Mechanical Properties of UV-Cured Urethane Films

S. NAKAZATO,* T. AMARI, and T. YAMAOKA, *Department of Image Science and Technology, Faculty of Engineering, Chiba University, Chiba, Japan 260*

Synopsis

A series of novel photosensitive urethane oligomers was synthesized in which methacryloyl group was contained in the hard segment. The hard segment was prepared by reacting 4,4'-diphenylmethane diisocyanate with glycerine mono methacrylate, which was successively reacted with three kinds of glycols involving 1,4-poly(butadiene glycol), poly(propylene glycol), and poly(caprolactone diol). The mechanical properties of synthesized urethane oligomers after irradiating with ultraviolet light were evaluated to elucidate the effect of the molecular structure and the content of the hard segment on the mechanical property.

INTRODUCTION

A polyurethane is composed of crystal domains due to hydrogen bonding of the hard segment and amorphous domains due to the soft segment. The good mechanical properties of the polyurethane in both strength and flexibility are considered to be due to the microphase separation of the hard and the soft segment.

Photosensitive urethane oligomers are presently in use throughout the coating engineering and most of them are urethane acrylates which have (meth)acryloyl group on the both ends of urethane molecule.

Relationships between the chemical structure and the mechanical property for photocrosslinked urethane oligomers have been studied[1-7] by varying the molecular weight of the soft segment and the amount of the monomeric compound added as the crosslinker.

Another type of photosensitive urethane oligomers were synthesized by Yamaoka et al.[8] in which the hard segment was composed of the repetition of 4,4'-diphenylmethane diisocyanate (MDI) and allyletherpropanediol (AEP), and 1,4-poly(butadiene glycol) was used as the soft segment. So the photoreactive double bondings were included at the inside of the hard segment. They showed for these photosensitive urethanes that the tensile strength and Young's modulus were increased with increasing the length of the hard segment while the ultimate strain was decreased.

The present study focuses on the effects of the chemical structure and the kinds of soft segments on physical properties in order to get good mechanical

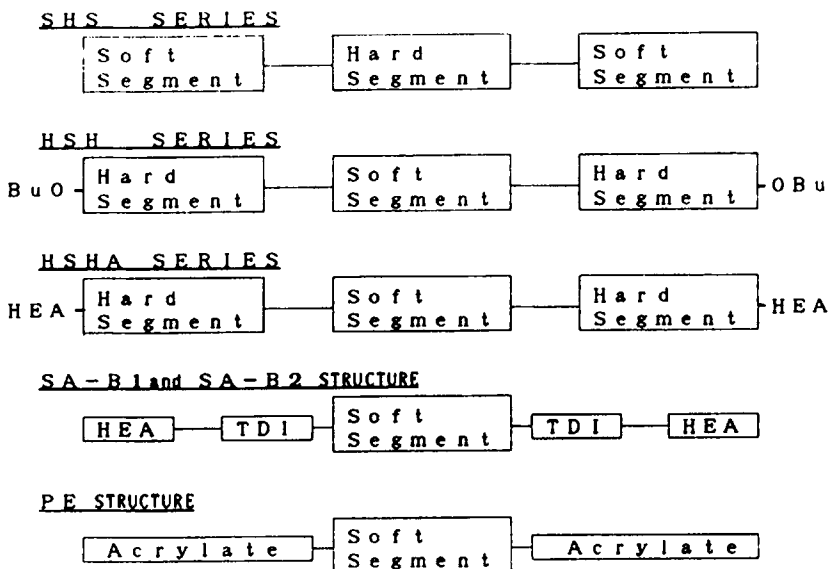*Present address: Oji Kako Co., Ltd., Product Research Laboratory, Utsunomiya Japan 321.

Fig. 1. The chemical structures of each oligomer.

properties, which are a good flexibility and a high strength, of pho-
tocrosslinked urethane oligomer.

A series of novel photosensitive urethane oligomers was synthesized in
which the hard segment was prepared by reacting MDI with glycerine
monomethacrylate (GMM) and the mechanical properties of these urethane
oligomers were evaluated, and then the dependence of molecular conformation
of the hard and the soft segment on the mechanical properties was examined.

EXPERIMENTAL

Structure of the Photosensitive Urethane Oligomers

The photosensitive urethane oligomers were prepared by reacting the hard
segment having methacryloyl group in its pendant chain with the soft seg-
ment. The structure and the abbreviation for the oligomers are shown in
Figure 1.

SHS series has the soft segments on the both ends of the hard segment, and
the photoreactive groups are located in the middle of the molecule. HSH
series has the hard segments on the both ends of the soft segment and the
isocyanate groups on the both ends are capped with butylalcohol, so that the
photoreactive groups are included at the ends of the molecule. HSHA series
has the same structure as HSH series except that the both ends are capped
with 2-hydroxyethylacrylate (2-HEA) instead of butylalcohol. As the soft
segment, 1,4-poly(butadiene glycol), poly(propyrene glycol), and poly(capro-
lactone diol) were used in order to make clear the effect of the kinds of soft
segments.

In order to clarify the effect of the molecular weight and the effect of urethane bondings, other types of oligomers, SA-B1, SA-B2, and PE, were prepared. SA-B1 and SA-B2 have the structure well known for urethane acrylate, and the soft segment is 1,4-poly(butadiene glycol) having the molecular weight $\overline{M}_n$ = 2800 for SA-B1 and $\overline{M}_n$ = 1120 for SA-B2, respectively.

PE is not urethane oligomer but the difunctional acrylate ester in which 1,4-poly(butadiene glycol) is esterified with acryloyl chloride.

Synthesis

The urethane oligomers were synthesized stepwise. For the first, the hard segment was prepared and then it was reacted with the soft segment and finally butylalcohol or 2-HEA to block the both ends of the oligomer. The hard segment was prepared by reacting four mol of 4,4'-diphenylmethanediisocyanate (MDI) with 2 mol of glycerine monomethacrylate (GMM) in purified dioxane at 60°C for 2 hr.

The molecular weight of the hard segment was determined by gel permeation chromatography (GPC). To measure its molecular weight, both ends of the hard segment was terminated with butylalcohol by adding the reaction solution into an excess amount of butylalcohol.

The structures of the hard segment and the end capped hard segment are shown in eq. (1). The average molecular weight of the hard segment was 2450 ($\overline{M}_n$), suggesting that the degree of polymerization (n) was about 5.

$$\text{(1)}$$
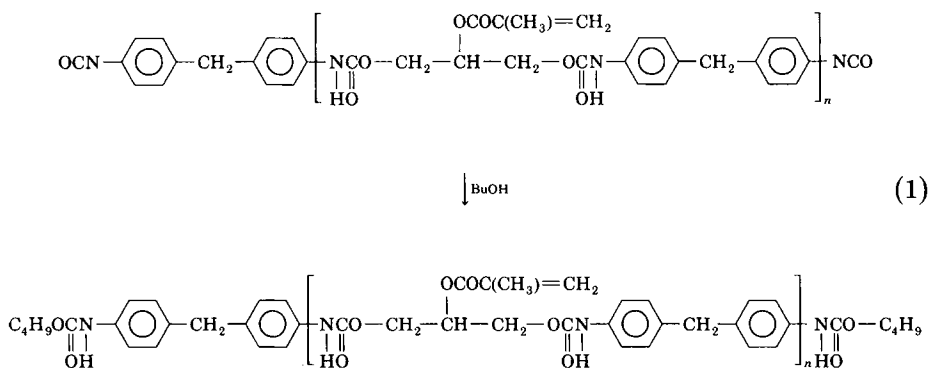
The urethane oligomers were synthesized by reacting its hard segment with the soft segment. One mole of the hard segment was reacted with 2 mol of the soft segment in dioxane at 60°C for 2 h to obtain SHS series. HSH series were prepared by reacting 1 mol of the hard segment with 0.5 mol of the soft segment in dioxane at 60°C for 2 h and successively reacted with butylalcohol to cap the both ends. For the preparation of HSHA series, 2-HEA was used as the capping reagent instead of butylalcohol. The reaction solution was poured into a large amount of n-hexane to precipitate the urethane oligomers. The precipitate was dried after filtration.
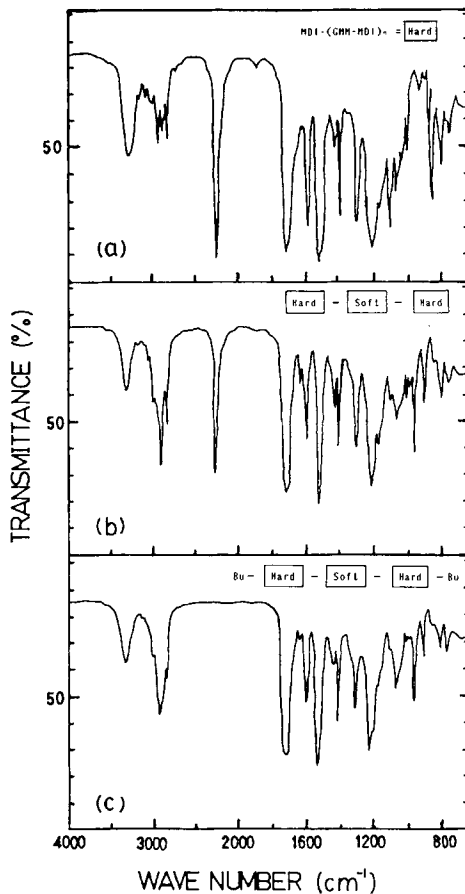
Fig. 2. The infrared spectrum of HSH-B during synthesis.

As mentioned above, three kinds of glycols were used as the soft segment and the oligomers were identified by adding B for 1,4-poly(butadiene glycol), P for poly(propylene glycol), and C for poly(caprolactone diol) to each abbreviation like SHS-B, SHS-P, and so on.

Figures 2(a) and 2(c) show the infrared spectra of the hard segment and HSH-B, respectively. It is noticed in Figure 2(c) that the absorption at 2250 cm^{-1} due to $-N=C=O$ stretching vibration has completely disappeared, indicating that the end isocyanates were successfully capped by butylalcohol.

The characterization of the urethane oligomer is listed in Table I.

Sample Preparation

The oligomers were dissolved in dioxane containing the photoinitiator, α, α-dimethoxy-α-phenyl acetophenone (2.4 wt % of the oligomer).

The 150–200-μm-thick films of each oligomer were cast from the dioxane solutions. The cast films were irradiated by a 3-kW high pressure mercury

TABLE I
The Molecular Weight of the Hard Segment, the Soft Segment, and the Oligomer

Sample name	Soft segment $\overline{M}_n(\overline{M}_w/\overline{M}_n)$	Hard segment $\overline{M}_n(\overline{M}_w/\overline{M}_n)$	Oligomer $\overline{M}_n(\overline{M}_w/\overline{M}_n)$	Structure	m
SHS-B	4336	2491 (1.7)	25090 (6.3)	Soft–(hard–soft)$_m$	3
HSH-B	(2.7)	2331 (1.5)	8811 (3.4)	Hard–(soft–hard)$_m$	1
HSHA-B		2462 (1.5)	9480 (3.6)	Hard–(soft–hard)$_m$	1
SHS-P	4232	2456 (1.5)	18770 (3.0)	Soft–(hard–soft)$_m$	2
HSH-P	(1.2)	2583 (1.6)	7642 (2.7)	Hard–(soft–hard)$_m$	1
HSHA-P		2338 (1.5)	8022 (1.5)	Hard–(soft–hard)$_m$	1
SHS-C	3119	2425 (1.7)	17800 (4.6)	Soft–(hard–soft)$_m$	2–3
HSH-C	(1.7)	2533 (1.8)	6447 (2.2)	Hard–(soft–hard)$_m$	1
HSHA-C		2449 (1.8)	7105 (2.2)	Hard–(soft–hard)$_m$	1
SA-B1	4336	—	5705 (3.1)	—	—
PE	(2.7)	—	4175 (3.0)	—	—
SA-B2	2130 (3.2)	—	5475 (2.3)	—	—

lamp from one side under a nitrogen atmosphere. These photocrosslinked oligomers were used as specimen for mechanical measurements.

Measurements of Mechanical Properties

The stress–strain curves of the cured films with 17 mm length and 2 mm width were obtained by using a tensile tester at 25°C and an extension rate of 600%/min. Tensile strength, ultimate strain, and Young's modulus of each cured film were determined from the curves.

In the stress relaxation measurement, 10% strain was applied to the cured films with 20 mm length and 4 mm width at an extension rate of 1000%/min at 25°C, and the arising stress was measured as a function of loading time.

In the creep measurement, the cured films with 25 mm length and 2 mm width were subjected to a constant stress by the creep testing apparatus which was laboratory made.[9] The strain of each cured film was measured as a function of time using a differential transformer. The stress was removed after a certain time and the creep recovery was measured. The creep and the creep recovery were measured at 25°C.

Dynamic mechanical data were obtained using a Rheovibron Dynamic Viscoelastometer at 110 Hz. The cured films with 20 mm length and 3 mm width were mounted in the instrument, and were quenched to -130°C and heated up to 130°C at about 2°C/min, while readings were taken every 5°C.

Photosensitivity

The dioxane solutions in which the oligomers and photoinitiator, α, α-dimethoxy-α-phenyl acetophenone (2.4 wt % of the oligomer) each were dissolved were coated on aluminum substrates to form 5-μm-thick films, which were irradiated by UV light and then washed with dioxane. The photosensitivity was determined as the minimum exposure energy to insolubilize the film.
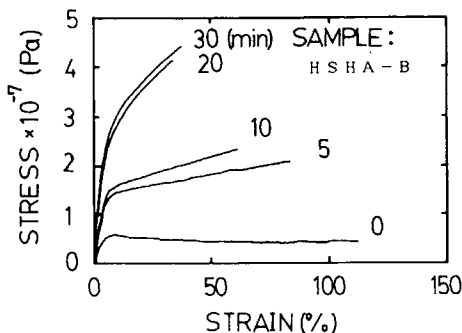
Fig. 3.   Stress–strain curves for HSHA-B at various irradiation time as indicated.

RESULTS AND DISCUSSION

Tensile Properties

The effect of irradiation time in HSHA-B on tensile properties is shown in Figure 3. We can estimate Young's modulus from the slope of initial linear portion.

With increasing the irradiation time, tensile strength and Young's modulus increase while ultimate strain decreases. It suggests that increasing the irradiation time increases the network density. The value of tensile strength of the cured film irradiated for 20 min is almost equal to that irradiated for 30 min. This fact means that the photocrosslinking may be completed after 20 min irradiation. The other oligomers were also irradiated for 20 min to measure their mechanical properties.

Tensile strength, ultimate strain, and Young's modulus of the photocrosslinked oligomers are listed in Table II. Figure 4(a) shows the stress–strain curves of the photocrosslinked oligomers of SHS-B, HSH-B, and HSHA-B whose soft segment is 1,4-poly(butadiene glycol). Figures 4(b) and 4(c) show the stress–strain curves for the photocrosslinked oligomers whose soft segment is poly(propylene glycol) (SHS-P, HSH-P, HSHA-P) and poly(caprolactone diol) (SHS-C, HSH-C, HSHA-C), respectively.

These figures indicate that the mechanical properties depend rather on the configuration of the hard and the soft segments than on the types of the soft segment. The tensile strength and Young's modulus of the HSHA, HSH, and SHS series decrease in that order, while their ultimate strains are in reverse order.

This is because, for SHS series, both ends of a molecule are comprised of soft segments which do not have photoreactive double bonds, so they can only make a low degree of photocrosslinking. On the other hand, for the SHS series, both ends of a molecule are comprised of hard segments which include photoreactive double bonds, so they can make a high degree of photocrosslinking. Furthermore, the tensile strengths for HSHA series are the highest among three series of chemical structures. This may be due to the fact that the acryloyl groups of 2-HEA at both ends of a molecule can photocrosslink to the soft segment, besides the photocrosslinking between hard segments.

The typical features due to chemical structure of soft segments are as follows. The photocrosslinked oligomers using poly(propyrene glycol) as the

TABLE II
Mechanical Properties of the Photocrosslinked Oligomer

Sample name	Soft segment	Mol ratio (MDI/GMM/soft)	Weight fraction of hard segment (%)	Tensile strength (Pa)	Ultimate strain (%)	Young's modulus (Pa)	Relaxation modulus (Pa)	Elastic modulus[a] (Pa)
SHS-B	Poly (butadiene glycol) ($\overline{M}_n = 2800$)	(2/1/1)	19.1	7.44×10^6	67.0	1.0×10^7	4.95×10^6	9.59×10^6
HSH-B		(8/4/1)	48.6	2.51×10^7	55.1	3.7×10^8	5.17×10^7	1.73×10^8
HSHA-B		(8/4/1)	48.6	3.94×10^7	33.0	5.4×10^8	1.09×10^8	3.38×10^8
SHS-P	Poly (propylene glycol) ($\overline{M}_n = 3000$)	(2/1/1)	18.0	3.38×10^6	37.5	6.0×10^6	2.01×10^6	2.90×10^6
HSH-P		(8/4/1)	46.8	2.30×10^6	18.1	3.9×10^8	2.41×10^7	5.65×10^7
HSHA-P		(8/4/1)	46.8	4.40×10^7	15.5	8.8×10^8	4.95×10^7	2.35×10^8
SHS-C	Poly (caprolactone diol) ($\overline{M}_n = 2000$)	(2/1/1)	24.8	3.98×10^6	57.9	$< 5.0 \times 10^6$	2.89×10^6	4.66×10^6
HSH-C		(8/4/1)	56.9	2.48×10^7	43.5	2.8×10^8	1.59×10^7	3.56×10^7
HSHA-C		(8/4/1)	56.9	5.13×10^7	34.7	1.0×10^9	4.31×10^7	1.56×10^8
SA-B1	Poly(buta diene glycol) ($\overline{M}_n = 2800$)	—	—	1.08×10^7	56.2	1.4×10^8	2.32×10^7	3.98×10^7
PE		—	—	5.98×10^5	28.6	$< 5.0 \times 10^6$	2.57×10^6	3.01×10^6
SA-B2	($\overline{M}_n = 1120$)	—	—	3.77×10^7	38.9	5.8×10^8	4.75×10^7	1.37×10^8

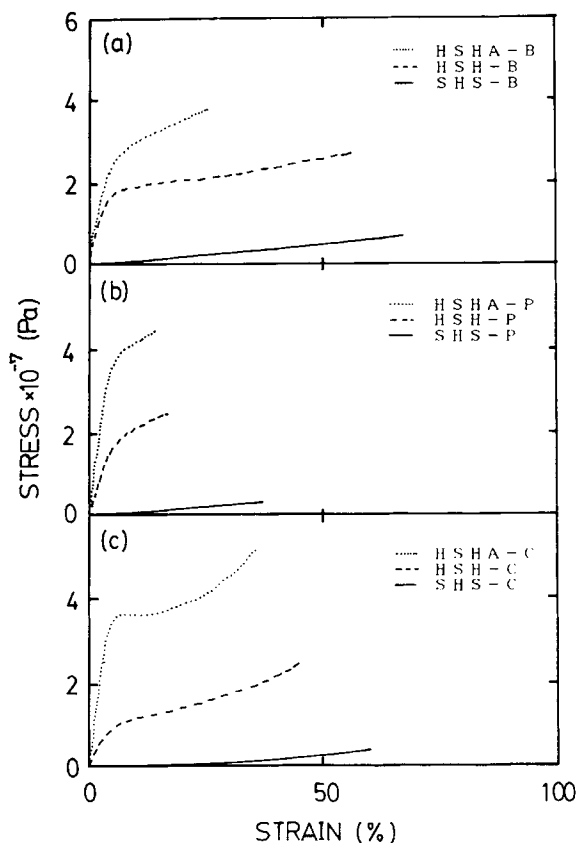[a] Estimated from the measurement of creep recovery.

Fig. 4. Stress–strain curves for the photocrosslinked urethane oligomers having various soft segments. Soft segment: (a) 1,4-poly(butadiene glycol); (b) poly(propylene glycol); (c) poly(caprolactone diol). (· · ·) HSHA; (- - -) HSH; (—) SHS.

soft segment indicate a lower degree of ultimate strain compared with those of the photocrosslinked oligomers using other two soft segments. The stress–strain curves of the photocrosslinked oligomers using poly(caprolactone diol) show the reverse sigmoid shape, which is attributable to the orientation of the molecules as the stress increases.

The value of the tensile strength of SA-B1 which has urethane bondings in the oligomer is 1.80×10^7 Pa as shown in Figure 5, whereas that of PE which has ester bondings in the oligomer is small, 5.98×10^5 Pa. Even though the structure of the oligomer and the molecular weight of the soft segment are the same for both oligomers, their mechanical properties become quite different due to having urethane bondings or not.

SA-B1 and SA-B2, as shown in Figure 5, were synthesized by using two different molecular weights of 1,4-poly(butadiene glycol) ($\overline{M}_n = 2800$, 1120, respectively). The tensile strength and Young's modulus of SA-B2 are higher compared with those of SA-B1, while the ultimate strain of SA-B2 is smaller.
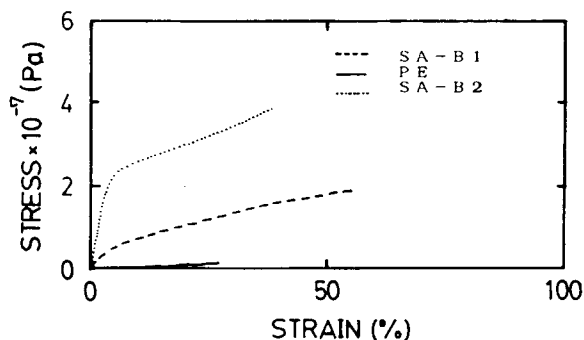
Fig. 5. Stress–strain curves for the photocrosslinked oligomers capped with acryloyl groups at the both ends of a molecule: (- - -) SA-B1; (—) PE; (· · ·) SA-B2.

Stress–Relaxation

The relaxation curves for three kinds of urethane oligomers composed of 1,4-poly(butadiene glycol) as the soft segment at various irradiation times are shown in Figures 6(a), 6(b), and 6(c). The relaxation curves for the photocrosslinked oligomer of which the irradiation time is longer than 5 min does not so depend on the irradiation time and they show an equilibrium modulus less than 10^7 Pa. Therefore, the degree of photocrosslinking of SHS-B may not increase with increasing the irradiation time. For HSH-B and HSHA-B, with increasing the irradiation time, the relaxation modulus increases. At the irradiation time of 20 min, the equilibrium modulus of the order of 10^8 Pa or more are observed. It is deduced that with increasing the irradiation time the states of network of HSH-B and HSHA-B obviously changed and a higher degree of photocrosslinking is formed in both cured films. These behaviors may be attributable to the quantity of photoreactive groups in the oligomer.

The relaxation curves for the photocrosslinked oligomers with different kinds of soft segments at the irradiation time of 20 min are shown in Figures 7(a), 7(b), and 7(c). The values of relaxation modulus at the time of 7200 s are listed in Table II with the values of the elastic modulus obtained from other methods.

The value of the relaxation modulus also does not depend on the kinds of soft segments, but depends on the kinds of chemical structures of the oligomers. For the H3H and HSHA series, the values of the relaxation modulus are in the neighborhood of 10^7–10^8 Pa. For SHS series, they are around 10^6 Pa. For the HSHA and HSH series, both the hard segment and the soft segment affect the relaxation modulus, whereas in the case of SHS series, the soft segment mainly affects the relaxation modulus.

For the oligomers composed of 1,4-poly(butadiene glycol) or poly(caprolactone diol) as the soft segment, the value of the relaxation modulus decreases with time. On the other hand, for that composed of poly(propylene glycol), the stress relaxes in a short time region and the value of the relaxation modulus seems to approach the equilibrium value in the long time region.

These results can be explained by the molecular movement which is restricted due to the existence of the double bond in butadiene or of the polar
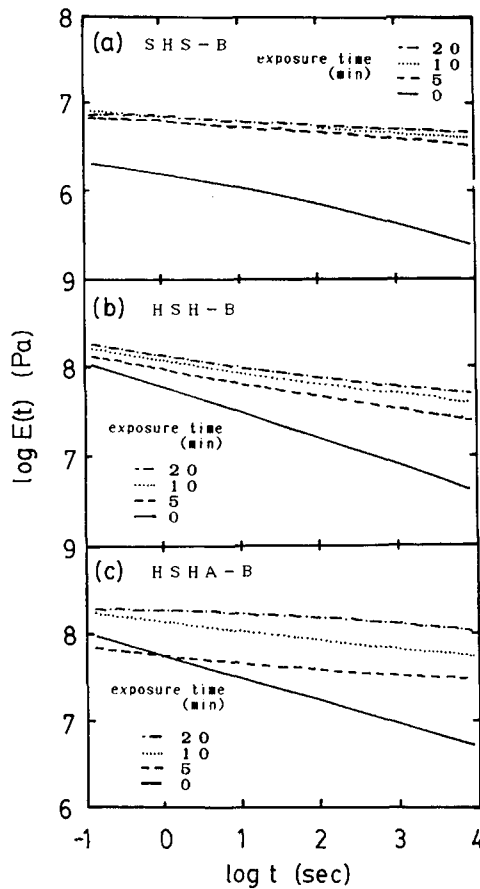
Fig. 6. Relaxation curves for the photocrosslinked urethane oligomers at various irradiation times (min): (·—) 20; (···) 10; (---) 5; (—) 0. Chemical structure: (a) SHS-B; (b) HSH-B; (c) HSHA-B.

bond of carbonyl group in caprolactone. For propylene, on the other hand, the molecular movement is not restricted and the molecules can move easily, so that this tendency of molecular movement affects the relaxation phenomena in the initial time region.

For the photocrosslinked oligomers composed of 1,4-poly(butadiene glycol), both ends of which are capped with the acryloyl group, as shown in Figure 8, the value of the relaxation modulus decreases in the order, SA-B2 > SA-B1 > PE. The results of this stress–relaxation measurement show the same tendency as the stress–strain measurement in Figure 5.

Creep and Creep Recovery

The creep and recovery curves for HSH-C are shown in Figure 9. The recoverable strain seems to be proportional to the applied stress as shown in Figure 10, and the elastic modulus can be calculated from its slope.

The values of elastic modulus for the other photocrosslinked oligomers were also obtained by the same creep measurement, and those data are listed in
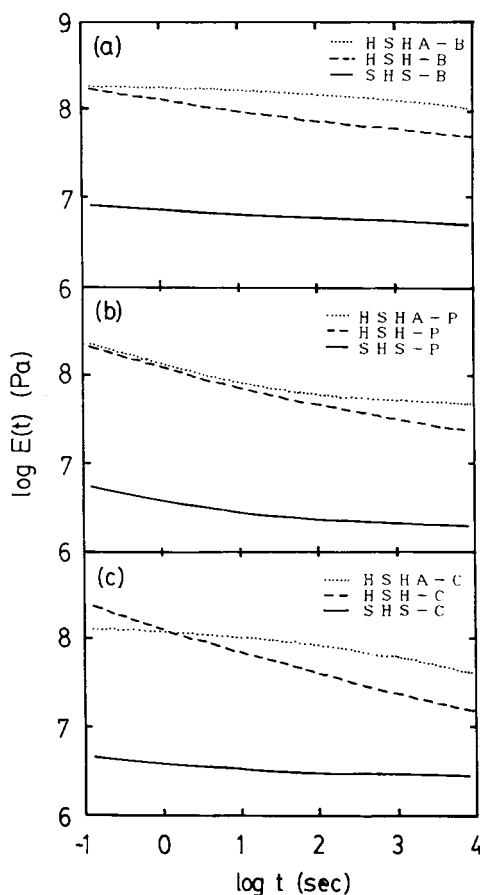
Fig. 7. Relaxation curves for the photocrosslinked urethane oligomers having various soft segments. Soft segment: (a) 1,4-poly(butadiene glycol); (b) poly(propylene glycol); (c) poly(capro-lactone diol). (· · ·) HSHA; (- - -) HSH; (—) SHS.

Table II. The modulus obtained from the stress–strain measurement and the stress–relaxation measurement are also shown in Table II.

These values of Young's modulus, relaxation modulus, and the elastic modulus obtained from creep measurement depend decisively on the chemical structure of the oligomer. The values of three kinds of elastic modulus decrease in the order, HSHA > HSH > SHS.

The creep and the creep recovery for each photocrosslinked oligomer are measured at a similar stress level, and the results are shown in Figures 11(a), 11(b), and 11(c). For the SHS series, an ideal elastic deformation is observed, and the behavior depends on the chemical structure of the soft segment. Especially for SHS-P, whose soft segment is poly(propylene glycol), the higher degree of recoverable strain due to active chain movement is observed. However, for the HSH and HSHA series, the photocrosslinked oligomers composed of poly(caprolactone diol) as the soft segment are apt to elongate and their irreversible strains are higher than the others.
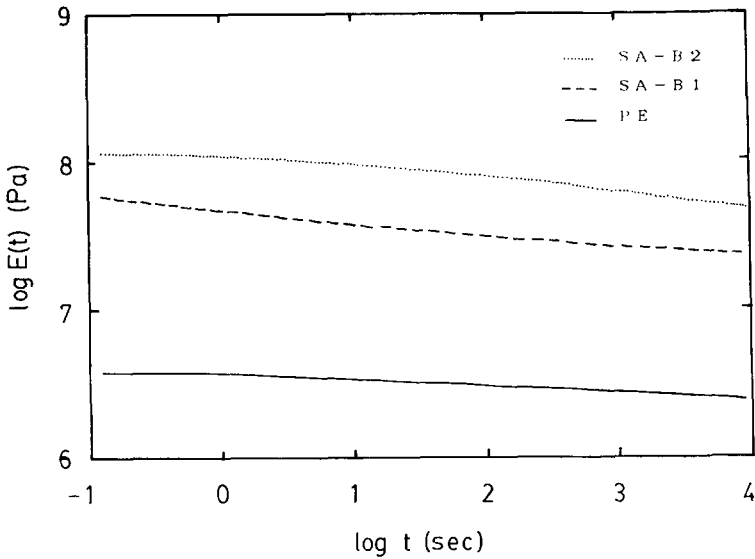
Fig. 8.   Relaxation curves for the photocrosslinked oligomers capped with acryloyl groups at the both ends of a molecule: ($\cdots$) SA-B2; (- - -) SA-B1; (—) PE.

Dynamic Viscoelastic Properties

The temperature dependences of storage modulus G' and loss tangent $\tan \delta$ for the photocrosslinked oligomers are shown in Figures 12(a), 12(b), 12(c), and 13.

In the curves of temperature dependence of G', the values of G' for the SHS series are smaller than those of other chemical structures, irrespectively of the kinds of soft segments. Since a large quantity of the soft segment exists in the SHS series, the photocrosslinked oligomer is comparatively soft and behaves more elastic materials.

For SHS-B composed of 1,4-poly(butadiene glycol) as the soft segment, the viscoelastic transition is observed around $-50°C$. On the other hand, for
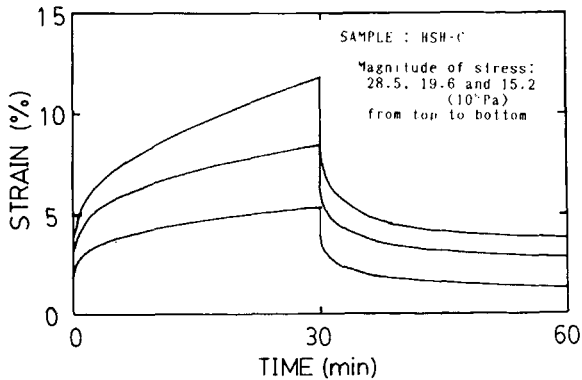

Fig. 9.   Creep and recovery curves for HSH-C at various magnitudes of stress (10^5 Pa): 28.5, 19.6, and 15.2, from top to bottom.
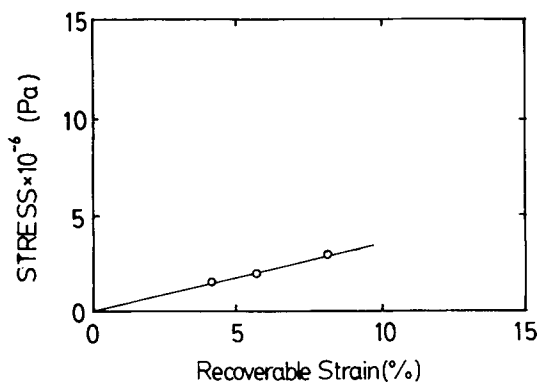
Fig. 10. The relaxation between recoverable strain and stress for HSH-C.

SHS-P composed of poly(propylene glycol) and SHS-C composed of poly(caprolactone diol), both viscoelastic transitions are observed around 0°C. It is thought that SHS-B behaves more elastically than SHS-P and SHS-C at low temperatures.

In the curves of temperature dependence of the tan δ, two peaks are observed around -50 and 110°C for HSH-B and HSHA-B. The curves of temperature dependence of tan δ for block copolymer show two distinct peaks, which are associated with the transition region of each phase as pointed out by Miyamoto et al.[10] for styrene–butadiene–styrene block copolymer.

Therefore, the two peaks observed in the tan δ curves for HSH-B and HSHA-B may be associated with the chain motion in the hard segment domains and that in the soft segment domains. In Figure 12(a), the peak value of tan δ for SHS-B around -50°C is higher than those of other structures; however, at higher temperature, the peak is vague, whereas other photocrosslinked oligomers show the distinct peak at the temperature around 110°C. And in Figure 13, which shows the curves for photocrosslinked oligomers capped with acryloyl groups at both ends of a molecule, only a single peak is observed around -50°C for PE which does not contain any hard segments. Therefore, the peak at higher temperatures is associated with the chain motion in the hard segment domains and the peak at lower temperatures is associated with the chain motion in the soft segment domains.

On the other hand, for the photocrosslinked oligomers composed of poly(propylene glycol) or poly(caprolactone diol) as the soft segment, a single broad peak is observed in the temperature dependence of tan δ as shown in Figures 12(b) and 12(c). For these single peaks, it may be suggested that only the single phase, where the hard and the soft segments are mixed homogeneously, exists in these cured films.

If the difference in the transition temperature between the soft and the hard segment is extremely large, the phase separation may occur. For the photocrosslinked oligomers composed of 1,4-poly(butadiene glycol) as the soft segment, the transition temperature of the soft segment is extremely low compared with that of the hard segment, so that discrete domains can be formed in each film. In the case of poly(propylene glycol) and poly(caprolac-
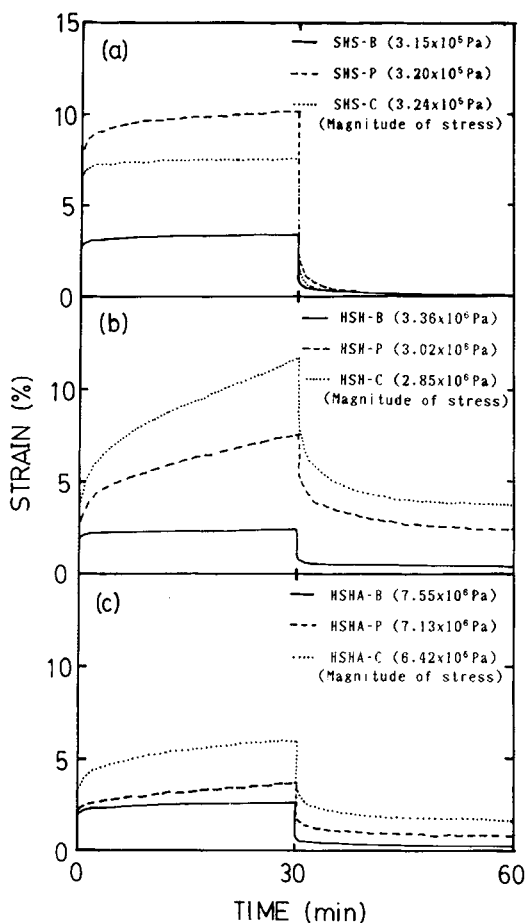
Fig. 11.   Creep and recovery curves for the photocrosslinked urethane oligomers at each stress as indicated. Chemical structure: (a) SHS series; (b) HSH series; (c) HSHA series. (a) (—) SHS-B (3.15 × 10⁵ Pa); (- - -) SHS-P (3.20 × 10⁵ Pa); (· · ·) SHS-C (3.24 × 10⁵ Pa). (b) (—) HSH-B (3.36 × 10⁶ Pa); (- - -) HSH-P (3.02 × 10⁶ Pa); (· · ·) HSH-C (2.85 × 10⁶ Pa). (c) (—) HSHA-B (7.55 × 10⁶ Pa); (- - -) HSHA-P (7.13 × 10⁶ Pa); (· · ·) HSHA-C (6.42 × 10⁶ Pa).

tone diol), there is a small difference between the transition temperature for the soft and the hard segment, so that no discrete domains can be formed.

As for PE, the value of storage modulus G' slightly increases with increasing in temperature above 0°C instead of decreasing, and this phenomenon corresponds to the entropy elasticity. Therefore, it is deduced that the network structure formed by polybutadiene molecules behaves as a rubbery elastic material.

Photosensitivity

The photosensitivity of each oligomer is shown in Table III. It shows that the photosensitivity does not depend on the kind of soft segment used, but depends on the chemical structure of the oligomer.
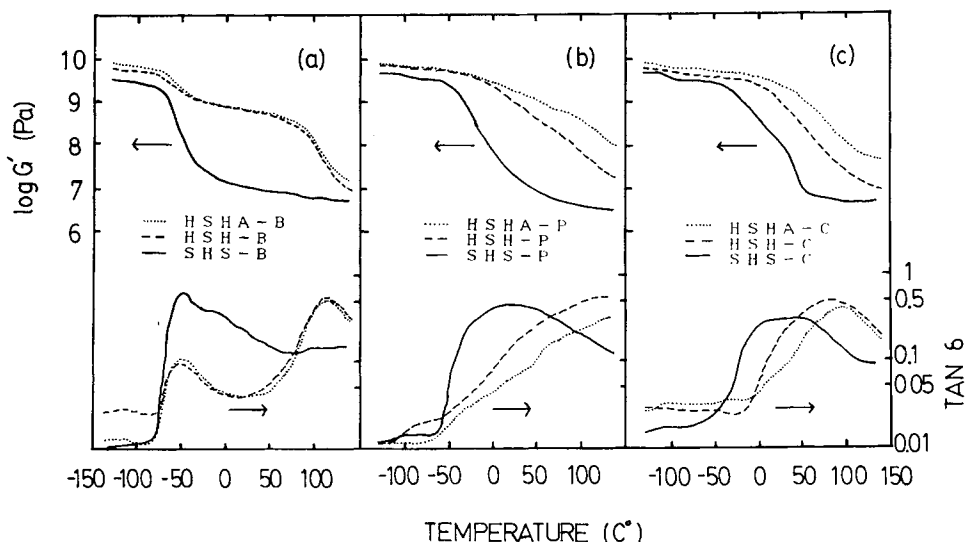
Fig. 12. Temperature dependence of dynamic viscoelastic properties for photocrosslinked urethane oligomers having various soft segments. Soft segment: (a) 1,4-poly(butadiene glycol); (b) poly(propylene glycol); (c) poly(caprolactone diol). ($\cdots$) HSHA; (---) HSH; (—) SHS.

HSHA series exhibits about two times higher photosensitivity than the HSH and SHS series, irrespective of using any kind of soft segment among three. This may be due to that acryloyl groups of 2-HEA, hanging both ends of a molecule in the HSHA series have a higher polymerization rate than methacryloyl groups in the hard segment.

For SA-B1, SA-B2, and PE, they have acryloyl groups at both ends of a molecule, but they exhibit a lower photosensitivity than the other oligomers. This is because that only reactive two acryloyl groups are contained in a molecule, so that the density of the photoreactive groups is lower than the other oligomers.

CONCLUSION

PE and SA-B1, in which acryloyl groups are introduced to the soft segment by ester bondings and by urethane bondings, respectively, are compared in terms of their mechanical properties. It was shown that SA-B1 has the better mechanical properties than PE, even though their chemical structures are analogous. This result indicates that the cohesion between hard segments due to their hydrogen bondings of the urethane group contributes largely to the mechanical properties.

From the experiment that the density of the photoreactive groups in the oligomer is varied by changing the molecular weight of the soft segment, it was found that SA-B2 having the smaller molecular weight of the soft segment ($\overline{M}_n = 1120$) has the higher tensile strength, relaxation modulus, and the network density than SA-B1, in which the molecular weight of the soft segment is higher ($\overline{M}_n = 2800$).

It was also found that HSH series, in which the content ratio of the hard segment is higher, is higher in both tensile strength and Young's modulus
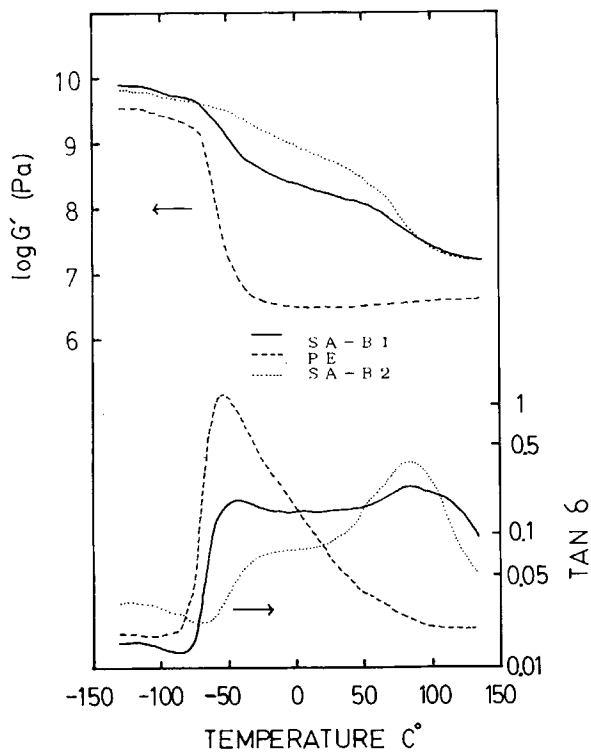
Fig. 13.   Temperature dependence of dynamic viscoelastic properties for the photocrosslinked oligomers capped with acryloyl groups at the both ends of a molecule: (—) SA-B1; (- - -) PE; (· · ·) SA-B2.

TABLE III
The Photosensitivity of the Oligomer

Sample name	Sensitivity (J/cm^2)
SHS-B	2.8
HSH-B	2.8
HSHA-B	1.4
SHS-P	2.1
HSH-P	2.6
HSHA-P	1.2
SHS-C	2.1
HSH-C	2.8
HSHA-C	1.8
SA-B1	3.9
SA-B2	3.3
PE	3.9

than that of SHS series. HSHA series having 2-HEA at both ends of the oligomer has much higher tensile strength, Young's modulus, and photosensitivity than the HSH series. These tendencies can be observed regardless of the kind of soft segments.

In the cured film where the soft segment is poly(propylene glycol), the stress relaxes faster than the other cured films. This fact means that the property of soft segments governs its stress–relaxation characteristics.

Using poly(caprolactone diol) as the soft segment, it was observed in the creep measurement that the cured film can elongate, compared with the cured films using other soft segments.

From the results of the dynamic viscoelastic properties, the cured film having 1,4-poly(butadiene glycol) as the soft segment has two peaks in the temperature dependence of $\tan \delta$ at $-50°C$ and $110°C$ which are associated with the chain motion in the soft segment domains and the hard segment domains, respectively. This indicates that phase separation in the cured film has occurred. In the case of poly(propylene glycol) and poly(caprolactone diol), only a single peak is observed. So it can be considered that these cured films have single phase, i.e., uniform morphology.

References

1. M. Koshiba, K. K. S. Hwang, S. K. Foley, D. J. Yarusso, and S. L. Cooper, *J. Mat. Sci.*, **17**, 1447 (1982).

2. Nippon Kokai Tokkyo Koho 49-13870 (Jpn. Pat.).

3. Nippon Kokai Tokkyo 48-58092 (Jpn. Pat.).

4. Nippon Kokai Tokkyo 49-105874 (Jpn. Pat.).

5. W. Oraby and W. K. Walsh, *J. Appl. Polym. Sci.*, **23**, 3227 (1979).

6. R. Kusaki and T. Yamaoka, *Jpn. Soc. Pri. Sci. Technol.*, **23**(4), 39 (1986).

7. R. Takiguchi and T. Uryu, *J. Polym. Mat.*, **2**, 35 (1985).

8. T. Yamaoka, T. Tsukada, H. Onogi, and K. Koseki, Proceedings of Conference on Radiation Curing ASIA, Preprint 107, 1986.

9. T. Amari et al., *Rep. Prog. Polym. Phys. Jpn.*, **24**, 101 (1981).

10. T. Miyamoto, K. Kodama, and K. Shibayama, *J. Polym. Sci.*, A-2 **8**, 2095 (1970).