation was achieved at elevated temperature to activate the photolysis of polystyrene.

The purpose of this experiment is to utilize photo- and thermal-effects simultaneously.

Fig. 4. Fluorescence spectra of polystyrene UV-irradiated in 1,2-dichloroethane. The concentration for the spectrum measurement is the same as in Fig. 2.

Fig. 5. Temperature dependence of the number of mainchain scission of degraded polystyrene in the five kinds of solvents, benzene; cyclohexane; ethylbenzene; ethylcyclohexane; decalin. The irradiation time was 8 h.
Temperature effects on mainchain scission of polystyrene are shown in Fig. 5. Ethylcyclohexane and cyclohexane enhance mainchain scission, but benzene and ethylbenzene depress the photolysis of polystyrene as seen in this figure. Number of scission shows maximum temperatures for ethylcyclohexane and decalin solutions. The mainchain scission in this experiment occurs via photo-oxidation, therefore, oxygen concentration in each solution controls number of scission. It is, however, difficult to identify significant roles in these complicated photodegradations.

Mainchain scission of polylactic acid

Polylactic acid is a well-known bio-degradable polymer. It seems that a bio-degradable polymer is also a photo-degradable polymer. From this point of view, photo-degradability of this polymer was studied.

Fig. 6 shows change of molecular weight of polylactic acid against irradiation time. In this case, polylactic acid films were irradiated in air and nitrogen atmosphere. As compared with the rates of polystyrene, polylactic acid decomposes very rapidly as seen in Fig. 6. Gel formation was not observed. Gel formation is generally observed for UV irradiation of polymer films.

Fig. 6. Relationship between irradiation time and number-average molecular weight of PLA in air (○) and in nitrogen (●).
Fig. 7 shows increase of -COOH group with increasing irradiation time. The quantity of -COOH group was determined by the infrared absorption at 3290 cm\(^{-1}\). -COOH end groups increase linearly with irradiation times. It is concluded from this fact that the Norrish II type photoreaction occurs by UV irradiation.

![Graph showing increase of -COOH group with irradiation time]

4. Conclusion

Photolysis of the waste polymers is believed to become one of available methods for treatment of polymeric garbages. It is, therefore, necessary to establish various processes of preparing photodegradable polymers having the controllable life.

All the materials utilized in our life must be mechanically, electrically stable during our use, but it turns afterwards to be degradable for prevention of environmental pollution. These materials are now expected.
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References