Synthesis of Polymer Materials by Low Energy Electron Beam. I. Polyurethane–Acrylate Materials Prepared by the EB and the UV Solid-State Polymerization

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Synopsis

Structure and properties of films obtained by the electron beam (EB) and the ultraviolet light (UV) solid-state polymerization of polyurethane–acrylate prepolymer were examined to reveal the characteristics of these radiation polymerizations. The prepolymer was synthesized by the reaction of poly(butylene adipate)diol, 4,4′-diphenylmethane diisocyanate, and 2-hydroxyethyl acrylate. EB polymerization behaviors of the prepolymer produced a unique polymer film different from that obtained by UV irradiation. Although polyurethane–acrylate films from the EB and the UV solid-state polymerizations consisted mainly of amorphous and crystalline phases, it was proved that the film from 10 Mrad of EB irradiation at 25°C had higher crystallinity and larger crystallite size than the film from UV irradiation. This is assumed to be due to the reason that EB irradiation below the melting point of the polyurethane–acrylate can lead to crosslinking without the destruction of the original crystalline structure. On the other hand, the UV polymerization proceeded with the melting of the crystalline structure by absorbing other lights than the UV absorbed by a photoinitiator. The EB-polymerized film which was crosslinked more densely than the UV-polymerized film showed higher mechanical strength than the latter film.

INTRODUCTION

A high-intensity radiation processing has been developed as one of the alternatives to a heat processing.[1] Research and development related to this processing cover such wide fields as coatings for metal and plastics, optical fiber,[2] magnetic media,[3] and printed circuit.[4] Recently, we reported the preparation of a pressure-sensitive adhesive.[5]

Radiation-curable compounds consist primarily of monomers and prepolymers with acryl double bonds.[1] Since the molecular structure and the composition are designed according to the end uses of cured polymeric materials, a large number of monomers and prepolymers have been prepared.[6,7]

Electron beam (EB) and ultraviolet light (UV), which have individual characteristics, have been primarily used as a high-intensity radiation for these monomers and prepolymers so far.

A few hundred KeV of low energy EB emitted from a tungsten filament can polymerize acryl double bonds via the electronic and the ionic excitation, and can penetrate through curable materials depending on both the initial electron energy and the density of irradiated materials.[8] Moreover, the secondary electrons which are formed by collision of the incident electron with molecules

play an important role in chemical reactions caused by the high energy radiation.

On the other hand, only UV of about 365 nm emitted from a high-pressure mercury lamp is effective for polymerization. Since the acryl double bonds which absorb only light at less than 250 nm of wavelength do not cause the reaction by UV irradiation, a photoinitiator with the optimum absorption of about 365 nm is necessary for the UV processing. This wave has only a few eV of energy and the penetration is dependent of the transparency of materials. In addition, the UV emitted from a high-pressure mercury lamp contains UV lights of other wavelength than 365 nm and infrared rays.[9]

Although there are possibly considerable differences in structure and properties between materials cured by EB and UV, a few studies have been reported on such subjects.[6,10] The solid-state polymerizations of polyurethane–acrylate were investigated using γ-ray and EB radiation to reveal the structure-properties relationships of the cured, crosslinked materials.[11,12]

In this study, we report the structural differences between the films obtained by the EB and the UV solid-state polymerization to manifest the characteristics of both processings. For this purpose, a semicrystalline polyurethane–acrylate prepolymer which was synthesized by the addition reaction of poly(butylene adipate)diol, 4,4'-diphenylmethane diisocyanate, and 2-hydroxyethyl acrylate was used as a EB- and UV-curable material. Properties of the EB- and UV-cured films were examined by optical, thermal, and mechanical methods, while the structure of the films was investigated by differential scanning calorimetry, X-ray diffractometry, and scanning electron microscopy. In addition, the extent of crosslinking was examined for each film by analyzing stress–strain curves and gel permeation chromatograms.

EXPERIMENTAL

Materials

Prepolymers. 2-Hydroxyethyl acrylate (HEA)-capped polyurethane–acrylate prepolymer (5, UA-251M) and ethyl alcohol-capped polyurethane prepolymer (7, U-251M) were synthesized according to Scheme I.
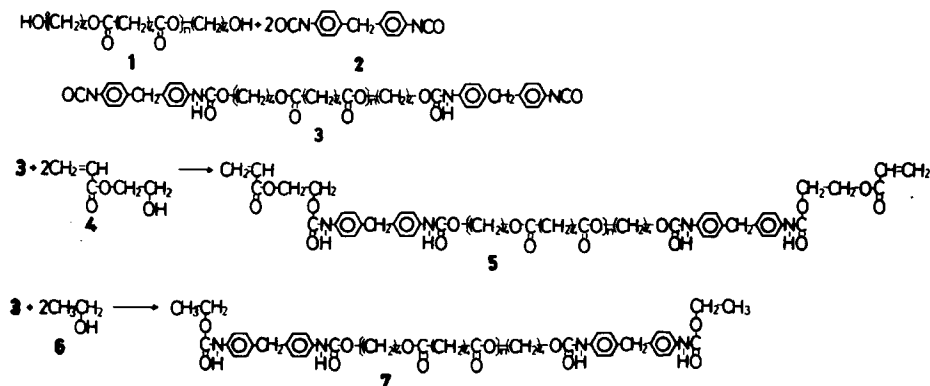
Scheme I. Synthesis of polyurethane–acrylate and polyurethane prepolymer: 1, Poly(butylene adipate)diol; 2, 4,4'-diphenylmethane diisocyanate; 3, isocyanate-capped intermediate; 4, 2-hydroxyethyl acrylate; 5, polyurethane–acrylate prepolymer (UA-251M); 6, ethyl alcohol; 7, polyurethane prepolymer (U-251M).

In the first step, 100 g of poly(butylene adipate)diol [1, PBAD, Nippon Polyurethane Industry Co., Ltd., the number average molecular weight $(\overline{M}_n)$ of about 2500] was reacted with 20 g of 4,4'-diphenylmethane diisocyanate (2, MDI) in methyl ethyl ketone (MEK, 70 wt %) under nitrogen atmosphere with di-n-butyltin dilaurate as catalyst according to the the established procedures.[13] The solution was successively stirred for 3 h at 40°C and for 3 h at 60°C to force the reaction to completion. In the second step, the iso-cyanate-capped intermediate (3) was reacted 9.8 g of HEA (4) or 3.9 g of ethyl alcohol (6) at 60°C for 10 h under oxygen atmosphere. Each reaction was undertaken in the same flask as the first step without recovery. The comple-tion of the reactions were confirmed by the disappearance of the peak due to N=C=O stretching absorption near 2270 cm^{-1} by IR spectroscopy. The final products (5, 7) were purified by reprecipitation and dried under vacuum.

Preparation of Irradiation Sample

For EB irradiations, films cast from MEK solutions and dried under vacuum were melted in the oven at 80°C for 0.5 h and cooled to room temperature. The thickness was about 40 μm. For UV irradiations, films were prepared by the similar method. But these films contained 5 wt % benzoin methyl ether as a photoinitiator, and they were covered by polypropylene film to remove the influence of oxygen.

Irradiation and Apparatus

An electro-curtain type accelerator (Energy Science Inc.) equipped with a linear filament was used as a low energy EB source. EB irradiations were carried out under nitrogen atmosphere and the irradiation dose ranged from 0.5 to 20 Mrad using beam current of 2 to 20 mA at an accelerated voltage of 175 KV. The irradiation at 65°C was performed by exposing the film to EB within 10 s after taking out it from the oven at 65°C. A bank of ozoneless high-pressure mercury lamp with the input of 80 W/cm was used as a UV irradiation source. The UV irradiation was carried out on the conveyer at a distance of 10 cm from the lamp. Irradiation time corresponding to the dose was calculated by assuming that the effective UV is irradiated 5 cm in length to the progressing direction of the conveyer.[14]

Characterization Methods

The gels of the polymerized sample were evaluated after extraction with tetrahydrofuran (THF) at 25°C for 72 h. The insoluble and the soluble part were dried under vacuum and weighed to give the gel fraction.

The glass transition temperature (T_g), the melting point (T_m), the heat capacity change (ΔC_p) at T_g, and the heat of fusion (ΔH) were determined for each sample using a Perkin-Elmer DSC-II. The measurements were carried out from -170 to 170°C at a heating rate of 20°C/min under nitrogen steam. The samples were placed in the DSC at 100°C and then quenched to -170°C at a cooling rate of 80 deg/min. Calibration was done by using indium as standard.

The percent transmittance over the wavelength between 400 and 700 nm was measured at 25°C using a UV/VIS recording digital spectrophotometer (Japan Spectroscopic Co., Ltd.).
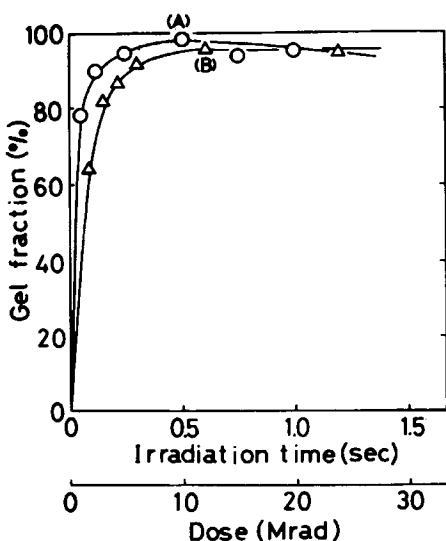
Fig. 1. Gel fraction of UA-251M films as function of dose for EB (○) and irradiation time for UV (△). UA-251M for UV process contains 5 wt % of benzoin methyl ether.

Stress–strain measurements at 25°C and 60°C were run on using Tensilon/UTM-III-100 (Toyo Baldwin Co., Ltd.) with a crosshead speed of 50 mm/min and a gauge length of 40 mm. Testing sample films were cut in 80 mm long and 10 mm wide. The engineering stress was calculated as the strength divided by the initial cross-sectional area.

Morphology of the film surface was observed using an Akashi scanning electron microscope (SEM, Model ALPHA-30W). SEM specimens were prepared by evaporating gold onto the film surfaces after drying under vacuum.

X-ray diffraction diagrams were obtained with Geigerflex (Rigaku Denki Co., Ltd.). The X-ray was nickel-filtered CuK_α ($\lambda = 0.1542$ nm) radiation from a sealed tube operated at 35 kV and 16 mA.

Gel permeation chromatography (GPC) was measured using a Toyo Soda HLC-802UR chromatograph with THF as eluent.

RESULTS AND DISCUSSION

Structure and Properties of Polyurethane–Acrylate Films Obtained by the EB and the UV Irradiation

The polyurethane–acrylate prepolymers were readily polymerized by both EB and UV irradiations to give higher molecular weight polymers and gels. The relations between gel fraction and irradiation dose or time are shown in Figure 1. The gel fractions of both films reached to more than 96 wt % in 0.6 s for UV irradiation and in 10 Mrad (approximately 0.6 s) for EB. It is noted that in spite of the opacity of the films due to the semicrystallinity, the UV solid-state polymerization proceeded readily with increasing irradiation time.

However, there was a significant visible difference in the physical property between a EB-irradiated film (EB-film) with a gel fraction of 98.4 wt % and a
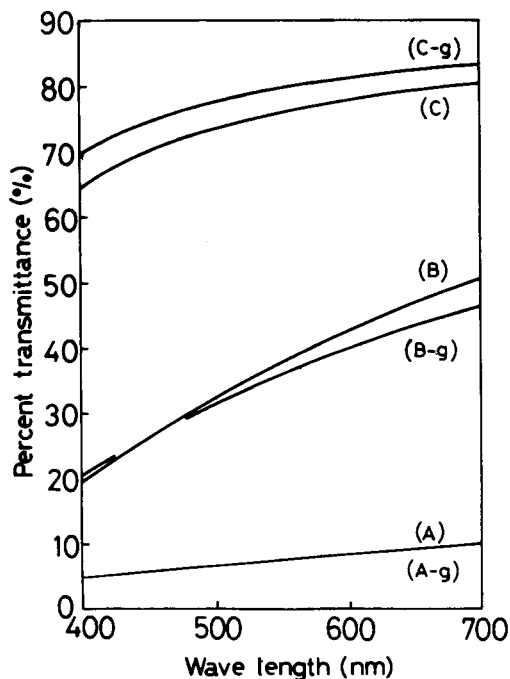
Fig. 2. Optical property of the UA-251M films cured by EB and UV: (A) film from EB irradiation of 10 Mrad at 25°C; (B) film from UV irradiation for 0.6 s at 25°C; (C) EB irradiation of 10 Mrad at 65°C; (A-g), (B-g), and (C-g) are gel films of (A), (B), and (C), respectively. Gel fraction: (A) 98.4% (B) 96.1%; (C) 97.2%.

UV-irradiated film (UV-film) with a gel fraction of 96.1 wt %, which are indicated as (A) and (B) in Figure 1, respectively.

As seen in Figure 2, since the EB film was opaque, the transmittance of visible light was 5–10% in the wavelength of 400 to 700 nm, while the transparent UV-film showed higher transmittance ranging from 20 to 50%, which depended on the wavelength.

To reveal the reason for the difference in the optical property between the two films, T_g and T_m were measured using DSC. As the results are shown in Table I, both T_g and T_m values of the EB-cured film were higher than those of the UV-cured film. Since T_g and T_m generally depend on the degree of crystallinity[15,16] and polymer materials with higher degree of crystallinity have higher T_g and T_m, the higher T_g and T_m values for EB film were due to the EB polymerization proceeded with less alternation of an original crystalline structure than the UV polymerization. However, it is assumed that the effect of the degree of crystallinity on T_g is small, though its effect may be attributed to the reason that the crystallites play a role as crosslinking junctions, and T_m must be intrinsically constant unless the change in crystalline structure occurs. Thus, other effects than the degree of crystallinity need to be added for explaining the above-mentioned differences. As described in the following sections, more flexible polymer chain in the amorphous phase which was induced by UV reduced the T_g of the UV film, and the crosslinking occurring within the backbone in the amorphous phase by EB enhanced the

TABLE I
Thermal Properties of UA-251M Films Cured by EB and UV

Materials	Irradiation condition	Gel fraction (%)	Glass transition temperature T_g (°C)	Melting point T_m (°C)
EB-cured UA-251M film[a]	10 Mrad[c] at 25°C[e]	98.4	−41.9	48.7
UV-cured UA-251M film[b]	0.6 s[d] at 25°C[e]	96.1	−43.7	44.0

[a] Film prepared from (A) in Figure 1.
[b] Film prepared from (B) in Figure 1.
[c] Dose of EB using electro-curtain type accelerator in 175 kV.
[d] Irradiation time of UV using 80 W/cm high-pressure mercury lamp.
[e] Temperature of UA-251M film before irradiating.

T_g of the EB film,[17] while the crystallites destroyed by UV decreased the T_m of the UV film.[18]

The mechanical property clearly reflected such structure. Both modulus and stress at yield of EB film were higher than those of UV film (Fig. 3).

These findings suggest that the semicrystalline polyurethane–acrylate prepolymer was polymerized by EB irradiation with retaining the original morphology arising from poly(butylene adipate) segment even after the reaction of acryl double bond, while the UV irradiation might cause its melting due to
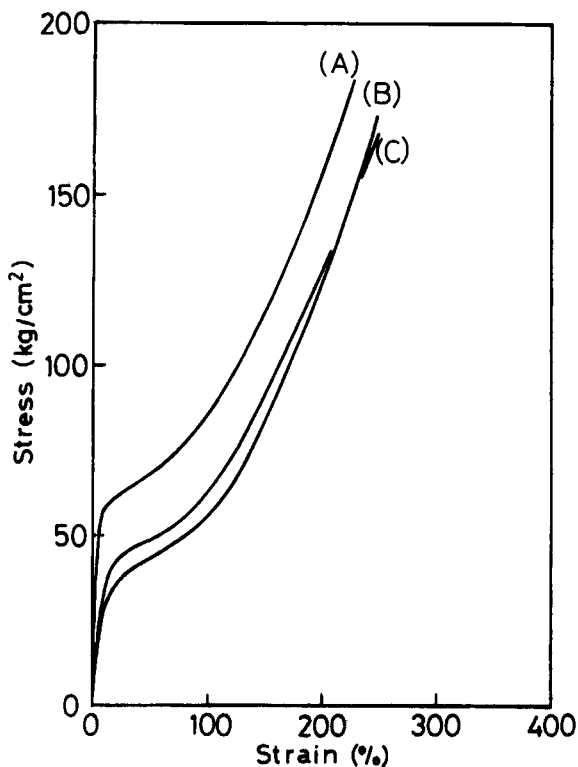

Fig. 3.   Mechanical property of the UA-251M films cured by EB and UV: (A) EB irradiation of 10 Mrad at 25°C; (B) UV irradiation for 0.6 s at 25°C; (C) EB irradiation of 10 Mrad at 65°C.

a temperature rise. In the polyurethane–acrylate prepolymer during polymerization, a temperature rise up to 65°C was observed for the UV irradiation, while the temperature did not rise to higher than 50°C for the EB irradiation in 10 Mrad. Thus, the EB irradiation at 65°C was performed, giving a film similar to UV film (Figs. 2 and 3). It was revealed that the temperature rise during UV irradiation produced a UV-film having higher transparency, lower T_g and T_m, and weaker mechanical strength in comparison with the EB film.

Structure of Polyurethane–Acrylate Gel Films

Subsequent experiments were performed using the gel films which remained after extraction with THF, because it was thought that an unreacted prepolymer included in the cured films might prevent to reveal the structure and properties intrinsic to the cured films.

In Figure 2, the percent transmittance of the gel films is shown against wavelength together with that of the as-polymerized films. These films were obtained from EB irradiation of 10 Mrad at 25°C (denoted as EB-gel-25), UV-irradiation for 0.6 s (UV-gel), and EB irradiation of 10 Mrad at 65°C (EB-gel-65). The transmittances of EB-gel-25 and UV-gel overlapped almost to those of the corresponding unextracted films. This fact suggests that the morphology in film is fixed by the EB and the UV irradiation.

As seen in Figure 2, EB-gel-65 which was obtained by the EB irradiation above the melting point is of the highest transparency, and the percent transmittance of UV-gel lies between that of EB-gel-25 and EB-gel-65. This result indicates that the crystalline state of polyurethane–acrylate prepolymer melts during the UV irradiation. However, for the UV irradiation, it is thought that, although the polymerization proceeded with melting of the crystalline phase, the morphology in dimension of visible light wavelength was not destroyed in comparison with the EB-gel-65 in which the complete melting occurred.

Figure 4 shows SEM photographs of film surfaces on the side of the poly(ethylene trephthalate) (PET) base film on which the prepolymer was applied. The observed rough surface of EB-gel-25 is presumed to be spherulitic texture due to the original morphology arising from poly(butylene adipate) portion of polyurethane–acrylate prepolymer, as was pointed out by Wilkes and coworkers.[12] On the other hand, the original morphology of UV-gel was almost destroyed and that of EB-gel-65 completely destroyed. The depressions found in the EB-gel-25 surface might be ascribed to the amorphous phases which were increased by the melting of the crystalline phase with polymerization of acryl double bonds.

Further investigations about the fine texture of the gel films were performed using DSC and X-ray diffractometry. From the DSC thermograms shown in Figure 5, Tg, Tm, ΔC_p, and ΔH were evaluated and the results are summarized in Table II.

Each value of UV-gel except T_g lies between the values of the EB-gel-25 and EB-gel-65, being similar to the tendency of the transmittance of visible lights.

The data from DSC measurements provided an information on other fine textures than those from the SEM observations. T_g was defined as the midpoint of the temperature interval before and after transition.
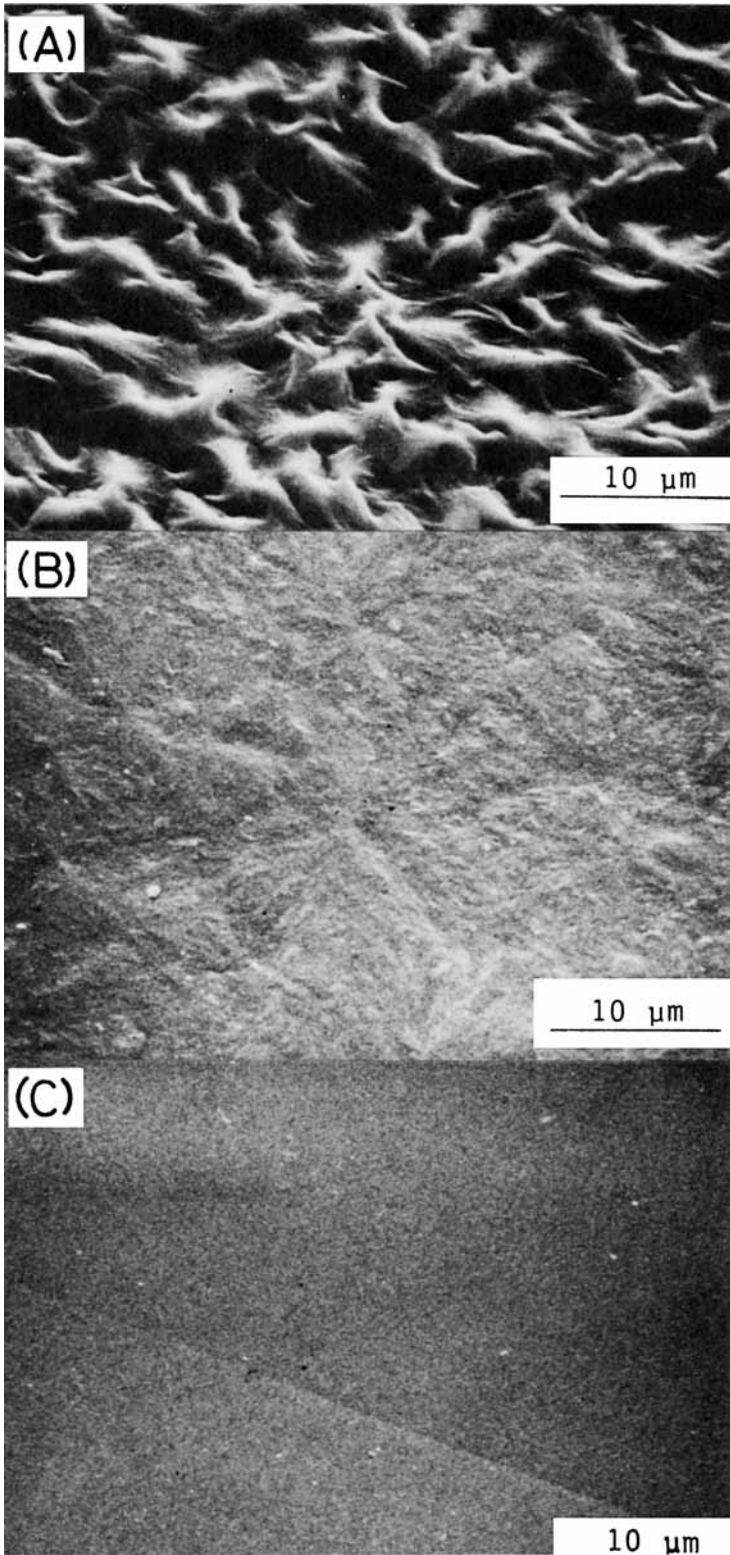
Fig. 4. Scanning electron micrographs of the gels obtained from UA-251M films cured by EB and UV: (A) EB irradiation of 10 Mrad at 25°C; (B) UV irradiation for 0.6 s at 25°C; (C) EB irradiation of 10 Mrad at 65°C.
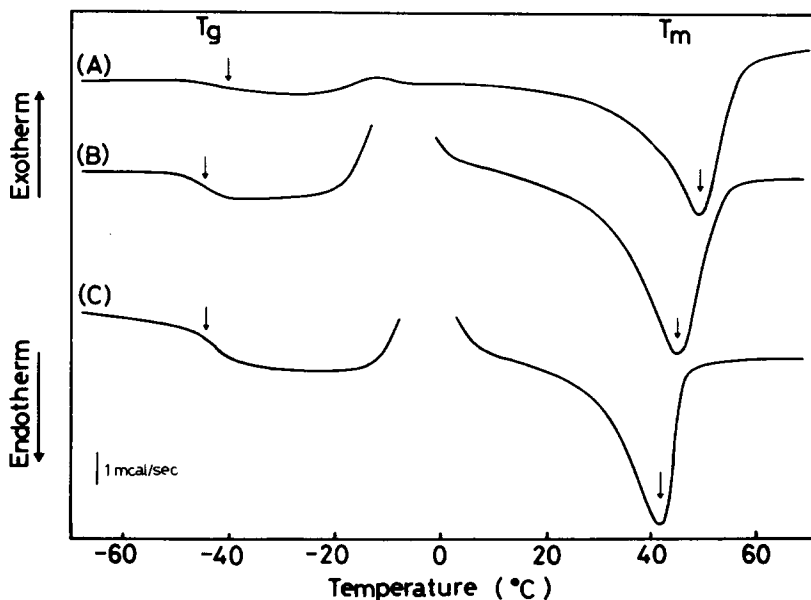
Fig. 5. DSC thermograms of the gels obtained from UA-251M films cured by EB and UV: (A) EB irradiation of 10 Mrad at 25°C; (B) UV irradiation for 0.6 s at 25°C; (C) EB irradiation of 10 Mrad at 65°C.

Of the three films, EB-gel-25 exhibited the highest T_g, implying that the crystalline phase of EB-gel-25 changed to the least extent into the amorphous phase. In addition, the following qualitative differences among them were recognized using ΔC_p.

ΔC_p at T_g was calculated from the following equation:[19]

$$\Delta J = m \cdot \Delta C_p \cdot r \qquad (1)$$

where ΔJ is a jump value (cal/s) at T_g between the lines drawn through the extrapolated base lines before and after transition, m is the weight of sample,

TABLE II

Results of DSC Measurements for the Gels Obtained from UA-251M Films Cured by EB and UV[a]

Materials	Irradiation condition	Glass transition temperature T_g (°C)	Melting point T_m (°C)	Heat capacity change ΔC_p $\times 10^{-2}$ (cal/g · deg)	Heat of fusion ΔH (cal/g)
Gel of EB-cured	10 Mrad at 25°C[b]	−41.5	48.2	5.9	8.1
UA-251M film	10 Mrad at 65°C[c]	−45.5	40.2	9.7	6.2
Gel of UV-cured UA-251M film	0.6 s at 25°C[d]	−45.8	43.8	7.6	7.3

[a] Original UA-251M: T_g, −35.9°C; T_m, 59.2°C, ΔC_p, 1.9 × 10^{-2} cal/g · deg; ΔH, 12.3 cal/g.
[b] Gel fraction 98.4%.
[c] Gel fraction 97.2%.
[d] Gel fraction 96.1%.

and r is the heating rate. According to Wunderlich,[20] ΔC_p per *bead*, which is the smallest unit of flexibility in polymer chain such as —CH_2—, —O—, and —$CH(CH_3)$—, is constant independently of materials. That is

$$\overline{M} \cdot \Delta C_p = 2.7 \pm 0.5 \ (cal/deg \cdot mol) \tag{2}$$

where $\overline{M}$ is *an average molecular weight of bead*. When this theory is applied to the polyurethane–acrylate film consisting of crystalline and amorphous phases, $\overline{M}$ implies the smallest molecular weight of a flexible unit in an amorphous phase. Thus, $\overline{M}$ decreases with increasing mobility of polymer chain in an amorphous phase. Recently, a study of phase separation of polyurethanes revealed that ΔC_p is effectively made use of understanding the amorphous phase structure.[21]

As shown in Table II, the ΔC_p values increased in order of EB-gel-25, UV-gel, and EB-gel-65, indicating that the degree of polymer chain mobility in the amorphous phase increased in that order. Accordingly, it was assumed that the UV solid-state polymerization must have proceeded by accompanying the alternation of a considerable portion of a crystalline phase to a flexible amorphous phase, and that lower T_g of UV-gel in comparison with EB-gel-25 might be due to this flexibility.

On the other hand, it is obvious that from ΔH and T_m values, the degree of crystallinity decreased in the order of EB-gel-25, UV-gel, and EB-gel-65.

The X-ray diffraction data support the results from the DSC measurements (Fig. 6). The degree of crystallinity decreased in the order of EB-gel-25, UV-gel, and EB-gel-65, while the diffuse scattering increased in the same order. The degree of crystallinity and the crystallite size calculated from main peak of the X-ray diffraction patterns are shown in Table III.

The degree of crystallinity was calculated using the true diffraction intensity which was defined as an intensity over the line drawn along the base of diffraction peaks.[19] The crystallite size D was calculated by Scherrer's equation[19]

$$D = 0.94\beta/\lambda \cdot \cos\theta \tag{3}$$

where β is the half-height width of the peak of $2\theta = 21°$, λ is the wavelength of X-ray (0.1542 nm), and θ is the Bragg's angle.

Although the degree of crystallinity of UV-gel (39.5%) was almost comparable to that of EB-gel-25 (36.5%), the crystallite size of UV-gel (85 Å) was much smaller than that of EB-gel-25 (120 Å). A higher T_m of EB-gel-25 is, therefore, due to a larger crystallite size. Also, it is extraordinary that T_m of EB-gel-65 was remarkably low in spite of the large crystallite size (141 Å), but it might be attributed to an imperfection of crystalline structure and low crystallinity. The shift of 2θ in Figure 6 seems to imply the imperfection in EB-gel-65.

Crosslinking Density of Polyurethane–Acrylate Gel Films

In Table II, the gel film obtained by EB irradiation of 10 Mrad at 65°C shows T_g of $-45.5°C$, which is almost the same as that of the UV-gel. Taking into account the ΔC_p and ΔH values, this value is too high. Thus, we assumed that this might be due to the crosslinking in the amorphous phase.
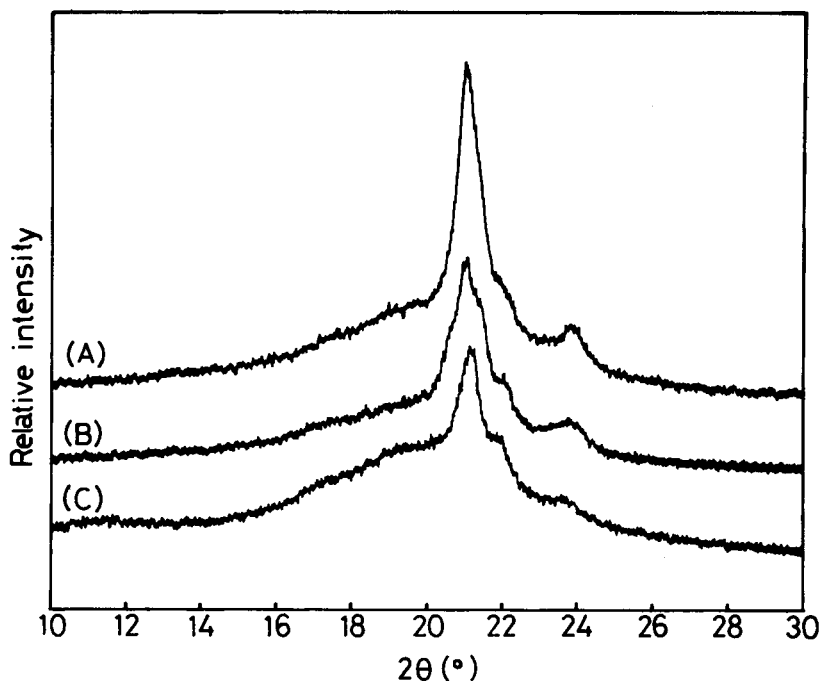
Fig. 6. X-Ray diffraction patterns for the gels obtained from UA-251M films cured by EB and UV: (A) EB irradiation of 10 Mrad at 25°C; (B) UV irradiation for 0.6 s at 25°C; (C) EB irradiation of 10 Mrad at 65°C.

To confirm this assumption, for three samples, stress–strain curves were measured at 60°C, and the crosslinking density was estimated from the stress–strain curves.

The crosslinking density was evaluated by the average molecular weight between crosslinking junctions, which is calculated according to the theoretical state equation for an ideal rubber,[22]

$$\tau = R \cdot T \cdot (1/v \cdot M_c) \cdot (1 - 2M_c/M) \cdot \left(\alpha - 1/\alpha^2\right) \qquad (4)$$

where R is the gas constant, T is the absolute temperature, M_c is the

TABLE III
Degree of Crystallinity and Crystallite Size of the Gels
from UA-251M Films Cured by EB and UV[a]

Materials	Irradiation condition	Degree of crystallinity (%)	Crystallite size (Å)
Gel of EB-cured UA-251M film	10 Mrad at 25°C	39.8	120
	10 Mrad at 65°C	21.8	141
Gel of UV-cured UA-251M film	0.6 s at 25°C	36.5	85

[a] Original UA-251M: Degree of crystallinity, 47.5%; Crystallite size, 234 Å.
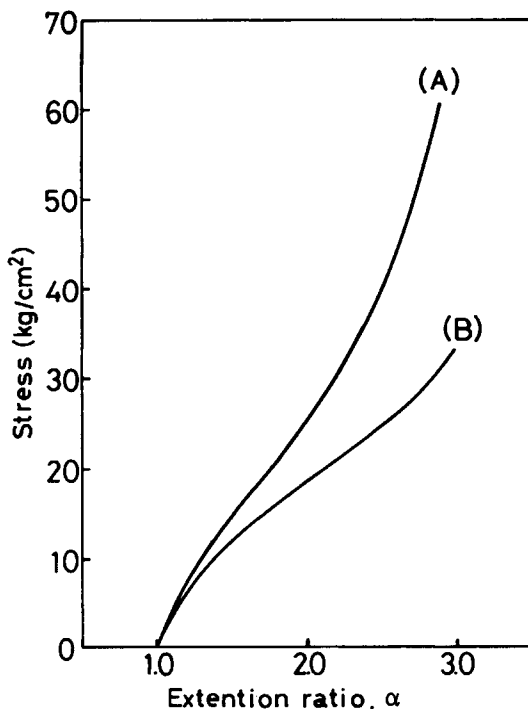
Fig. 7. Stress-extension ratio (α) curves at 60°C of the gels obtained from UA-251M films cured by EB and UV: (A) EB irradiation of 10 Mrad at 25°C; (B) UV irradiation for 0.6 s at 25°C.

molecular weight between crosslinking junctions, M is the molecular weight of an original polymer, τ is the engineering stress, v is the molecular volume, and α is the extension ratio.

However, since the term $(1 - 2M_c/M)$ is a correction for so-called dangling of free ends, the term hardly needs to be added in this system on account of the crosslinking at the end groups of the prepolymers. Accordingly, eq. (4) must be replaced by the following equation in this system:

$$\tau = R \cdot T \cdot (1/v \cdot M_c) \cdot \left(\alpha - 1/\alpha^2\right) \tag{5}$$

In Figure 7 is shown the stress–strain curves obtained from the tensile testing performed at 60°C. Since such equation holds for equilibrium thermodynamics, the tensile testing was carefully carried out slowly enough and was performed at the sufficiently high temperature so that these films might be a nearly ideal rubber. Therefore, when the stress was plotted against $(\alpha - 1/\alpha^2)$, the straight lines was obtained in low elongation range (Fig. 8). Accordingly,

$$a = \rho \cdot R \cdot T/M_c \tag{6}$$

where a is the slope of the straight line and ρ the density. The molecular weight between crosslinking junctions was calculated from eq. (6).

As shown in Table IV, the gel film obtained by UV irradiation for 0.6 s exhibited the molecular weight between crosslinking junctions of about 2500.
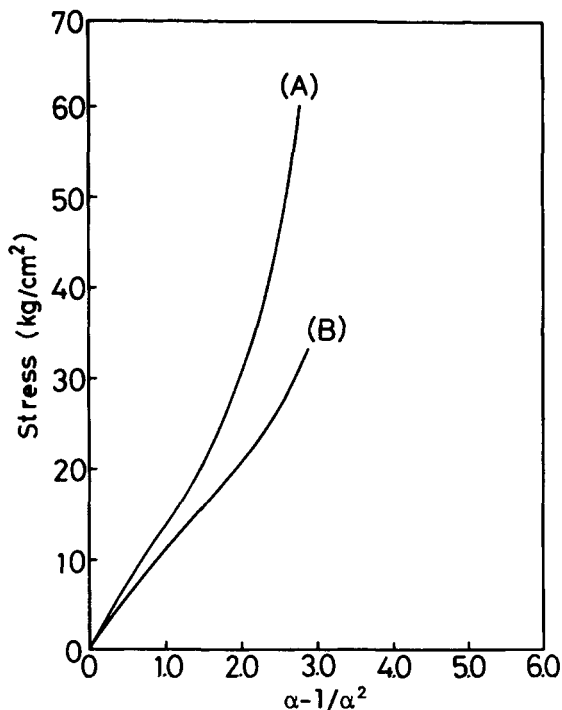
Fig. 8. Stress–$(\alpha - 1/\alpha^2)$ plots from stress–extension ratio (α) data at 60°C obtained from the gels of UA-251M films cured by EB and UV: (A) EB irradiation of 10 Mrad at 25°C; (B) UV irradiation for 0.6 s at 25°C.

Because $\overline{M}_n$ of the original polyurethane–acrylate prepolymer is about 3200, it is supposed that the reaction by UV irradiation occurred almost exclusively with acryl double bonds. On the other hand, smaller M_c values (1930 and 1700) for the EB-gels indicate that the reaction by EB irradiation occurred not only with acryl double bonds but also in polymer chains. In addition, as the reaction in polymer chains takes place in an amorphous phase more readily than in a crystallite phase,[23] it is reasonable that the M_c of EB-gel-65 was smaller than that of EB-gel-25.

TABLE IV

Molecular Weight between Crosslinking Junctions Calculated from Stress–$(\alpha - 1/\alpha^2)$ Plot

Materials	Irradiation condition	Molecular weight between crosslinking junctions M_c, $\times 10^3$
Gel of EB-cured UA-251M Film	10 Mrad at 25°C[a]	1.93
	10 Mrad at 65°C[b]	1.70
Gel of UV-cured UA-251M film	0.6 s at 25°C[c]	2.51

[a] Gel fraction 98.4%.
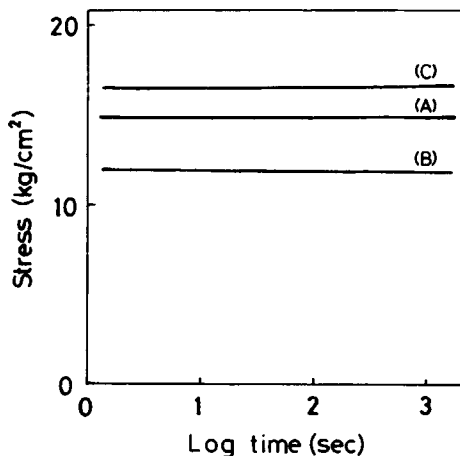[b] Gel fraction 97.2%.
[c] Gel fraction 96.1%.

Fig. 9. Stress–time plot for the gels of UA-251M films cured by EB and UV above the melting point (at 60°C) in a stress relaxation experiment ($\alpha = 1.5$): (A) EB irradiation of 10 Mrad at 25°C; (B) UV irradiation for 0.6 s at 25°C; (C) EB irradiation of 10 Mrad at 65°C.

It is obvious that the crosslinking brought about predominantly by the polymerization at the terminal acryl double bonds. In addition, the crosslinking density obtained from the stress–strain measurement was supported by the stress relaxation measurements above the T_m (60°C) and under $\alpha = 1.5$ (Fig. 9). Stress–time plots for the gel films show the given stress depending on the crosslinking density but no stress–relaxation. This indicates that the relaxation due to entanglements of dangling polymer chains does not occur and agrees well with the results obtained by Wilkes and co-workers.[12] But, in this system, it is assumed that the differences of crosslinking densities depend on the crosslinking between the poly(butylene adipate) portions.

To confirm the above assumption, the EB and the UV irradiation to the ethyl-alcohol-capped polyurethane prepolymer (U-251M) without acryl double bond were carried out, and the GPC measurements of the irradiated prepolymers were done. As for the UV irradiation, there was neither an increase in molecular weight nor the formation of gel (Table V). In contrast, the EB irradiation caused an increase in molecular weight and a gel formation. Therefore, the film obtained by EB irradiation had higher crosslinking density than that by UV irradiation because of the crosslinking between polymer chains in the amorphous phase.

TABLE V
Results Obtained from GPC Chromatograms[a] and Gel Fraction about U-251M[b]

Irradiation condition	Gel Gel fraction (%)	Soluble part Weight average molecular weight $\overline{M}_w, \times 10^4$	Number average molecular weight $\overline{M}_n, \times 10^4$	Dispersity $\overline{M}_w/\overline{M}_n$
10 Mrad at 25°C	5.9	1.90	1.22	1.56
0.6 s at 25°C	1.2	1.56	1.10	1.45

[a]Soluble parts of U-251M cured by EB and UV.
[b]$\overline{M}_w$, 1.56×10^4; $\overline{M}_n$, 1.08×10^4; $\overline{M}_w/\overline{M}_n$, 1.44 (the original U-251M).

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