

Bulk Polymerization of Polyurethane under High Pressure

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Synopsis

The pressure effect on the reaction kinetics, molecular weight, and the microphase separation of the soft and hard segment of the polyurethane, synthesized under high pressure, was studied. The polymerization rate increased with increasing synthesis pressure and the activation energy of polymerization decreased with increasing synthesis pressure from 22.4 kcal/mol at 1 kg/cm² to 19.4 kcal/mol at 3000 kg/cm². The volume of activation of the polyurethane polymerization was -19.8 cm³/mol at 60°C. Microphase separation between soft and hard segment decreased with increasing synthesis pressure and increased with increasing synthesis temperature. Molecular weight and molecular weight distribution were not influenced by the synthesis pressure.

INTRODUCTION

Reaction Kinetics

The rate of reaction in the liquid state is dependent on pressure. The rate change is often much greater than the volume change caused by pressure, and sometimes is not directly related to the volume change. It reflects the pressure effect on the molecular structure of the participating species, and on the nature of the reaction mechanism.¹

It is well known that the dependence of the rate constant k on pressure is expressed as

$$\left(\frac{\partial \ln k}{\partial P} \right)_T = - \frac{\Delta V^\ddagger}{RT} \quad (1)$$

where ΔV^\ddagger is the volume of activation, the change in molar volume from the reactant to the transition state. According to eq. (1), the effect of pressure on the rate constant depends on the sign and magnitude of the volume of activation. The effect of pressure on addition polymerization has been extensively investigated; Increased pressure usually results in the increased polymerization rate and molecular weight.²⁻⁴ However, the effect of pressure on the condensation polymerization kinetics is not well known.

The effect of pressure on the polyurethane polymerization in the bulk state is studied in this paper.

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Microphase Separation

Elastomeric polyurethane block copolymers consist of alternating blocks of soft segment of low glass transition and highly polar, relatively rigid, hard segment. The soft segment generally consists of polyether or polyester segment such as poly(tetramethylene ether) and poly(tetramethylene adipate) in the molecular weight range from about 600 to 3000. The hard segment is formed from the reaction of the diisocyanate such as diphenylmethane diisocyanate (MDI) or tolylene diisocyanate (TDI) with a low molecular weight glycol or amine such as 1,4-butanediol (1,4-BD) and 3,3'-dichloro-4,4'-diamine diphenyl methane (MOCA).

A considerable amount of research was carried out on the structure and properties of the segmented polyurethane elastomers. These studies, employing small angle X-ray diffraction,⁵ transmission electron microscopy,⁶ and birefringence,⁷ have suggested the existence of domain structure on the order of 100Å in size. Dynamic mechanical studies⁸ have shown the existence of a major glass transition in the soft segment as well as the melting of the hard segment. It is now widely accepted that many of the unusual properties of these elastomers can be attributed to the microphase separation of the hard segment into domains dispersed in the matrix of soft segment.⁹ The rigid domains reinforce the elastomeric matrix by functioning both as the tie-down points and as the filler particles. Such a segmented block polymer exhibits the characteristic properties of the crosslinked elastomer at moderate temperature but flows at temperature above the softening point of the hard domain. This microphase separation is recognized as the principal feature controlling the properties of these elastomers.

The purpose of the present study is to consider the effect of the pressure on the reaction kinetics, the microphase separation, and the molecular weight of the linear segmented polyurethanes synthesized under high pressure.

EXPERIMENTAL

Materials. Commercial grade of the 4,4'-diphenylmethane diisocyanate (MDI) and poly(tetramethylene ether) glycol (PTMG) were used. MDI was stored at 70°C in the oven and filtered prior to use. PTMG was dried at 60°C for 10 h under vacuum before use, and had a number average molecular weight of 1044 g (OH value of 107). Reagent grade 1,4-butanediol (BD) with the moisture content less than 0.02% was used.

PU-Prepolymer Synthesis. The isocyanate-terminated polyurethane prepolymer was prepared by reacting 1 eq poly(tetramethylene ether) glycol with 2 eq 4,4'-diphenylmethane diisocyanate at 60°C without any catalyst. Into a four-neck flask equipped with a high-torque stirrer, thermometer, nitrogen inlet, and reflux condenser were put 2 eq MDI which were heated to 60°C. One equivalent of PTMG was slowly added with stirring. The reaction was carried out until the theoretical isocyanate content was reached as determined by the di-*n*-butylamine method.¹⁰

Kinetics. PU prepolymer and 1,4-butanediol were mixed thoroughly, and the air entrapped during mixing was removed by applying a vacuum. The mixture was charged into a lead capsule (11 mm O.D., 9 mm I.D., 45 mm H), and the capsule was inserted into a cylindrical cavity of a mold made of

SNCM8 alloy steel (100 mm O.D., 11.5 mm I.D., 100 mm H). Pressure was applied through a piston rod in a 12-ton hydraulic press (Fred S. Caver Inc., Model-C12). The mixture was polymerized at 40, 50, 60, and 70°C under varying pressure from atmospheric to 3000 kg/cm². The hard segment content of these polyurethanes synthesized from the above mixture is 37 wt %. To avoid additional reaction, the sample was kept in liquid nitrogen before and after the experiment. The reacting mixtures were withdrawn at fixed time intervals, and dissolved in 10 mL standard di-*n*-butylamine solution. The NCO % was determined by backtitrating the excess di-*n*-butylamine with aqueous HCl solution, using 100 mL isopropanol as a coupling agent.

Dynamic Mechanical Analysis (DMA). The dynamic mechanical properties were measured using a DuPont Model 981-990 dynamic mechanical analyzer. A constant heating rate of 10°C/min was employed over a temperature range of -70-50°C. The oscillation amplitude was 0.2 mm and the gap setting was 13 mm. The DMA was a resonant frequency type, and the frequency range was 3-20 Hz. The test specimens were prepared in a rectangular shape of about 1.5 mm in thickness, 8 mm in width, and 20 mm in length.

Differential Scanning Calorimetry (DSC). The differential scanning calorimetry measurements were made using a Perkin-Elmer DSC-4. The sample weight was about 10 mg, and the heating rate was 10°C/min under nitrogen flow of 30 cm³/min. The transition temperatures were obtained from the first heating scan.

Molecular Weight. The molecular weight and the molecular weight distribution of polyurethane synthesized under different conditions were determined by gel permeation chromatography.

RESULTS AND DISCUSSION

Reaction Kinetics

The bulk polymerization reaction of the isocyanate terminated polyurethane prepolymer and 1,4-butanediol were carried out at 40, 50, 60, and 70°C under pressure range between 1 and 3000 kg/cm². In order to compare the effect of the synthesis pressure on the reaction rate, a second-order reaction was assumed.^{11,12} With equal initial concentration of the isocyanate and the alcohol, the second-order kinetic equation becomes

$$-dC/dt = kC^2 \quad (2)$$

and after integration yields

$$1/C - 1/C_0 = kt \quad (3)$$

where C_0 is the initial concentration (eq/kg), C is the concentration at time t (eq/kg), t in s, and k is the reaction rate constant (kg/eq s). The curves of Figure 1 were drawn by use of the second-order kinetic equation, and are almost straight lines up to a determined reaction time. The reaction rate constants are plotted in Figure 2 and listed in Table I. The polymerization

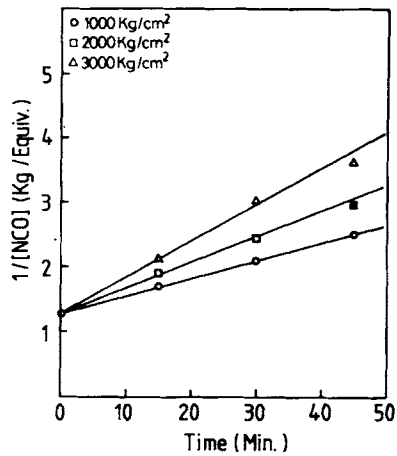


Fig. 1. Second-order plots for the reaction of NCO-terminated prepolymer and 1,4-butanediol at 40°C.

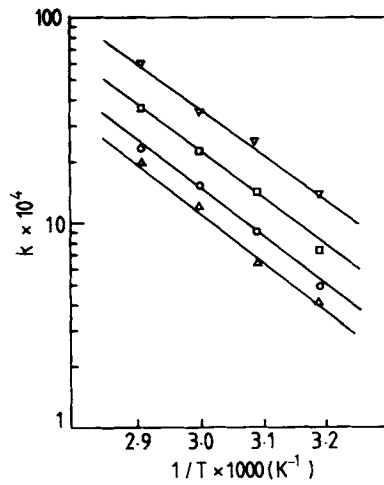


Fig. 2. Rate constant k vs. the reciprocal of absolute temperature $1/T$ at: (Δ) 1 kg/cm²; (\circ) 1000 kg/cm²; (\square) 2000 kg/cm²; (∇) 3000 kg/cm².

TABLE I
Rate Constant $k \times 10^3$ (kg/eq s)

Temperature (°C)	Pressure (kg/cm ²)			
	1	1000	2000	3000
40	0.42	0.44	0.74	1.04
50	0.63	0.95	1.40	2.05
60	1.21	1.54	2.25	3.56
70	1.96	2.29	3.63	6.16

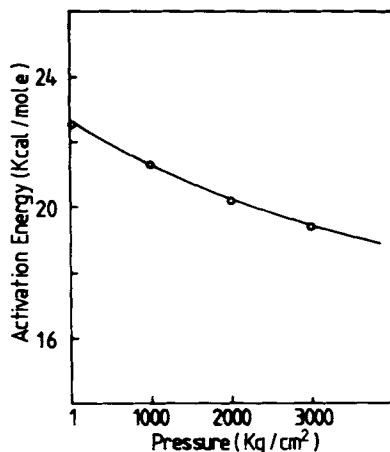


Fig. 3. Effect of the synthesis pressure on the activation energy of the polyurethane polymerization.

rate increases with increasing synthesis pressure. The rates at 3000 kg/cm² in each temperature are about three times faster than that of the atmospheric pressure.

Activation energy of reaction was calculated from Figure 2 and was 22.4 kcal/mol at 1 kg/cm², 21.4 kcal/mol at 1000 kg/cm², 20.2 kcal/mol at 2000 kg/cm², and 19.4 kcal/mol at 3000 kg/cm². Figure 3 shows the change of activation energy with synthesis pressure. The activation energy of the polyurethane polymerization rate decreases with synthesis pressure. Similar effect also appears in the addition polymerization of styrene under pressure.³ The activation energy can be expressed as

$$E = E_0 + P\Delta V^\ddagger \quad (4)$$

The rate constant is expressed as

$$k = k_0 \exp\left[-(E_0 + P\Delta V^\ddagger)/RT\right] \quad (5)$$

$$\ln k = \ln k_0 - \frac{E_0}{RT} - \frac{\Delta V^\ddagger}{RT}P \quad (6)$$

where E_0 is activation energy at atmospheric pressure, P is the external pressure (synthesis pressure), ΔV^\ddagger is volume of activation, and k_0 is the frequency factor. A plot of the $\ln k$ vs. pressure (Fig. 4) was linear over the pressure range examined, confirming the validity of eq. (5). The volume of activation was calculated from Figure 4 and listed in Table II. The volume of activation decreases as the synthesis temperature is increased; thus the pressure effect is enhanced at high temperature.

Microphase Separation

Figures 5 and 6 show the dynamic mechanical properties of the polyurethanes synthesized under different conditions. Peak temperatures

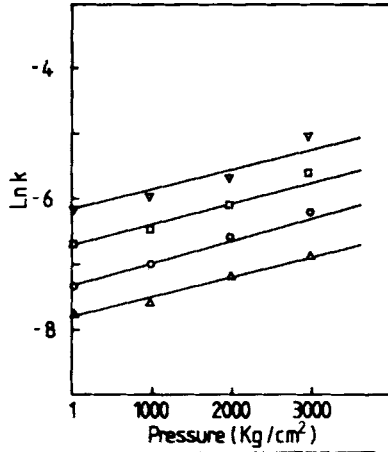


Fig. 4. Effect of the synthesis pressure on the rate constant k at: (Δ) 40°C; (\circ) 50°C; (\square) 60°C; (∇) 70°C.

TABLE II
Volume of Activation at Different
Polymerization Temperatures

Temperature (K)	ΔV^\ddagger (cm ³ /mol)
313	-16.2
323	-21.4
333	-19.8
343	-21.6

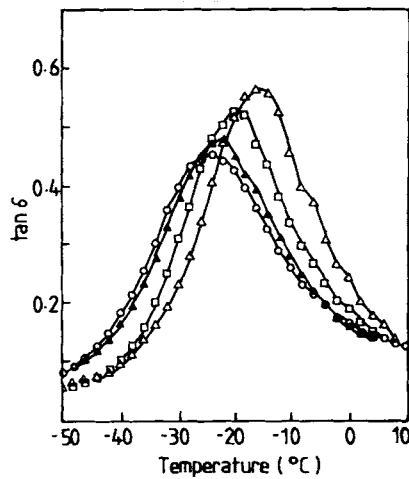


Fig. 5. Effect of the synthesis pressure on $\tan \delta$ of the polyurethane synthesized at 80°C under: (\circ) 1 kg/cm²; (Δ) 1000 kg/cm²; (\square) 2000 kg/cm²; (∇) 3000 kg/cm².

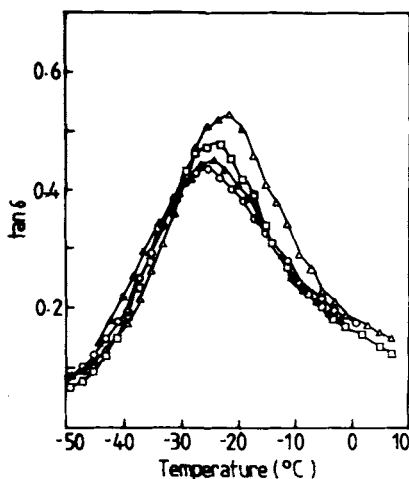


Fig. 6. Effect of the synthesis pressure on $\tan \delta$ of the polyurethane synthesized at 90°C under: (○) 1 kg/cm^2 ; (▲) 1000 kg/cm^2 ; (□) 2000 kg/cm^2 ; (Δ) 3000 kg/cm^2 .

which correspond to the glass transition temperature of the soft segment move toward higher temperature as the synthesis pressure is increased. This means that the phase separation between the soft and hard segment is restricted under pressure and the soft segment is intermixed with the hard segment. The intensity of the loss peak also increases with increasing synthesis pressure because the role of the physical crosslinking of the hard segment is decreased as the synthesis pressure is increased due to the partial mixing of the hard segment into the soft segment. The shift of the glass transition

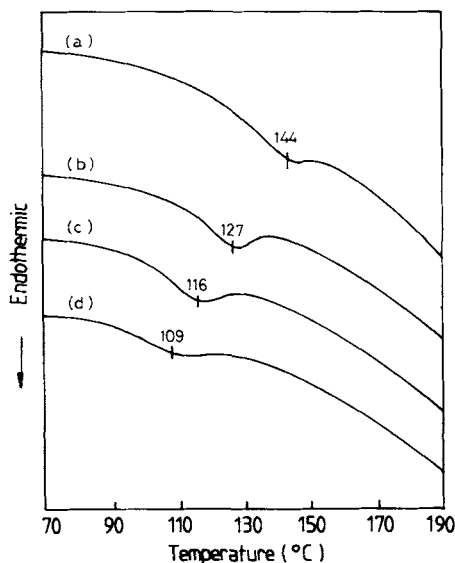


Fig. 7. Effect of the synthesis pressure on the melting point of the hard domain in the polyurethane synthesized at 80°C under: (a) 1 kg/cm^2 ; (b) 1000 kg/cm^2 ; (c) 2000 kg/cm^2 ; (d) 3000 kg/cm^2 .

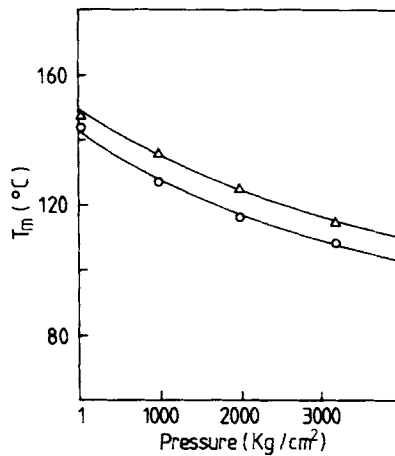


Fig. 8. Decrease of the melting point of the hard domain with increasing synthesis pressure for the polyurethane synthesized at 80°C (○) and 90°C (Δ).

temperature of the soft segment is more pronounced when the polyurethane is synthesized at 80°C than at 90°C due to the increased rate of phase separation at high temperature with increased mobility of the polymer chain.

Figure 7 shows the melting point of the hard segment in polyurethanes synthesized at 80°C. The T_m is 144°C at atmospheric pressure, 127°C at 1000 kg/cm², 116°C at 2000 kg/cm², and 109°C at 3000 kg/cm². The melting point decreased as the synthesis pressure is increased due to the restricted phase separation of the polyurethanes synthesized under high pressure. Figure 8 shows the change of melting point of the hard segment with synthesis pressure on samples synthesized at two different temperatures. The T_m of the polyurethanes synthesized at 90°C are about 5°C higher than that of the polyurethanes synthesized at 80°C due to the advanced level of phase separa-

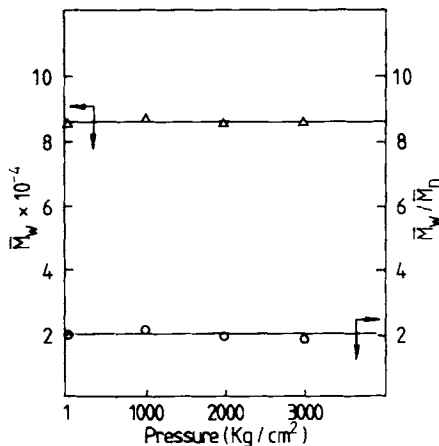


Fig. 9. Effect of the synthesis pressure on the molecular weight and polydispersity of the polyurethane synthesized at 80°C.

tion with higher mobility of the polymer chains when synthesized at high temperature.

Molecular Weight

The molecular weight and molecular weight distribution of the polyurethanes synthesized under different pressure were analyzed. Figure 9 shows the effect of the synthesis pressure on the molecular weight and molecular weight distribution of the polyurethanes synthesized at 80°C. For the addition polymerization it was reported that the molecular weight increases with increasing synthesis pressure.^{2,3} In the polyurethane polymerization, molecular weight and molecular weight distribution were not influenced by the synthesis pressure.

CONCLUSIONS

The rate of reaction increased with decrease in the activation energy during the polyurethane polymerization in the bulk state as the synthesis pressure was increased. The volume of activation was about $-20 \text{ cm}^3/\text{mol}$ and increased with increasing synthesis temperature.

Glass transition temperature of the soft segment shifted towards higher temperature and the glass transition temperature of the hard segment was lowered as the synthesis pressure was increased. It is presumed that high synthesis pressure depresses the microphase separation of the soft and hard segment during the reaction due to the reduced mobility of chain segments.

The molecular weight and molecular weight distribution of the polyurethane synthesized under pressure were not affected by the synthesis pressure.

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