Synthesis of polymer materials by low-energy electron beams: 5. Effects of prepolymer molecular weight on structure and properties of electron-beam-cured gel films

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The effects of prepolymer molecular weight on the structure and properties of electron-beam-cured (EB-cured) gel films were investigated. The molecular weight of the urethane–acrylate prepolymer, which was synthesized by reaction of poly(butylene adipate) diol (PBAD), 4,4′-diphenylmethane diisocyanate (MDI) and 2-hydroxyethylacrylate (HEA), was varied between 1450 and 3200 by changing the molecular weight of PBAD. Above a prepolymer molecular weight of 2700, the crystallinity arising from PBAD moieties decreased with decreasing molecular weight for both the prepolymer films and EB-cured gel films. Below a molecular weight of 1700, these films had no crystallinity and gave an amorphous film. But the rigidity of the polymer chains in the amorphous phases increased with decreasing molecular weight of prepolymer below 2700 because of an increase in the MDI content. The production of crosslinking junctions by EB polymerization, which contain the crosslinking between PBAD chains, contributed dominantly to decreases both in the crystallinity above 2700 and in the polymer chain mobility below 2700. Such phase and crosslinking structure played an important role in thermal properties and resulted in different mechanical properties. The Young's modulus, tensile strength and elongation at break showed minimum values at a prepolymer molecular weight of 1700. The stress at yield was found only in the semicrystalline gel film above 2700.

(Keywords: electron-beam solid-state polymerization; urethane–acrylate; phase structure; crosslinking density; morphology; hydrogen bond; mechanical properties)

INTRODUCTION

Various kinds of electron-beam-curable (EB-curable) resins composed of EB-curable acryloyl monomers and/or prepolymers have been prepared for coating applications[1–3]. However, there are only a few fundamental investigations on the structure and properties of EB-cured materials[4–6]. In order to design new EB-curable materials, it is important to elucidate correlations among the structure of EB-curable monomers and prepolymers, the properties of EB-cured polymers and the features of EB polymerization.

So far, we have studied EB solid-state polymerization of a semicrystalline urethane–acrylate prepolymer. Comparisons of an EB-cured film with a u.v.-cured one were reported[7,8]. It has been revealed that EB solid-state polymerization of the semicrystalline urethane–acrylate prepolymer produces highly crosslinked polymer materials with retention of the original crystalline structure[7]. In addition, it was found that there is an optimum EB irradiation dose for the mechanical properties of the EB-cured film[8]. Since such characteristics of the EB-cured film might be governed by the prepolymer structure, the molecular design of prepolymers for EB solid-state polymerization is important for properties of the resulting polymer materials.

In this study, it is reported that the change in molecular weight of urethane–acrylate prepolymers to a large extent affects their crystalline and amorphous structure, and mechanical properties of the EB-cured film.

EXPERIMENTAL

Materials

A series of urethane–acrylate prepolymers of different molecular weights ($\bar{M}_n$) were synthesized through two-step reactions in the same way as in the previous paper[7]. After 2 equivalents of poly(butylene adipate) diol (PBAD) (from Nippon Polyurethane Ind. Co. Ltd) were allowed to react with 1 equivalent of 4,4′-diphenylmethane diisocyanate (MDI), 2.1 equivalents of 2-hydroxyethylacrylate (HEA) were added to the isocyanate-capped intermediate. The formula of the urethane–

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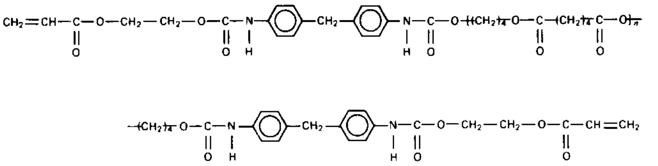
acrylate prepolymer is given as follows:



Four kinds of PBAD with different molecular weights ($\bar{M}_n$) were used to vary the molecular weight of the prepolymer.

Electron-beam irradiation

The prepolymer films were cast from the prepolymer solutions. Methyl ethyl ketone (MEK) was used as solvents for UA-251M and UA-201M, and dimethylformamide (DMF) for UA-101M and UA-071M. After casting, the films were dried at room temperature and then under vacuum. They were melted in an oven at 80°C for 0.5 h and cooled to room temperature before EB irradiation. The thickness was about 40 μm.

An electro-curtain type accelerator (Energy Science Inc.) equipped with a linear filament was used as an electron-beam source. EB irradiation was performed under nitrogen atmosphere. The irradiation dose ranged from 0.5 to 20 Mrad using a beam current of 1 to 20 mA at an acceleration voltage of 175 kV.

Characterization methods

For EB-cured films, the following measurements were performed using gel films extracted with tetrahydrofuran (THF) to avoid the effect of unreacted components similarly to the previous paper[7]. For instance, the gel film obtained from UA-251M is designated as UA-251M gel film.

The gel fraction was measured by means of extraction with THF at 25°C for 72 h. The soluble and insoluble parts were dried under vacuum and weighed to give the gel fraction.

Table 1 Characterization of urethane–acrylate prepolymers

Prepolymer[a]		PBAD[b]	PBAD content	MDI content
Symbol	$\bar{M}_n$	$\bar{M}_n$	(wt%)	(wt%)
UA-251M	3200	2500	78.1	15.6
UA-201M	2700	2000	74.1	18.5
UA-101M	1700	1000	58.8	29.4
UA-071M	1450	750	51.7	34.5

[a] Calculated from $\bar{M}_n$ of poly(butylene adipate) diol (PBAD), 4,4'-diphenylmethane diisocyanate (MDI) and 2-hydroxyethylacrylate (HEA)
[b] Estimated by end-group assay

The per cent transmittance at the wavelength of 700 nm was measured at 25°C using a u.v./vis recording digital spectrophotometer (Japan Spectroscopic Co. Ltd).

The degree of crystallinity and the crystallite size were calculated from the X-ray diffraction pattern, which was obtained using a Geigerflex (Rigaku Denki Co. Ltd).

The glass transition temperature (T_g), the melting point (T_m), the heat capacity change (ΔC_p) at the glass transition and the heat of fusion (ΔH) were determined by differential scanning calorimetry (d.s.c.). D.s.c. measurements were performed from −100 to 100°C using a Perkin–Elmer DSC-II. The heating rate was 20°C min^{-1}. The samples were placed in the DSC-II at 100°C and then cooled to −100°C at a cooling rate of 80°C min^{-1}.

The morphology of the gel film surface was observed using an Akashi scanning electron microscope (SEM) (model Alpha-30W).

I.r. spectra were obtained by using a Hitachi infra-red spectrophotometer (model 260-10).

Stress–strain curves were measured using a Tensilon model UTM-III-100 (Toyo Baldwin Co. Ltd). Testing sample films were 80 mm long and 10 mm wide. The measurements were run with a crosshead speed of 50 mm min^{-1} and a gauge length of 40 mm at 25°C.

RESULTS AND DISCUSSION

Electron-beam solid-state polymerization of urethane–acrylate prepolymers

The characteristics of the four prepolymers (UA-251M, UA-201M, UA-101M and UA-071M), which were synthesized by using poly(butylene adipate) diol (PBAD) of different molecular weights, are summarized in *Tables 1* and *2*.

The casting films of UA-251M and UA-201M were opaque, while those of UA-101M and UA-071M were transparent. This is due to the difference in crystallinity of the prepolymers. It is obvious that comparing UA-251M of $\bar{M}_n = 3200$ with UA-201M of $\bar{M}_n = 2700$, the decrease in the molecular weight caused the decrease in the crystallinity. As the molecular weight decreased to about 1700, the prepolymer showed no crystallinity (*Table 2*). Accordingly, the formation of crystalline region needs PBAD moieties with molecular weight more than about 2000. On the other hand, the glass transition temperature (T_g) increased with decreasing molecular weight.

The heat capacity change (ΔC_p) at the glass transition rose as the molecular weight was increased up to 2700, and then the ΔC_p value for UA-251M largely decreased. The gradual rise in ΔC_p might be due to a decrease in the MDI content, and the large decrease due to a reduction in polymer chain mobility in an amorphous phase because of high crystallinity[9].

Table 2 Structure and properties of urethane–acrylate prepolymers

	X-ray diffraction		Differential scanning calorimetry			
Prepolymers	Degree of crystallinity (%)	Crystallite size (Å)	Glass transition temperature, T_g (°C)	Melting point, T_m (°C)	Heat capacity change, $\Delta C_p \times 10^2$ (cal g^{-1} °C^{-1})	Heat of fusion, ΔH (cal g^{-1})
UA-251M	47.5	234	−35.9	59.2	1.9	12.3
UA-201M	31.0	211	−36.5	48.5	9.1	8.5
UA-101M	–	–	−21.6	–	8.6	–
UA-071M	–	–	−13.9	–	8.0	–

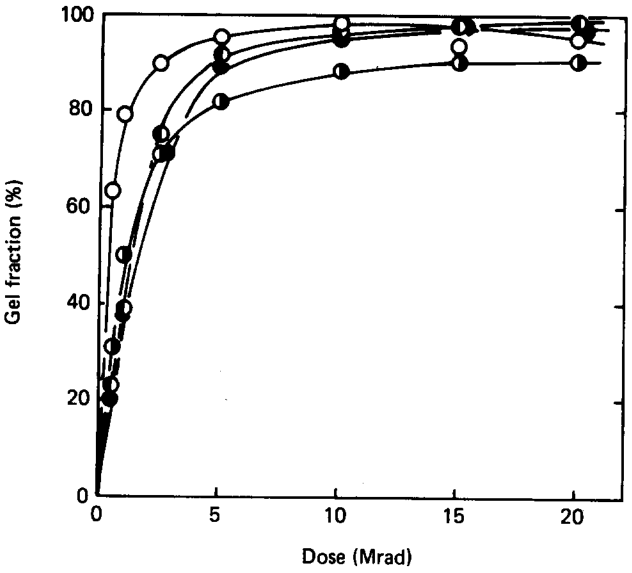


Figure 1 Gel fraction as a function of dose for the urethane–acrylate prepolymers with different molecular weights: (○), UA-251M ($\bar{M}_n$=3200), (◑), UA-201M ($\bar{M}_n$=2700); (◐), UA-101M ($\bar{M}_n$=1700); (●), UA-071M ($\bar{M}_n$=1450)

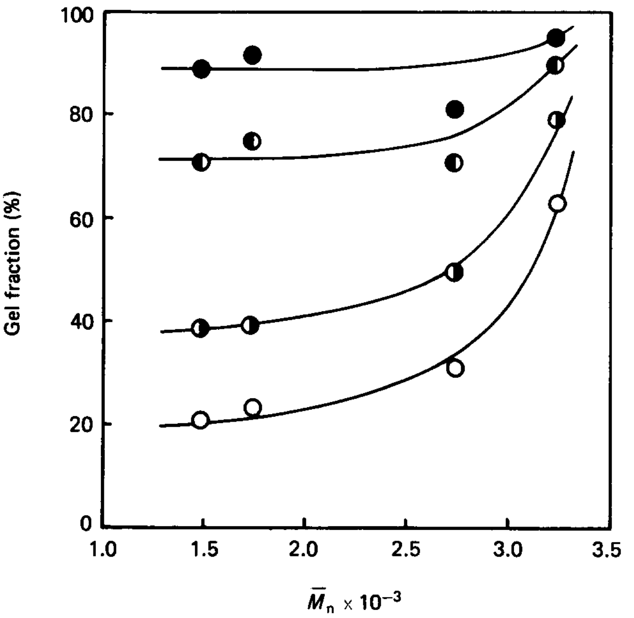


Figure 2 Gel fraction as a function of the prepolymer molecular weight ($\bar{M}_n$). Dose (Mrad): (○), 0.5; (◑), 1.0; (◐), 2.5; (●), 5.0

When the prepolymers were exposed to an electron beam, the gel fractions reached saturation at 10 Mrad irradiation (*Figure 1*). But it is perceived that the rate of gel formation is different among the prepolymers below 5 Mrad. To clarify this point, the gel fraction was plotted against prepolymer molecular weight (*Figure 2*). The gel fraction rose with increasing prepolymer molecular weight, the tendency appearing more remarkably at lower doses. It is assumed that as the crystallinity increased, acryloyl groups might be localized in positions favourable to EB reaction.

Morphology of electron-beam-cured gel films

Transparency and morphology of the gel films were measured on films that reacted completely at 10 Mrad irradiation. Per cent transmittance of the gel films after extraction with THF is shown in *Figure 3*. In analogy with the prepolymer films, the gel films obtained from UA-251M and UA-201M were opaque, while those from UA-101M and UA-071M were transparent. Thus, it was assumed that the morphologies of prepolymers were maintained after EB irradiation.

As shown in *Figure 4*, the scanning electron micrographs of the gel film surfaces apparently changed with molecular weight of prepolymers. The gel film obtained from UA-251M with $\bar{M}_n$ = 3200 showed a rough surface originating from a spherulitic texture[6]. This texture nearly disappeared on the gel film surface obtained from UA-201M with $\bar{M}_n$ = 2700. The surfaces obtained from prepolymers of lower molecular weights had perfect flatness. It was concluded that such changes in transparency and morphology were caused by decrease in crystallinity resulting from the PBAD moieties.

Structure of electron-beam-cured gel films

The crystallinity of the prepolymers played an important role in the reactivity of the prepolymer and therefore in the morphology of the resulting gel film. The degree of crystallinity and the crystallite size were evaluated from X-ray diffraction patterns for the semicrystalline gel films. The results are outlined in *Table 3*.

The degree of crystallinity of UA-251M gel film (39.8 %) was about 2.4 times as large as that of UA-201M gel film. An analogous tendency was found for the crystallite size. However, comparing the gel film with its prepolymer film, both the degree of crystallinity and the crystallite size decreased after EB polymerization. For UA-251M, the degree of crystallinity and the crystallite size of the gel film were about 84 % and 51 % of the prepolymer, respectively. For UA-201M, these values decreased to about 53 % and 42 %, respectively. Thus, it was revealed that the crystalline region is destroyed by EB polymerization in the prepolymer with smaller molecular weight more

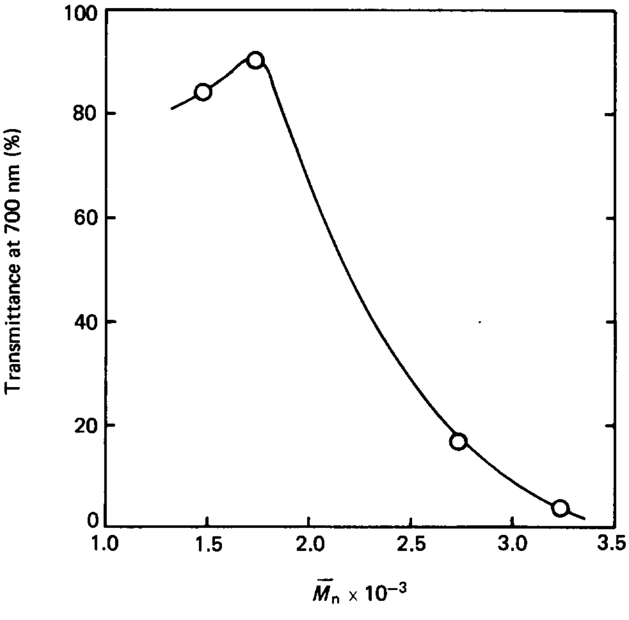


Figure 3 Transmittance as a function of the prepolymer molecular weight ($\bar{M}_n$) for gel films obtained from 10 Mrad irradiated prepolymer films

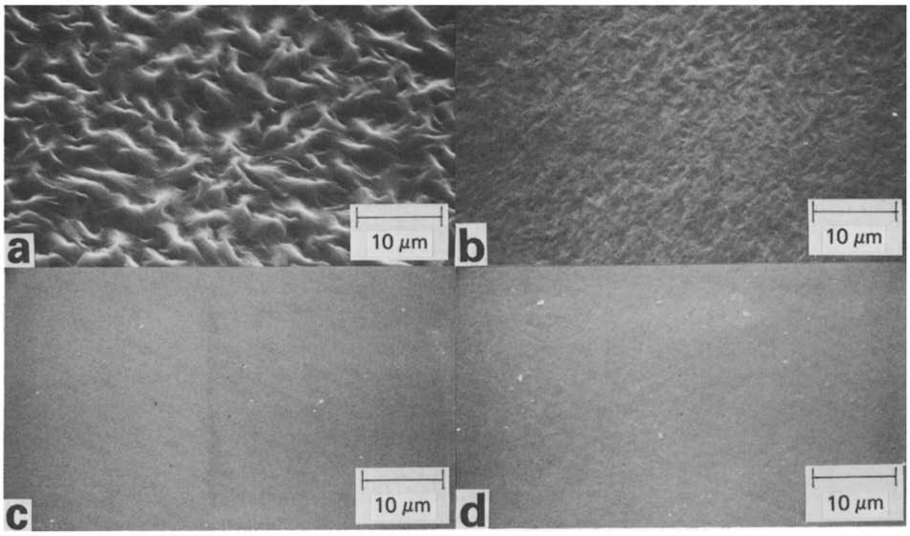


Figure 4 Scanning electron micrographs of the gel film surfaces obtained from 10 Mrad irradiated prepolymer films: (a), UA-251M; (b), UA-201M; (c), UA-101M; (d), UA-071M

Table 3 Structure and properties of EB-cured polyurethane–acrylate gel films

		X-ray diffraction		Differential scanning calorimetry			
Prepolymers	Gel fraction[a] (%)	Degree of crystallinity (%)	Crystallite size (Å)	Glass transition temperature, T_g (°C)	Melting point, T_m (°C)	Heat capacity change, $\Delta C_p \times 10^2$ (cal g^{-1} °C^{-1})	Heat of fusion, ΔH (cal g^{-1})
UA-251M	98.4	39.8	120	−41.5	48.2	5.9	8.1
UA-201M	88.5	16.3	89	−34.8	41.0	4.1	0.1
UA-101M	96.8	–	–	−18.5	–	3.5	–
UA-071M	95.1	–	–	−3.9	–	1.4	–

[a] Irradiation dose: 10 Mrad

readily than in that with larger molecular weight. Since the crystallinity is destroyed by the crosslinking junctions, this phenomenon might be ascribed to the difference in the crosslinking density, which is based not only on the molecular weight of the prepolymer but also on the crosslinking between PBAD chains[8]. Particularly, it is thought that the crosslinking between PBAD chains occurred to a larger extent in prepolymers with smaller molecular weight, considering the crystallinity of the prepolymers.

D.s.c. measurement also revealed that the degree of crystallinity of gel films decreased with decreasing molecular weight of prepolymers (*Table 3*). Both T_m and ΔH diminished with decreasing molecular weight of the prepolymer. The former factor reflects the crystallite size and the perfection of the crystalline structure, and the latter corresponds to the degree of crystallinity.

Moreover, the d.s.c. measurement afforded information about an amorphous phase which is not obtained by X-ray diffraction. As shown in *Figure 5*, T_g and ΔC_p for both gel and prepolymer films were plotted against prepolymer molecular weight.

With decreasing molecular weight, T_g of the gel films increased, whereas ΔC_p decreased. Such tendencies of T_g and ΔC_p for the gel films correspond mainly to an increase in the MDI content and the crosslinking density due to a decrease in the molecular weight of PBAD (*Table 1*).

Effects of EB irradiation on T_g and ΔC_p were remarkably different between the molecular weights of 3200 and less than 2700. For the prepolymers with $\bar{M}_n < 2700$, the T_g values were slightly increased by polymerization, and the ΔC_p values were to a large extent decreased. This is due to the decrease in polymer chain mobility which was caused by crosslinking[10–12].

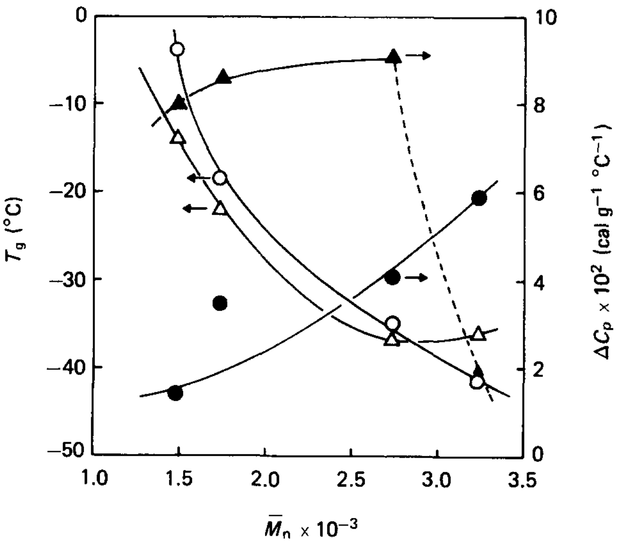


Figure 5 Glass transition temperature (T_g) and heat capacity change (ΔC_p) at the glass transition as functions of the prepolymer molecular weight ($\bar{M}_n$) for the prepolymers and their gel films at 10 Mrad: (△, ▲), prepolymers; (○, ●), gel films

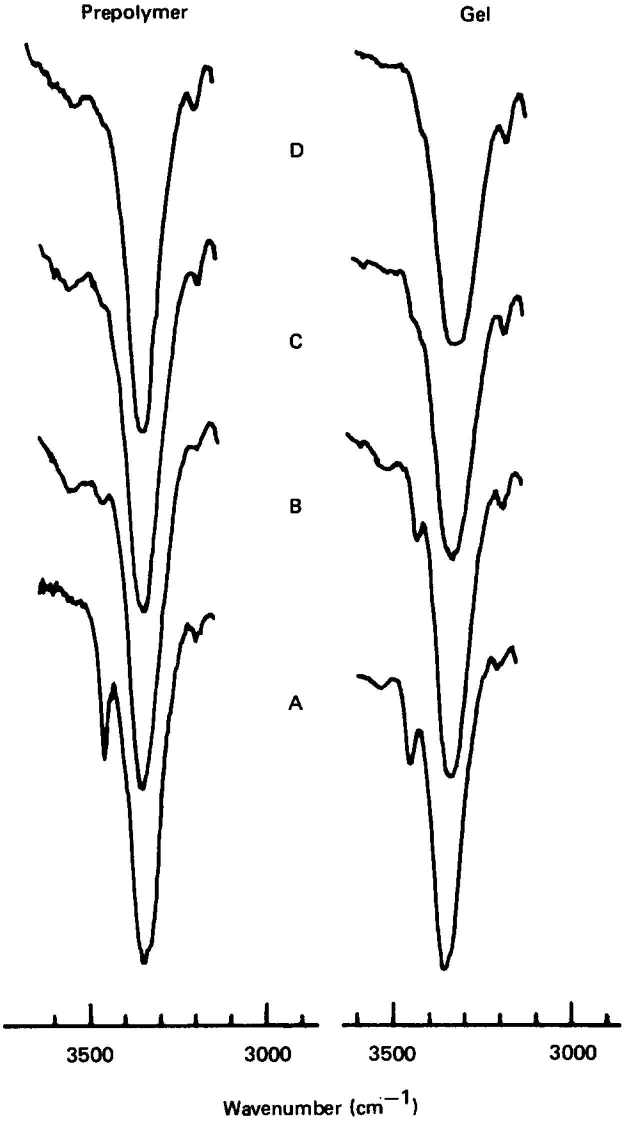


Figure 6 I.r. spectra of the prepolymers and their gel films at 10 Mrad: (A), UA-251M; (B), UA-201M; (C), UA-101M; (D), UA-071M

Accordingly, the effects of EB irradiation on T_g and ΔC_p below 2700 depends dominantly on the crosslinking, which contains the crosslinking between PBAD chains.

On the other hand, for the prepolymer with $\bar{M}_n = 3200$, the molecular weight between crosslinking junctions was so large that the crosslinking junctions could not decrease the polymer chain mobility. However, the crystalline phases, which work as crosslinking junctions or filler[13,14], could be destroyed by the crosslinking junctions. Therefore, such alternation from the crystalline phase to the amorphous phase by EB polymerization enhances the polymer chain mobility in the amorphous phase, leading to a decrease in T_g and an increase in ΔC_p. Above $\bar{M}_n = 3200$, the change of crystallinity mainly influences T_g and ΔC_p. Although there is this effect also at $\bar{M}_n = 2700$, the crosslinking junctions play an important role in the destruction of the crystallinity as mentioned above. That is to say, in the case of $\bar{M}_n = 2700$, it might be proper to think that the effect of crosslinking is larger than that of the crystallinity change.

Nest, i.r. spectra were measured to examine the interaction between polymer chains. Hydrogen bonds are assumed to result from the hydrogen atoms of NH groups of urethane bonds and the C=O groups of urethane or ester bonds, in the urethane–acrylate prepolymers and EB-cured gel films. As shown in *Figure 6*, an NH stretching absorption changed with factors such as the molecular weight of prepolymer, the crosslinking and the crosslinking density.

Above $\bar{M}_n = 2700$ (UA-251M and UA-201M), a free NH stretching absorption near 3450 cm^{-1} was observed, while below $\bar{M}_n = 1700$, the free NH stretching absorption was not observed in either the prepolymers or the gel films. It is suggested that the crystallinity originating from PBAD moieties to some extent prevented the MDI units from interacting with other polymer chains, and that hydrogen bonds were not formed.

In addition, the bonded NH stretching absorption around 3350 cm^{-1} was broadened by EB irradiation. Since the extent of broadening was larger in the prepolymer with lower molecular weight, the broadening might be caused mainly by crosslinking with terminal acryloly groups and PBAD chains.

Mechanical properties of electron-beam-cured gel films

EB-irradiated films showed good mechanical properties. Representative stress–strain curves for the gel films obtained with 10 Mrad irradiation are shown in *Figure 7*. The shape of the stress–strain curve, showing a combination of various mechanical properties, differed with change in the prepolymer molecular weight. To elucidate this difference, the Young's modulus, stress at yield, elongation at break and tensile strength were determined from the stress–strain curves and then each value was plotted against the prepolymer molecular weight. These results are shown in *Figures 8* and *9*.

It is noteworthy that the Young's modulus, tensile strength and elongation at break indicated minimum

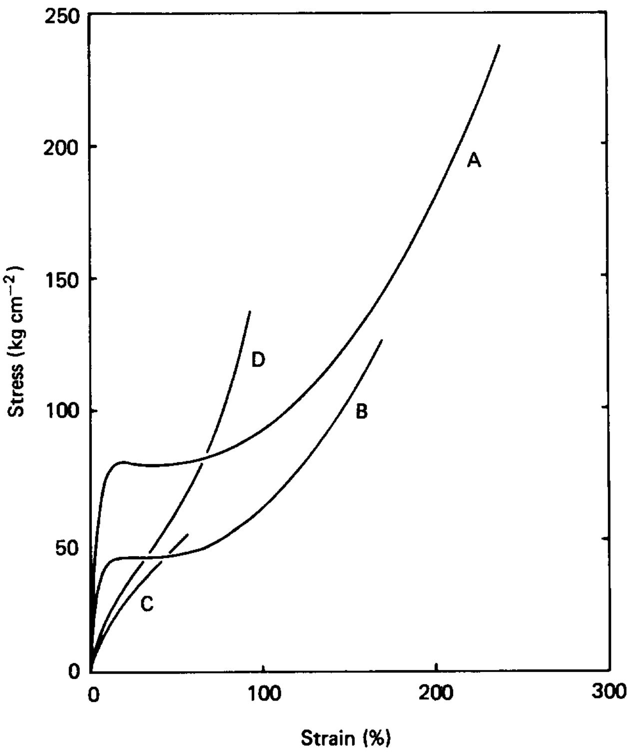


Figure 7 Stress–strain curves of the gel films obtained from 10 Mrad irradiated prepolymer films: (A), UA-251M; (B), UA-201M; (C), UA-101M; (D), UA-071M

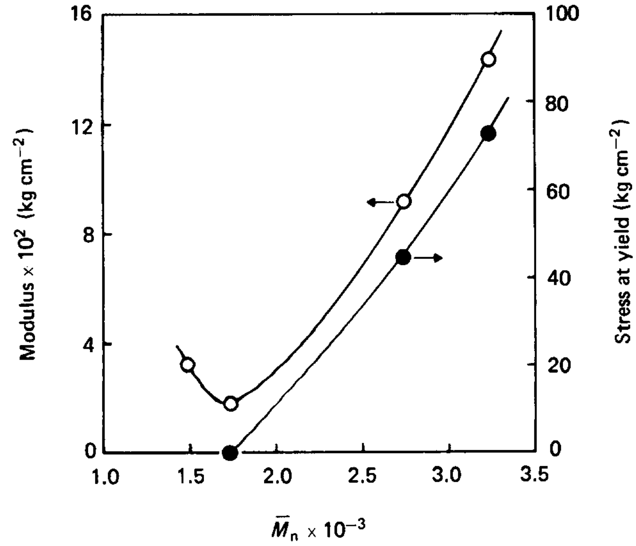


Figure 8 Young's modulus and stress at yield as functions of the prepolymer molecular weight ($\bar{M}_n$) for the gel films obtained from 10 Mrad irradiated prepolymer films

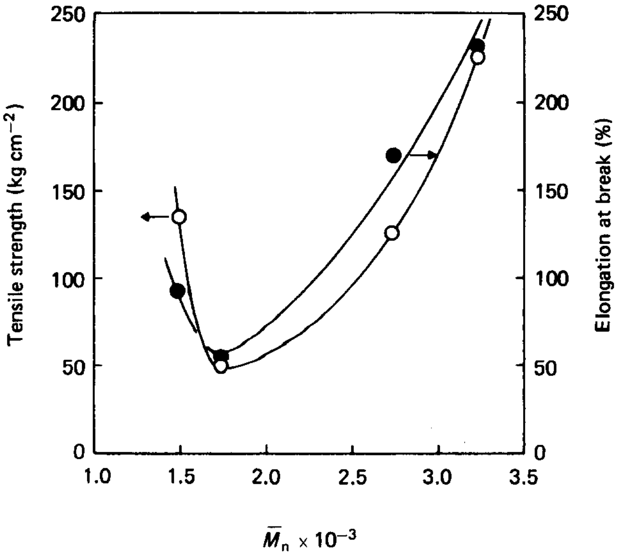


Figure 9 Tensile strength and elongation at break as functions of the prepolymer molecular weight ($\bar{M}_n$) for the gel films obtained from 10 Mrad irradiated prepolymer films

values at the molecular weight of 1700. Previously, it was reported by Walsh and Oraby[4] that, in polyurethane–acrylate based on poly(ethylene adipate), the modulus and tensile strength decrease with increasing prepolymer molecular weight. In the case of poly(ethylene adipate)-based polymer, the relationships between the mechanical property and prepolymer molecular weight seem to be ascribed to such film morphology as one-phase structure[5]. On the contrary, in the present study, the structure of gel films changed from an amorphous film to a semicrystalline film with change of prepolymer molecular weight.

Above $\bar{M}_n = 1700$, the modulus and the tensile strength increased possibly with an increase in the crystallinity. The elongation was also enhanced with an increase in the molecular weight. This is possibly attributed to a decrease in crosslinking junction.

Below $\bar{M}_n = 1700$, the modulus and the tensile strength rose again because of increases in both the MDI content and the crosslinking density. Some arrangements of MDI might be related to this behaviour.

The stress at yield was found only in UA-251M and UA-201M gel films containing the crystalline region, and was dependent on the degree of crystallinity. UA-101M and UA-071M gel films, consting of an amorphous phase, showed a rubber-like elasticity.

As a conclusion, EB polymerization of polyurethane–acrylate can provide gel films with different phase structure and good mechanical properties by changing the molecular weight of the prepolymer.

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