

Synthesis of Polymer Materials by Low Energy Electron Beam. III. Effects of Polymerization Temperature in EB Solid-State Polymerization of Semicrystalline Urethane-Acrylate Film

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Synopsis

In an electron beam (EB) polymerization of a urethane-acrylate prepolymer, the polymerization temperature greatly affected the structure and properties of the resulting gel film. Urethane-acrylate, which was synthesized by the reaction of poly(butylene adipate)diol, 4,4'-diphenylmethane diisocyanate, and 2-hydroxyethyl acrylate, was used as a prepolymer. The prepolymer was semicrystalline and showed a melting point in the region of 50–60°C. The maximum polymerization rate of the prepolymer was obtained when the prepolymer film was irradiated in the temperature range of 25–40°C. EB polymerization below the melting point (T_m) of the prepolymer produced semicrystalline polyurethane-acrylate gel films with a spherulitic texture. On the other hand, EB polymerization above the T_m destroyed the crystalline phase of the prepolymer to give transparent gel films. The gel film cured below the T_m had higher stress at yield, Young's modulus, and tensile strength than those cured above the T_m . Such temperature effects are attributed to whether or not the EB polymerization proceeds with retention of crystalline structure of the prepolymer.

INTRODUCTION

Low-energy electron beam (EB) processing has developed as an alternative to conventional heat processing from energy-saving, ecological, and economical viewpoints.¹ Most EB-curable resins are composed of reactive prepolymers and/or monomers, both of which have acryloyl or methacryloyl groups. These EB-curable materials and components have been prepared for coating applications.^{2–5}

However, EB processing can be used not only as a substitute for heat processing, but also for production of new materials with excellent properties which could be induced by the high energy of EB. It has been reported that the polymeric reactions of polymer–monomer mixture by EB cause crosslinking, homopolymerization, and graft polymerization. When pressure-sensitive adhesives were produced by EB irradiation, the resulting crosslinking networks and graft polymer had an important influence on their physical properties.⁶

Recently, we reported the relationships between the structure and properties of gel films obtained by EB and ultraviolet (UV) solid-state polymeriza-

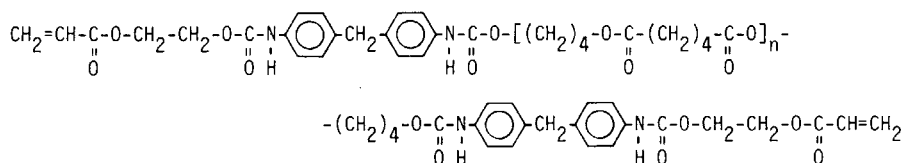
tions of a semicrystalline urethane-acrylate film.⁷ It was revealed that the gel film produced by EB had higher crystallinity and better mechanical properties than that produced by UV. This may be because the prepolymer is crosslinked by EB irradiation with retention of the original crystalline phase, while UV polymerization, which is accompanied by an increase in polymerization temperature, proceeds with destruction of the crystalline phase.

In this report, focusing our attention on the effects of a polymerization temperature, EB solid-state polymerizations of the semicrystalline urethane-acrylate were performed at different polymerization temperatures, and the structure and properties of gel films obtained were examined.

EXPERIMENTAL

Materials

The semicrystalline urethane-acrylate prepolymer (UA-251M) was synthesized by the reaction of poly(butylene adipate)diol (PBAD, number-average molecular weight (\bar{M}_n) ~ 2500; Nippon Polyurethane Ind. Co., Ltd.), 4,4'-Diphenylmethane diisocyanate, and 2-hydroxyethyl acrylate according to the previous paper.⁷ The prepolymer chemical structure is given as follows:



The UA-251M films, which were cast on polyethylene terephthalate (PET) film from methyl ethyl ketone (MEK) solution of UA-251M 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.

Irradiation

An electrocurtain-type accelerator (Energy Science Inc.) equipped with a linear filament was used as an electron beam source. EB irradiation was performed under a nitrogen atmosphere and the irradiation dose range was 0.13–10 Mrad using a beam current of 0.5–10 mA at an accelerated voltage of 175 kV.

Polymerization temperature was controlled by heating the film in a thermostatted oven. The UA-251M film kept at the prescribed temperature was exposed to EB within 10 s after removing it out of the oven.

Characterization Methods

Characterization was performed according to the previous paper.⁷ The gel fraction was evaluated by extracting a soluble fraction with tetrahydrofuran (THF) at 25°C for 72 h. The soluble and insoluble parts were dried under vacuum and weighed to give the gel fraction.

The following characterizations of the EB-cured UA-251M films were performed using the gel films which remained after extraction with THF.

The percent transmittance at the wavelength of 700 nm was measured using a UV/VIS recording digital spectrophotometer (Japan Spectroscopic Co., Ltd.) at 25°C.

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.

For each gel film, the melting point (T_m), the heat of fusion (ΔH), the glass transition temperature (T_g), and the heat capacity change (ΔC_p) at T_g were measured calorimetrically using a Perkin-Elmer DSC II. Each thermal property was determined according to a conventional method.⁸ The samples were placed in the DSC at 100°C and then cooled to -100°C at a rate of 80°C/min. The measurements were performed from -100 to 100°C at a heating rate of 20°C/min under a nitrogen stream.

X-ray diffraction patterns were obtained using a Geigerflex (Rigaku Denki Co., Ltd.) with nickel-filtered CuK_α ($\lambda = 0.1542$ nm) radiation. The degree of crystallinity and the crystallite size were estimated in the usual way.⁸

Tensile testing was run on at 25°C using a Tensilon (model 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 80 mm long and 10 mm wide.

RESULTS AND DISCUSSION

Polymeric Reaction of Semicrystalline Urethane-Acrylate

The prepolymer UA-251M exhibited an endothermic peak corresponding to the melting point in the region of 50–60°C on DSC thermogram. This peak rose from PBAD moieties and seemed to be composed of two peaks, which involved crystalline phases with different crystallite sizes. EB solid-state polymerizations of such prepolymer films were carried out under various polymerization temperatures. In Figure 1, the gel fractions are plotted against dose in the polymerization at 25 and 80°C. Both polymerizations were completed by exposure of 5 Mrad. However, in the low dose of 0–1 Mrad, gel formation at 80°C was less than that at 25°C.

To further investigate this phenomenon, the effects of the polymerization temperature on gel fraction were examined in the region of 0.13–1.0 Mrad under a constant dose rate of 1.52 Mrad/s. The results are shown in Figure 2. The gel fraction indicated a maximum value in the 25–40°C range, and the dependence of the gel fraction on the polymerization temperature decreased with an increase in dose.

These features can be elucidated according to a simple kinetic equation (1) for radical solid-state polymerization of vinyl monomer.⁹

$$R_p = -\frac{d(M)}{dt} = k_p \cdot k_i \cdot f \cdot I \cdot t \cdot (M) \quad (1)$$

where R_p denotes an overall reaction rate, (M) a monomer concentration, k_p a propagation rate constant, k_i an initiation rate constant, f an initiation

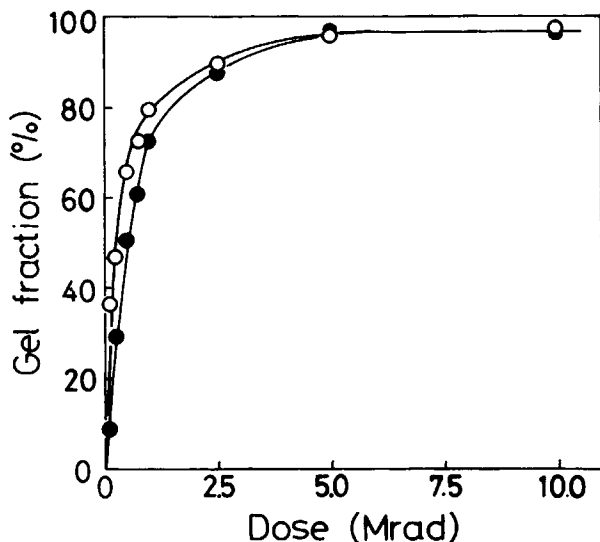


Fig. 1. Gel fraction as function of dose for EB solid-state polymerization of UA-251M film. The polymerization temperature ($^{\circ}\text{C}$): (○), 25; (●), 80.

efficiency, I a dose rate, and t an irradiation time. Below the T_m of the prepolymer, it is assumed that acryloyl double bonds are to some extent concentrated because of ordering of PBAD moieties. This concentration caused an acceleration of gel formation. On the other hand, it is considered that above the T_m , acryloyl double bonds are not localized because of higher chain mobilities, causing the decrease in the reaction rate. This suggests that

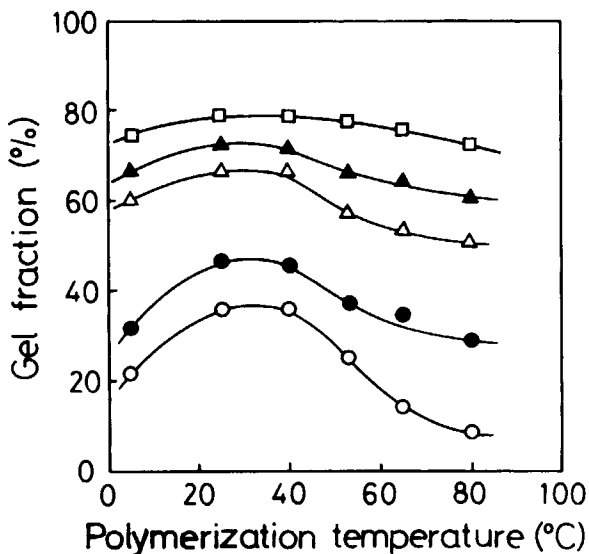


Fig. 2. Gel fraction as function of polymerization temperature for EB solid-state polymerization of UA-251M film. Dose (Mrad): (○), 0.13; (●), 0.25; (△), 0.50; (▲), 0.75; (□), 1.00. Dose rate: 1.52 Mrad/s.

in Eq. (1), the concentration (M) of an acryloyl double bond depends on the phase structure. In addition, the effect of (M) on R_p is thought to be much larger than that of the thermodynamic effects due to k_p and k_t . However, below 20°C, the reactivity decreased probably because of the temperature effect. In this way, the phase structure change and the temperature effect resulted in the maximum gel fraction.

In the case of higher doses, the rate of gel formation is affected mainly by the strength of the electron beam, and hence the effects of the polymerization temperature might be neglected. In Eq. (1), such a tendency is represented by a remarkable increase in $I \times t$.

Structure of EB-Cured Polyurethane-Acrylate Gel Films

In order to elucidate the temperature effect, the structure of gel films polymerized at different temperatures in a constant irradiation dose of 5 Mrad was examined.

Although the gel films obtained at 5 Mrad had the same gel fraction independent of the polymerization temperature, the percent transmittance at 700 nm increased steeply in the polymerization at 40–50°C and reached more than 80% of transmittance at 80°C (Fig. 3). This is assumed to be due to the morphological change in the dimension of visible light wavelength.

Representative SEM photographs of gel films are shown in Figure 4. The gel film obtained at 25°C (a) had an uneven surface, where a convex part indicates a spherulitic texture originating from PBAD moieties. On the contrary, the gel film obtained at 65°C (b) was a smooth surface, and the texture observed in (a) was not observed. It is evident that such differences in morphology lead to a marked change in the transmittance.

The finer structure of the gel films was investigated. Structural changes associated with polymerization temperature were clearly recognized on DSC

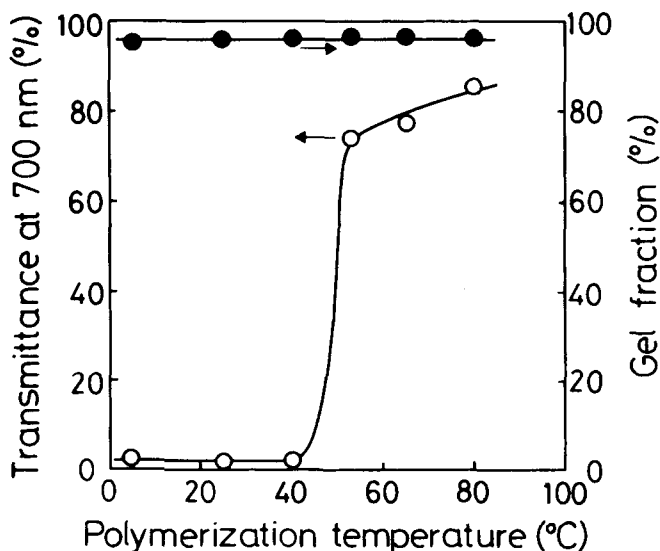


Fig. 3. Transmittance of the gel film obtained from 5 Mrad-irradiated UA-251M film and its gel fraction as functions of polymerization temperature.

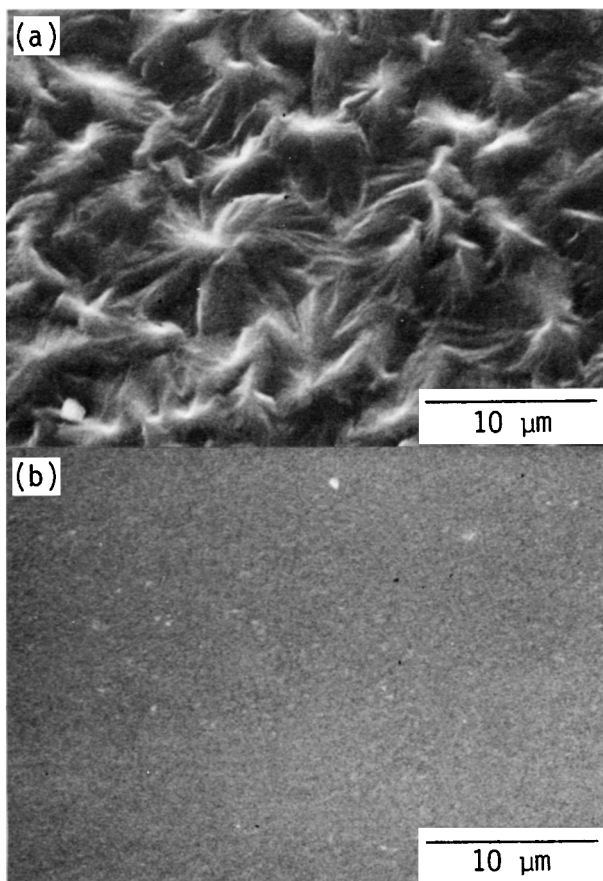


Fig. 4. Surfaces of the gel films obtained from 5 Mrad-irradiated UA-251M films at polymerization temperatures of (a) 25°C and (b) 65°C.

thermograms and x-ray diffraction patterns, and were discussed using four thermal parameters, which contain T_m , ΔH , T_g , and ΔC_p , and two crystallographic parameters, which contain the degree of crystallinity and the crystallite size.

At polymerization temperatures lower than T_m (50–60°C) of the prepolymer UA-251M, T_m of the gel films showed about 53°C, while, at temperatures higher than T_m of UA-251M, it was decreased by about 13 degrees (Fig. 5). Although T_m generally depends on the crystallite size or the imperfection of crystalline structure, the decrease in T_m might be due mainly to the imperfection of the crystalline structure as can be seen from the change of crystallite size (see Fig. 7). It is thought that this imperfection was brought about by inhibition of the recrystallization by the crosslinking junctions,¹⁰⁻¹² which is also supported by the shift of x-ray diffraction peak to a lower angle.

Moreover, as seen in Figure 6, the heat of fusion ΔH , which corresponds to the degree of crystallinity of the gel films, also decreased remarkably in the polymerization around the T_m of the prepolymer. This behavior agreed with the result on the degree of crystallinity from x-ray diffraction (Fig. 7).

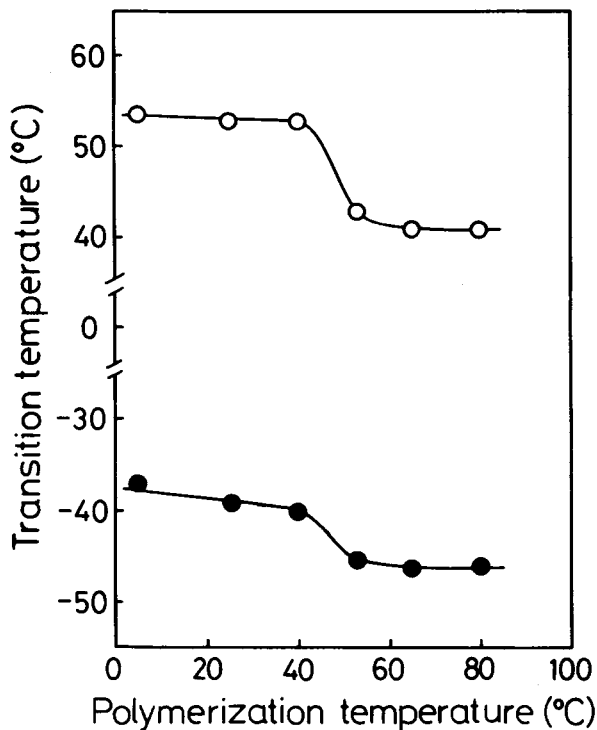


Fig. 5. Thermal properties of the gel film obtained from 5 Mrad-irradiated UA-251M film as functions of polymerization temperature. (○), Melting point, T_m ; (●), Glass transition temperature, T_g .

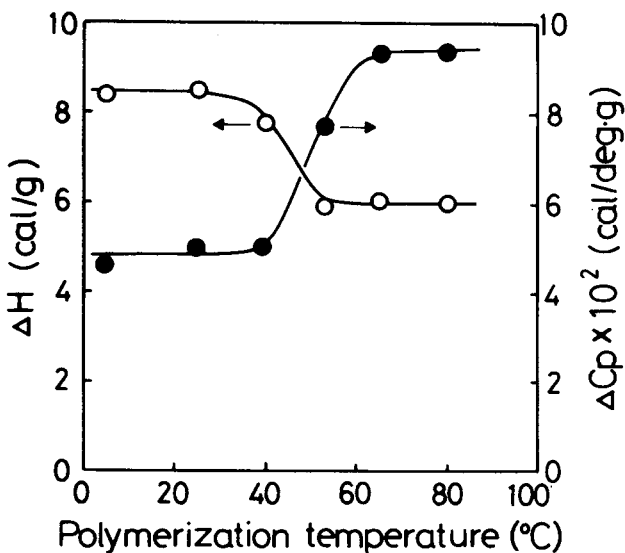


Fig. 6. Heat of fusion (ΔH) and heat capacity change (ΔC_p) of the gel film obtained from 5 Mrad-irradiated UA-251M film as functions of polymerization temperature.

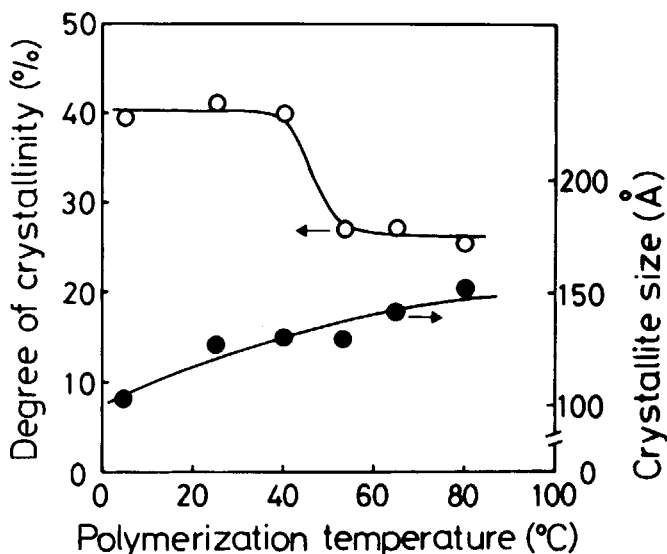


Fig. 7. Degree of crystallinity and crystallite size of the gel film obtained from 5 Mrad-irradiated UA-251M film as functions of polymerization temperature.

The structure change seems to have occurred also in the amorphous phases. T_g of the gel film decreased steeply in the polymerization near the T_m of UA-251M as shown in Figure 5. Although in a few cases T_g depends on the degree of crystallinity,¹³ relationships between T_g and the degree of crystallinity seem not to be evident and the effect of the degree of crystallinity on the T_g is generally known to be small.¹⁴ Thus, effects of polymerization temperature on T_g were discussed using ΔC_p .

According to Wunderlich,¹⁵ ΔC_p per bead, which is the smallest unit of flexibility in polymer chains such as $-\text{CH}_2-$, $-\text{O}-$, and $-\text{CH}(\text{CH}_3)-$, is constant independent of materials. That is,

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

where M is an average molecular weight of bead. This equation means that with increasing ΔC_p , M decreases and hence the mobility of polymer chains in an amorphous phase is enhanced in our case.

ΔC_p increased steeply in the polymerization near the T_m of UA-251M, as shown in Figure 6. This behavior suggests that the flexible polymer chains free of the crystalline segments were generated in the amorphous phase during EB irradiation above 50–60°C. Accordingly, it was concluded that a decrease in T_g was caused by such an increase in the polymer chain mobility.

Mechanical Properties of EB-Cured Polyurethane-Acrylate Gel Films

Tensile testing was performed using the gel films which were produced by the irradiation of 5 Mrad under prescribed polymerization temperatures. The stress at yield, the Young's modulus, the tensile strength, and the elongation

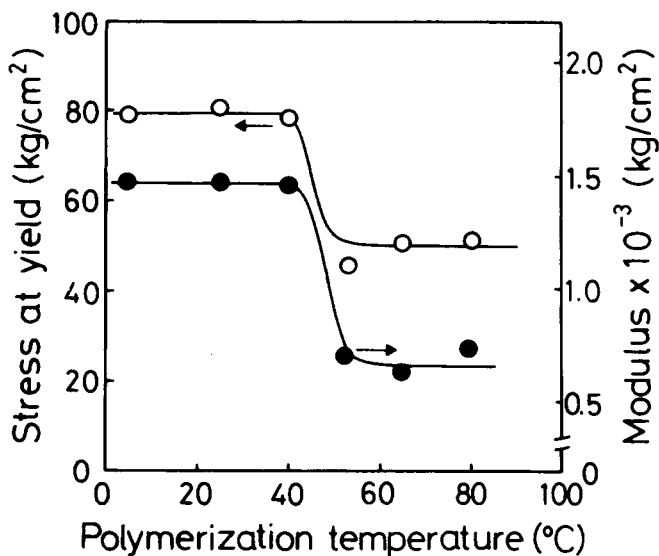


Fig. 8. Stress at yield and Young's modulus of the gel film obtained from 5 Mrad-irradiated UA-251M film as functions of polymerization temperature.

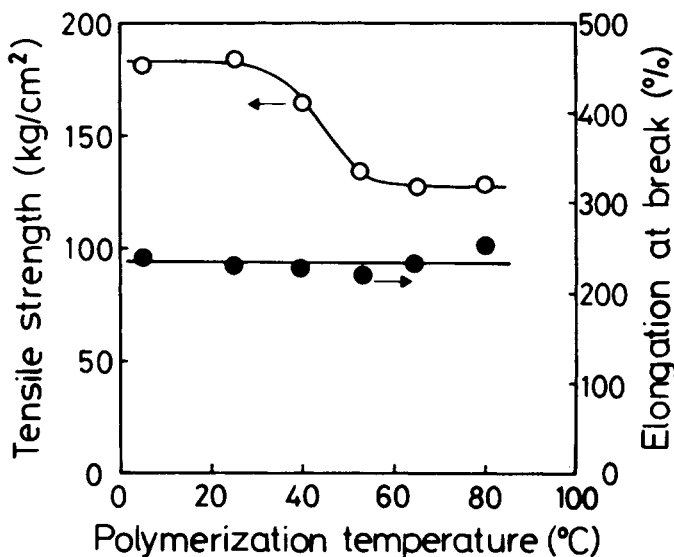


Fig. 9. Tensile strength and elongation at break of the gel film obtained from 5 Mrad-irradiated UA-251M film as functions of polymerization temperature.

at break were estimated from the stress-strain curves obtained, and were plotted against the polymerization temperature. The results are shown in Figures 8 and 9.

All the mechanical properties except the elongation at break decreased steeply in the polymerization near the T_m of UA-251M. Since the gel obtained below the T_m had higher crystallinity than that obtained above the T_m , the crystallites possibly act as a filler or a crosslinking junction.¹⁴

On the other hand, elongation was independent of polymerization temperature. Since, in 5 Mrad irradiation, the reaction occurs predominantly at the terminal acryloyl double bonds,¹⁶ the molecular weight between the cross-linking junctions might be constant in each polymerization temperature, which causes a constant elongation.

Accordingly, polymer films with markedly different structure and properties can be produced by changing solely the polymerization temperature without exchange of a chemical composition. This finding presents a novel synthetic method of polymer materials by low-energy electron beam.

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