Mechanism of Degradation and Crosslinking of Polyurethane When Irradiated by Gamma-Rays

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SYNOPSIS

We conducted a study to clarify the mechanism of crosslinking and degradation of thermoplastic polyurethane (PU) when irradiated with gamma-rays. Changes in molecular weights as a result of gamma-ray irradiation, the UV absorption, the amount of PUs with amino groups, and the elution of oligomers to an organic solvent were determined to estimate characteristic changes in PU caused by irradiation. The amount of PUs with primary amino groups as a degradated PU products at *p,p'*-methylenediphenyl diisocyanate–1,4-butanediol (MDI–BU) hard segments increased linearly with increasing irradiation level. The amount of this products by gamma-ray irradiation was approximately 10–20% of the calculated amount, indicating that predominant degradation occurred at polytetramethyleneglycol (PTMG) soft segments (about 80–90% of the degradation). Characteristic differences were seen in crosslinking between non-chain-extended thermoplastic PUs based on the molecular weights of PTMG (M_w of PTMG = 640–2800). The crosslinking ratio is linearly proportional to the molecular weights of PTMG, indicating that crosslinking at PTMG soft segments was major (the ratio of crosslinking at PTMG was more than 90%). Methanol extract of PU indicated elution of PU oligomers ranging from 13 to 1 as a polymerization degree.

INTRODUCTION

Polyurethane (PU) is synthesized by the reaction of methylene bis(*p*-phenylisocyanate) (MDI) and polytetramethyleneglycol (PTMG). 1,4-Butanediol (BU) is used as the chain-extending agent of PU. *n*-Butanol is added to terminate a polymerization process.

PU is widely used in health care applications, specifically in a large variety of medical devices because of its compatibility with blood.[1]

Gamma-ray irradiation, pressurized steam (autoclave), and chemical agents are used in sterilization practices. There have been reports of hazardous effects of sterilization on plastic materials.[2] With gamma-ray irradiation and autoclave sterilization, high molecular weight materials may decompose, yielding toxic low molecular weight compounds such as 4,4'-methylenedianiline (MDA, *p,p'*-diaminodiphenylmethane), a carcinogen.[3] With the use of ethylene oxide (EO) for chemical sterilization, significant amounts of it may remain in PU.[4] EO has been reported to be mutagenic, carcinogenic, and antigenic.[5]

The mechanism of characteristic changes in gamma-ray-irradiated PU, including degradation and crosslinking, has not previously been studied qualitatively or quantitatively using gel permeation chromatography (GPC) and GPC detected by an electrochemical detector (ECD).

In order to clarify the mechanism of crosslinking, we synthesized PUs fabricated from PTMGs of various molecular weights. The change in the amount of PUs with secondary amino groups, the UV absorption, GPC elution, and other parameters with irradiation levels were studied.

In order to clarify the mechanism of degradation, the change in the amount of PUs with primary amino groups, GPC elution pattern detected by

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ECD, the UV absorption, and other parameters with irradiation levels were determined.

Elution of PU oligomers from organic solvent extracts of irradiated and nonirradiated PUs was confirmed and their constituent was studied.

MATERIALS AND METHODS

Materials

Thermoplastic PU samples were synthesized by the reaction of PTMG (M_w of PTMG = 640–2800) with MDI in *N,N*-dimethylformamide (DMF). Polymerization was terminated by adding *n*-butanol after various reaction times: Non-chain-extended thermoplastic PU samples thus obtained had weight average molecular weights (M_w) of 233,000 (PU-1), 192,000 (PU-2), 175,000 (PU-3), 300,000 (PU-12), 184,000 (PU-9, M_w of PTMG = 640), 232,000 (PU-11, M_w of PTMG = 2800), and 214,000 (PU-10, M_w of PTMG = 2000). The M_w of PTMG of PU-1–3 and -12 was 1000.

To provide chain-extended thermoplastic PUs, 1,4-butanediol (BU) was added to the reaction mixture before the addition of *n*-butanol. Thus, the chain-extended thermoplastic PU samples with M_w of 255,000 (PU-4), 198,000 (PU-5), and 152,000 (PU-6) were obtained. The M_w of PTMG of PU-4–6 was 1000. The structures of chain-extended PU samples were similar to that of Pellethane, currently available on the market.[1] The structures of PU samples are shown in Figure 1.

These PU samples were dissolved in DMF to prepare a 30% solutions. Fifteen-gram samples of each solution were placed into glass Petri dishes 9 cm in inner diameter to form a uniform layer. A PU film with a thickness of about 1 mm was obtained in the Petri dish after complete removal of DMF by evaporation at room temperature over 2 weeks following vacuum evaporation for 2 days. The covered dishes were subjected to gamma-ray irradiation.

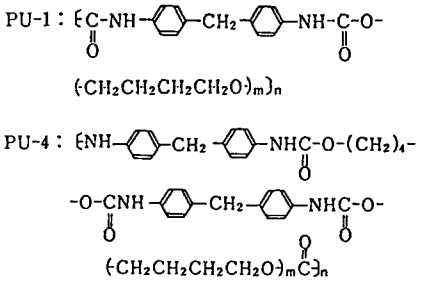

Figure 1 Structure of non-chain-extended polyurethane (PU) in the upper section and that of chain-extended PU in the lower section.

Instrumentation

GPC analysis was performed on a Toso Co. Ltd. Gel Permeation Chromatograph HLC-8020 equipped with a refractive index (RI) detector. Other detectors used were a Shimadzu Co. Ltd. UV spectrophotometer SPD-2A and a Toa Electronics Co. Ltd. electrochemical detector (ECD) ICA-3000. The ECD is specific for detecting the compounds with aromatic amino groups, OH or SH groups. A Yokogawa-dennki Co. Ltd. Type 3066 recorder and a SIC Co. Ltd. Chromatocorder 12, a data acquisition system, were used. A Toa Electronics Co. Ltd. AUT-301, an autotitrator for the nonaqueous titration method, was used to determine PUs with primary and secondary amino groups dissolved in an organic solvent. A Shimadzu Co. Ltd. UV-160A spectrophotometer was used to determine UV absorption.

Sterilization

PU samples were subjected to ^{60}Co gamma-ray irradiation at a rate of 2.5 Mrad/25 h from 0 to 10 Mrad at intervals of 2.5 Mrad.

Conditions of GPC analysis

A Toso-GPC column (7.8 × 300 mm) packed with a TSK gel GMH (molecular weight exclusion limit 400,000,000) was coupled with a TSK guard column HM (7.5 × 75 mm). Two-hundred-microliter sample volumes were applied. Elution was accomplished with DMF containing 10 mM LiBr or with tetrahydrofuran (THF) containing 0.03% butylhydroxy toluene at a flow rate of 1.0 mL/min. DMF eluent was used for ECD detection. LiBr addition to DMF is favorable for ECD detection, which was carried out by applying 1000 mV and other conditions were the same as in the previous report.[3] The column and injection temperature was kept at 40°C. The eluate was monitored at 290 nm by UV, RI, and ECD. PU samples for GPC analysis were dissolved in the GPC eluent at a concentrations of 0.05–0.1%. Weight average molecular weight, M_w, was computed by a resident program in the SIC chromatocorder 12. Polystyrene SM-105 supplied from a Showa Denkou Co. Ltd. was used as a standard and reference compound for GPC analysis. Polystylene 706 and 705 from National Bureau of Standard USA were used to evaluate the accuracy of the standard GPC analysis curve.

Determination of PUs with Primary and Secondary Amino Groups by the Nonaqueous Titration Method

For the determination of PUs with primary amino groups, 2 g PU samples were dissolved in 50 mL of DMF containing 0.1% LiCl. Then 2 mL of acetic acid was added and the solution was titrated with 0.01 N $HClO_4$ in dioxane, noting microburette recording potential values after each portion of the titrant. The blank sample was simultaneously titrated.

For the determination of PUs with secondary amino groups, the procedure was somewhat different from above as secondary amino groups in urethane bonds in MDI–BU hard segments are acidic. The procedure was as follows. Two grams of PU were dissolved in 50 mL of DMF containing 0.1% LiCl. The titrant was 0.01 N NaOH in DMF containing 0.1% LiCl. NaOH (0.4 g) was dissolved with a trace of water, after which DMF containing 0.1% LiCl was added to 1 L. The rest of the titration procedure was the same as that used in the determination of PUs with primary amino groups.

RESULTS AND DISCUSSION

Molecular Weight Changes before and after Gamma-Ray Irradiation

Irradiated and nonirradiated PU samples were dissolved in GPC eluent. The solution was subjected to GPC analysis.

The G values (the number of molecules increased or decreased when absorbed at 100 eV) were calculated with equations representing the relationship between irradiation level and $1/M_w$ (Fig. 2)[6–10]. In calculating the G values, the unit molecular weight of the PUs (w = the monomer molecular weight) was 1250. The greater the G values, the greater the degree of degradation or crosslinking.

In samples PU-4–PU-6 of chain-extended PUs, the M_w typically decreased with increasing irradiation level as a result of degradation (Table I). In samples PU-1–PU-3 of non-chain-extended PUs, in contrast, the M_w increased with increasing irradiation level presumably because of increased crosslinking (Table I). The G values for PU-1–PU-3 and those for PU-4–PU-6 were 0.2 (crosslinking) and 1.1 (degradation), respectively (Fig. 2). These values clearly agree with those reported in the literature.[6]

GPC chromatograms of samples exposed to different irradiation levels are superimposed in Figure 3. Chromatograms detected by UV (290 nm) and RI are shown in the upper and lower sections, respectively, indicating that both detections gave identical chromatograms. The peak area of chromatograms was almost identical at every level of irradiation.

The left section in Figure 3 shows the superimposed GPC chromatograms of PU-1–PU-3 of non-chain-extended PUs. The commencement of GPC elution decreased while, at the same time, completion time for GPC elution increased with increasing irradiation levels. This indicated that both an in-

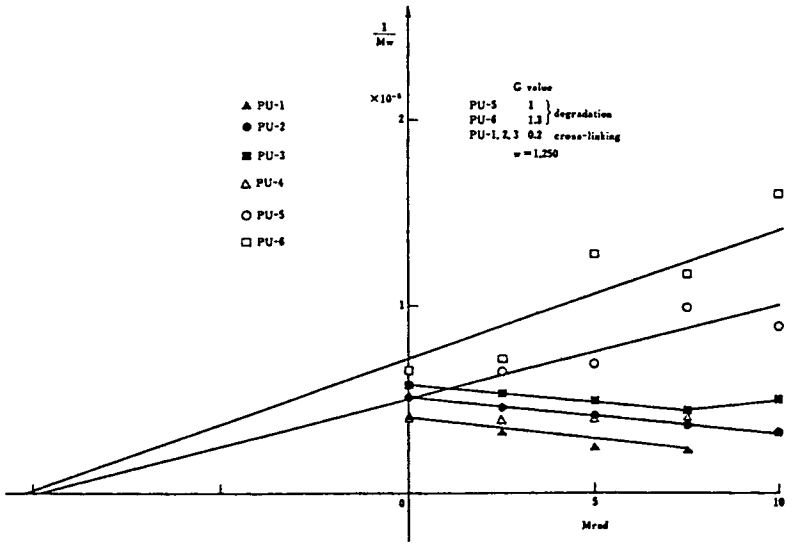

Figure 2 Relationship between irradiation level (Mrad) and $1/M_w$.

Table I Change in Weight Average Molecular Weight (M_w) by Gamma-Ray Irradiation[a]

	Non-Chain-Extended PUs			Chain-Extended PUs	
Sample	(Mrad)	M_w	Sample	(Mrad)	M_w
PU1	0	233,447	PU4	0	254,868
	2.5	299,981		2.5	254,348
	5.0	391,755		5.0	254,553
	7.5	423,762		7.5	253,198
	10.0	Undissolved		10.0	318,970
PU2	0	191,510	PU5	0	197,545
	2.5	215,012		2.5	150,780
	5.0	239,525		5.0	144,073
	7.5	269,538		7.5	101,143
	10.0	340,021		10.0	109,313
PU3	0	174,586	PU6	0	152,031
	2.5	185,646		2.5	138,655
	5.0	200,147		5.0	76,258
	7.5	222,860		7.5	84,248
	10.0	203,454		10.0	61,025

[a] M_w of PTMG = 1000.

crease and a decrease in molecular weight occurred simultaneously. Furthermore, the distribution of molecular weights increased with increasing irradiation levels and the retention time of the peak maximum increased, indicating the peak top molecular weight, MGPC, decreased with increasing irradiation levels. These results indicated that in non-chain-extended PUs, irradiation led to crosslinking and to some extent to degradation simultaneously. The total irradiation effect on non-chain-extended PUs was crosslinking due to an increase in the M_w with increasing irradiation levels (Table I).

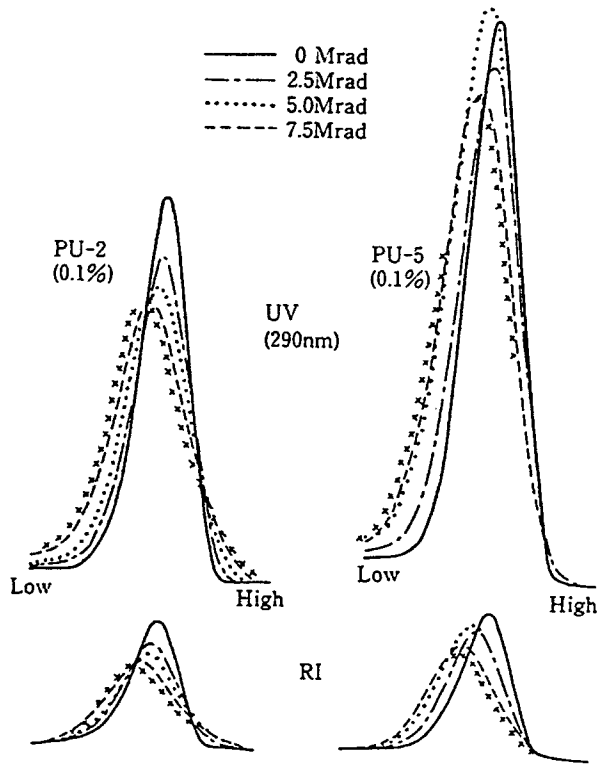

Figure 3 Superimposed GPC chromatograms of PU-2 (non-chain-extended PU) and PU-5 (chain-extended PU) detected by UV (290 nm) and RI.

In contrast, for PU-4–PU-6 of chain-extended PUs, as shown on the right section in Figure 3, the commencement of GPC elution was almost identical at every level of irradiation. At the same time, completion time for GPC elution increased with increasing irradiation level, indicating that irradiation caused only a decrease in molecular weight. The distribution of molecular weights increased with increasing irradiation level. The retention time of the peak maximum increased, indicating the MGPC decreased with increasing irradiation levels. These results indicated that, in chain-extended PUs, irradiation led solely to degradation.

It is interesting to note that PU samples synthesized with and without BU chain-extending respond to irradiation in such contrasting ways.

Chain-extended PUs were more rigid than non-chain-extended PUs. The former was resistant to autoclaving; therefore, no MDA was formed by autoclaving.[11] MDA was formed, however, from the latter treated by autoclaving.[11]

Mechanism of Degradation

We have clarified the mechanism of degradation of chain-extended PUs by gamma-ray irradiation. The

superimposed UV spectra in irradiated and nonirradiated chain-extended PUs are presented in Figure 4. PUs dissolved in THF were used in the UV absorption experiments. The UV absorption spectra were identical in irradiated and non-irradiated PUs. However, UV absorbance at 248 nm, UV maximum wavelength, decreased with increasing irradiation levels. If degradation occurred only at polytetramethyleneglycol (PTMG) soft segments, UV absorbance at 248 nm would be unchanged. Therefore, we speculated that the decrease in UV absorbance would be due to degradation at the urethane bonds in MDI–BU hard segments.

The molar absorptivity of 4,4′-methylenedianiline (MDA) and that of the two successive urethane derivative of MDA at 248 nm was 20,000 and 45,200, respectively, as shown in Figure 5. The concentration of each substance in middle and lowest UV spectra in Figure 5 was not identical.

If cleavage occurred at MDI–BU hard segments, PU with terminal amino groups would be produced. The UV absorbance in the compound cleaved at one urethane bond and at two successive urethane bonds

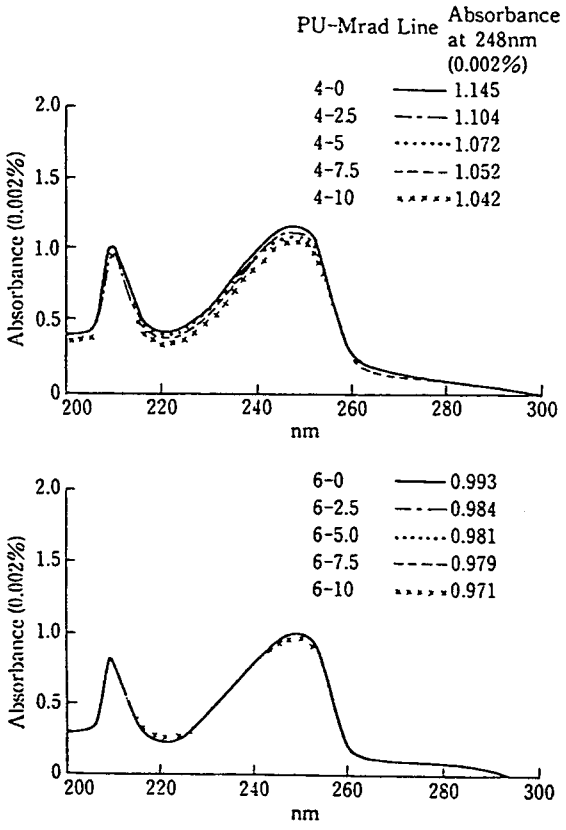

Figure 4 Superimposed UV spectra and UV absorbance at 248 nm in irradiated and nonirradiated chain-extended PUs (PU-4 and -6).

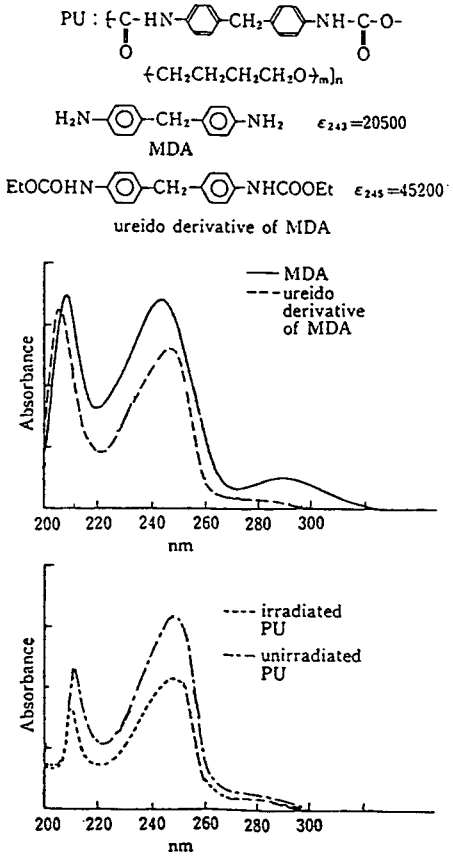

Figure 5 Molar absorptivity and UV spectra in MDA and that in urethane derivative of MDA in the upper section and UV spectra in irradiated and nonirradiated chain-extended PUs in the lower section.

(MDA) was almost 73 and 45% of that in the original absorbance of nonirradiated compound, respectively (Fig. 5).

If cleavage and degradation occurred at MDI–BU hard segments, the following reaction would occur (Fig. 6). If two successive MDI–BU hard segments were cleaved at urethane bonds, MDA would be formed. Experimental results in fact indicated no MDA formation from degradated chain-extended PUs by irradiation.[11] If MDA was produced by degradation, UV spectra of degradated PU would be different from that of nondegradated PU, corresponding to the difference in UV absorption spectra in MDA and that in the urethane derivative of MDA (middle section in Fig. 5). They were different, for example, the maximum wavelength and the absorption spectrum from 270 to 320 nm. In fact, the UV absorption spectra in degraded and nondegraded PUs were almost identical, as shown in Figure 4 and lowest section in Figure 5, indicating no MDA formation.

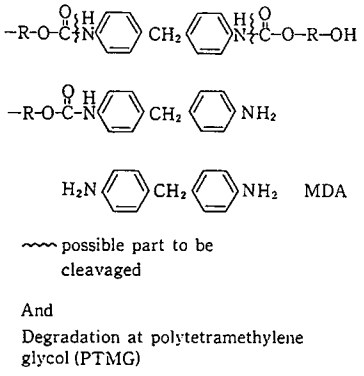

Figure 6 Proposed mechanism of degradation occurring at MDI–BU hard segments of chain-extended PUs.

If one urethane bond was cleaved, PUs with primary amino groups such as those seen in the middle section in Figure 6 would be produced. The molar absorptivity in PUs with one primary amino groups was approximately 27% less than that in the original PUs (Fig. 5). The UV spectra of PUs with one primary amino groups and that of the original PUs was almost identical. We have studied whether the amount of PUs with primary amino groups may increase with increasing gamma-ray irradiation levels.

The amount of PU with one primary amino groups increased linearly with increasing irradiation levels (Fig. 7). The GPC results detected by electrochemical detector (ECD) showed that the elution of PU oligomers with amino groups increased exponentially with increasing irradiation levels. The amount of PU with primary amino groups at 10 Mrad irradiation of PU-5 and -6 was approximately 0.23 and 0.14 g eq/sample mol. This amount was quite similar to that estimated from the UV absorbance change due to the following reason: In one urethane bond cleavage, 27.5% of the absorbance would be diminished (Fig. 5). In PU-5 and -6, 8 and 3% of UV absorbance decreased at 10 Mrad irradiation (Fig. 4), corresponding to the production of 0.29 and 0.11 g eq/mol PU with primary amino group.

If degradation was restricted only to MDI–BU hard segments, the degree of degradation of PU-5 would be greater than that of PU-6 from the result of Figure 7. However, the result was quite the contrary. M_w's of PU-5 and -6 at 10 Mrad irradiation were $\frac{1}{2}$ and $\frac{1}{3}$ of the original M_w, respectively (Fig. 7), and the G values of PU-5 and -6 were 1 and 1.3, respectively (Fig. 2), indicating that the total degree of degradation of PU-6 was greater than that of PU-5.

If degradation was restricted to only MDI–BU hard segments to reduce the M_w to half of the original M_w, the calculated amount of PU with primary amino groups to be formed was 5 μeq/sample g for PU-5 and 6.7 μeq/sample g for PU-6. In fact, experimental results indicated that the amount of PU with primary amino groups formed by reducing the M_w to half of the original M_w was 1.02 μeq/sample g for PU-5 and 0.63 μeq/sample g for PU-6 (Fig. 7), indicating that the degree of degradation occurring at MDI–BU hard segments was approximately 20 and 10% of the total degradation for PU-5 and PU-6, respectively (Fig. 7). The remainder of degradation occurred at PTMG soft segments (80–90% of the total degradation).

Mechanism of Crosslinking

In order to clarify the mechanism of crosslinking by gamma-ray irradiation in non-chain-extended PUs, we prepared several PU-1–3 analogues from various molecular weights of polytetramethyleneglycol (PTMG), as shown in Table II.

Molecular weight change dependent on the irradiation levels, crosslinking ratio, and UV absorbance are shown in Table III. The UV absorbance at 248 nm was measured from nonirradiated PU

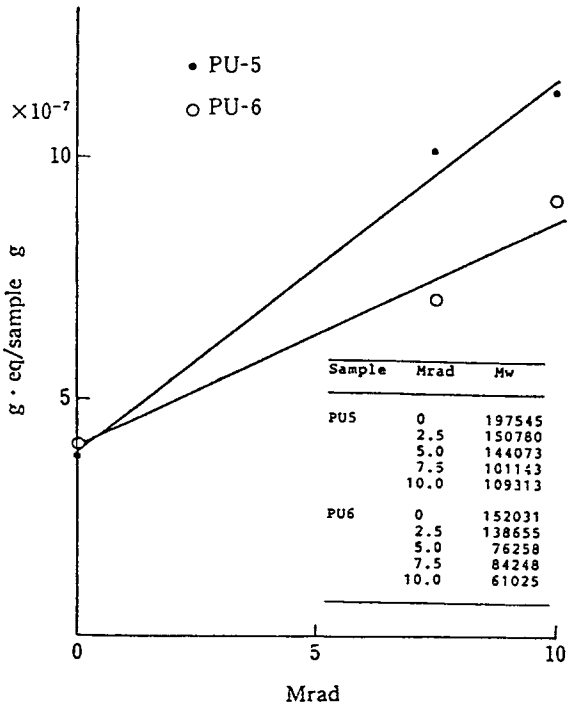

Figure 7 Relationship between irradiation level and amount of PUs with primary amino groups.

Table II M_w of Non-Chain-Extended PUs from Various M_w of PTMG

	M_w of PTMG	M_w of PU
PU-1	1000	206,000
PU-9	641	184,000
PU-12	1011	302,000
PU-11	2805	232,000
PU-10	1986	214,000

samples dissolved in THF at the concentration of 0.54 μM (Table III). The UV absorbance at 248 nm was proportional to the concentration of MDI–BU hard segments in PU. The PTMG soft segments showed no UV absorbance at 248 nm. The M_w increased with increasing irradiation levels. PU-10–12, irradiated at more than 5 Mrad, were not dissolved completely in DMF or THF, indicating that the degree in an increase in crosslinking in PU-10–12 was much greater than that in PU-1 and PU-9; 10.5 Mrad irradiated PU-1 and PU-9 were also undissolved in DMF and THF (Table III).

The G values of crosslinking in PU-9, −1, and −12 were 0.28, 0.36, and 0.64, respectively, which was the same order in an increase as in crosslinking. The greater the G value, the greater the ratio of crosslinking.

Irradiation caused both crosslinking and degradation simultaneously in non-chain-extended PUs (left section in Fig. 3). GPC results indicated that for up to 2.5 Mrad of irradiation, the irradiation effect was restricted mainly to crosslinking (left section in Fig. 3). Therefore, we studied the relationship between the M_w of PTMG and the ratio of M_w at 2.5 Mrad irradiated and nonirradiated levels in the upper section in Figure 8 and the relationship between the UV absorbance at 248 nm and the ratio of M_w at 2.5 Mrad irradiated and nonirradiated levels in the lower section in Figure 8.

The degree of crosslinking and the ratio of M_w at 2.5 Mrad irradiated and nonirradiated levels was directly proportional to the M_w of PTMG, except in the case of PU-12, and was in inverse proportion to the concentration of MDI–BU hard segments, indicating that crosslinking at PTMG soft segments

Table III Changes in M_w with Irradiation, UV Absorbance in Nonirradiated PU and Crosslinking Ratio

PU-Mrad	M_w	Abs at 248 nm in Nonirradiated PU (0.54 μM)	Ratio of M_w at 2.5 Mrad/ M_w at 0 Mrad
9-0	184,232	4.05	1.03
9-2.5	189,930		
9-5.0	250,908		
9-8.0	315,806		
9-10.5	Undissolved		
1-0	206,626	3.59	1.18
1-2.5	244,178		
1-5.0	326,506		
1-8.0	431,902		
1-10.5	Undissolved		
12-0	301,870	4.92	2.01
12-2.5	605,276		
12-5.0	Undissolved		
12-8.0	Undissolved		
12-10.5	Undissolved		
11-0	232,110	1.89	2.12
11-2.5	491,516		
11-5.0	Undissolved		
11-8.0	Undissolved		
11-10.5	Undissolved		
10-0	214,234	2.20	1.80
10-2.5	385,621		
10-5.0	Undissolved		
10-8.0	Undissolved		
10-10.5	Undissolved		

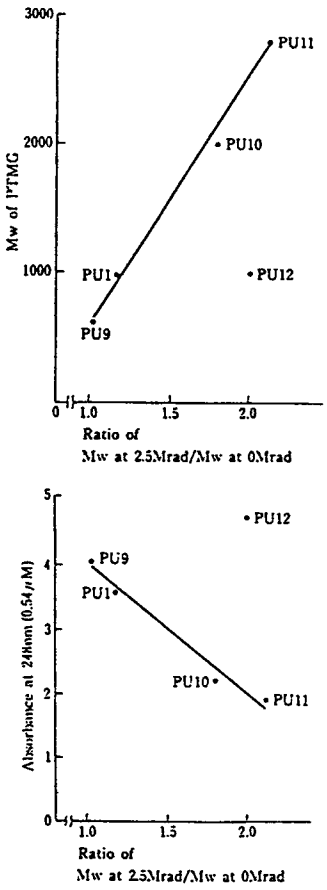

Figure 8 Relationship between the Mw of PTMG and the ratio of M_w at 2.5 Mrad irradiated and nonirradiated levels in the upper section and the relationship between the absorbance at 248 nm and the ratio of M_w at 2.5 Mrad irradiated and nonirradiated levels in the lower section.

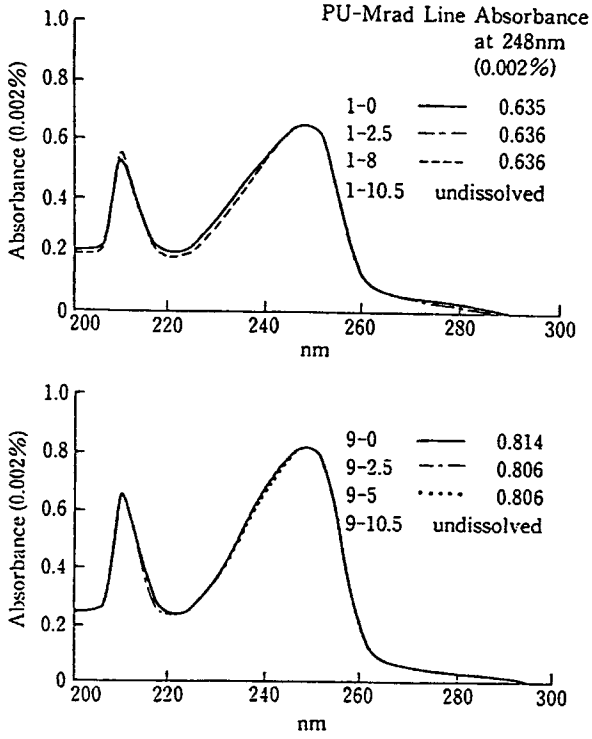

Figure 9 Superimposed UV spectra and UV absorbance at 248 nm in irradiated and nonirradiated non-chain-extended PUs (PU-1 and -9).

was major and at MDI–BU hard segments was minor. The M_w's of PU-1 and PU-9–11 were approximately 200,000 and that of PU-12 was about 300,000 (Table II). Exceptional behavior of PU-12 may be due to this M_w difference and possible crosslinking at MDI–BU hard segments.

In Figure 9, superimposed UV spectra in irradiated and nonirradiated non-chain-extended PU-1 and -9 dissolved in THF are presented. Predominant crosslinking at PTMG soft segments indicated no change in UV absorbance at 248 nm. Therefore, the change in UV absorbance at 248 nm and that in the absorption spectra was almost negligible as shown in Figure 9.

If crosslinking occurred at MDI–BU hard segments as a minor reaction, secondary amino groups in the urethane bonds would be crosslinked to produce tertiary amino groups, thus reducing secondary amino groups in PUs (Fig. 10). The production of tertiary amino groups may cause a decrease in UV absorbance at 248 nm. We studied whether the amount of PUs with secondary amino groups may decrease with increasing irradiation levels.

The amount of secondary amino groups in urethane bonds decreased with increasing irradiation levels. The decreased amount of PUs with secondary amino groups at 8 Mrad irradiation was 0.31 μeq/sample g for PU-9 and 0.27 μeq/sample g for PU-1. These amounts were approximately 6% that of

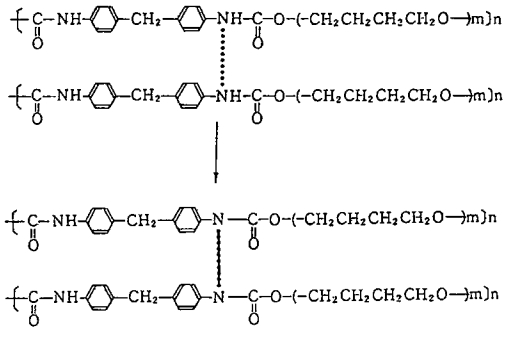

Figure 10 Proposed mechanism of crosslinking occurring at MDI–BU hard segments of non-chain-extended PUs.

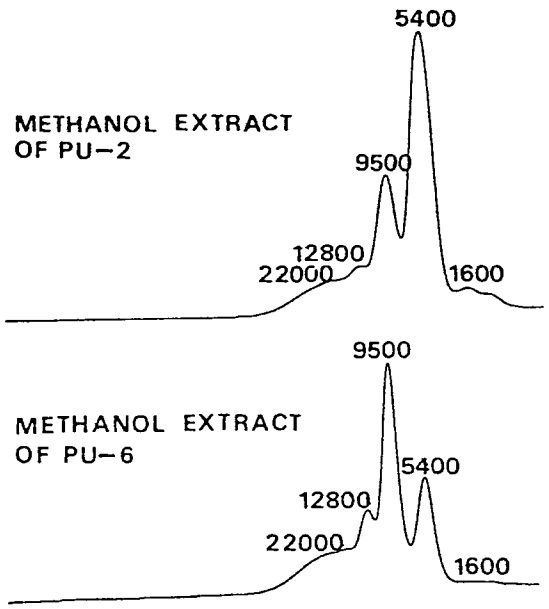

Figure 11 GPC chromatograms of methanol extract of non-chain-extended PU (PU-2) and that of chain-extended PU (PU-6).

the calculated amounts, indicating that the crosslinking ratio at the urethane bonds in MDI–BU hard segments was approximately 6% for PU-9 and PU-1 and the remainder (94% of the total crosslinking) was crosslinked at PTMG soft segments.

In PU-1–3 analogues of non-chain-extended PUs, irradiation caused both degradation and crosslinking simultaneously (left section in Fig. 3). There was no significant difference of the amount of PUs with primary amino groups between irradiated and non-irradiated PU-1 and PU-9, indicating no significant degradation at urethane bond in MDI–BU hard segment in PU-1 and PU-9 of non-chain-extended PUs. Predominant degradation and crosslinking occurred at PTMG soft segments, which showed no change in UV absorbance at 248 nm.

Methanol Extracts of Irradiated and Nonirradiated Thermoplastic PUs

Methanol extracts of non-chain-extended and chain-extended PU samples were analyzed by GPC detected by UV at 290 nm (Fig. 11). Five peaks appeared at molecular weights of 22,000, 12,800, 9500, 5400, and 1600 as MGPC, corresponding to polyurethane oligomers containing, per molecule, 13, eight, six, and three urethane oligomers and a monomer, respectively. The constituent of these PU oligomers was PTMG combined with MDI. The quantity of MDI was the greatest in the 9500 peak as MGPC.

The oligomer of MGPC 5400 was prominent in methanol extracts in non-chain-extended PUs (upper section in Fig. 11). In contrast, methanol extracts in chain-extended PUs yielded the highest peak at MGPC, 9500 (lower section in Fig. 11).

Additionally, we detected the elution of PTMG, 1,4-butanediol (BU) and *n*-butanol in this elution order in GPC chromatogram from methanol extracts of chain-extended and non-chain-extended PUs detected by RI.

The elution of higher oligomers from methanol extracts in chain-extended and nonchain-extended PUs, i.e., those in MGPC 22,000 increased with increasing irradiation level.

CONCLUSION

Crosslinking and degradation occurred mainly at PTMG soft segments by gamma-ray irradiation.

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