

Phase Separation in Segmented Polyurethanes

T. K. KWEI,* *Bell Laboratories, Murray Hill, New Jersey 07974*

Synopsis

Phase separation in a segmented polyurethane has been studied by differential scanning calorimetry. The glass transition temperature of the soft phase decreases logarithmically with time to a limiting value at each annealing temperature. The magnitude of the decrease is larger at low annealing temperatures, but the normalized rate of logarithmic decrease is smaller. At high annealing temperatures, long sequences of hard segments are excluded from the soft phase in which short segments are still soluble. At low temperatures, even short hard segments separate from the soft phase. The exclusion of the hard segments from the soft phase is a relatively fast process, but the development of order in hard domains takes longer time to reach steady state.

INTRODUCTION

Phase separation in segmented polyurethanes has been the subject of many recent investigations.¹⁻¹² The segregation of hard and soft segments at low temperatures and the mixing of these domains at elevated temperatures have been studied by a variety of techniques including microscopy,⁹ X-ray measurement,^{2,5,7,9,11} pulsed nuclear magnetic resonance,^{3,4} mechanical relaxation,^{6,8} and calorimetry.^{1,5,9,10} In differential scanning calorimetry studies,¹ the thermograms revealed three endothermic events. A relatively sharp melting peak near 200°C was attributed to the fusion of microcrystalline domains comprised of long sequences of hard segments because it was not found in the thermograms of materials containing only short lengths of hard segments. In addition to the sharp melting peak, two broad endotherms were detected at lower temperatures, one below 100°C (I) and the other below 180°C (II). Annealing moved endotherm I upscale in temperature to merge with endotherm II. These two endotherms were thought to represent the disordering of hard segment domains with relatively short-range order.

In light of the above interpretation of the nature of endotherms I and II, there seems to be a need to acquire quantitative information about the enthalpy changes associated with the two disordering processes. We have now undertaken such a study with a material which contains only a small amount of hard segments because the absence of large crystalline domains in this material simplifies the interpretation of experimental results. In the course of our study we have also examined, in some detail, the effect of annealing on the magnitude of the enthalpy change, the temperature span of the endotherm, and the glass transition temperature of the soft phase.

* Now at Industrial Technology Research Institute, Taiwan, R.O.C.

EXPERIMENTAL

Materials. The material used in this study is a thermoplastic elastomer obtained from B. F. Goodrich Co. It is a polyether urethane having a hard segment formed from *p,p'*-diphenylmethane diisocyanate (MDI), chain extended with butanediol. The polyether portion has been identified, using C^{13} NMR analysis,¹³ as $[(CH_2)_4-O-]_{14}$. The molar ratio of polyol to butanediol was estimated to be 1.4 ± 0.07 from NMR signal intensities; however, elemental analysis (C, 66.24%; H, 8.99%; N, 3.41%) seems to agree better with a molar ratio of 1.07 if one assumes that the polymer contains stoichiometric amount of MDI (calcd. C, 66.83%; H, 8.95%; N, 3.40%). As a point of reference, the weight percent of hard segments in a 1:1 polymer is 22.6%.

The polyurethane material was compression-molded at 170°C between Teflon films into sheets approximately 1 mm in thickness. All calorimetric studies were conducted on samples cut from the same sheet.

Calorimetry. Differential scanning calorimetry data were obtained with the use of DuPont 990 thermal analyzer equipped with a DSC cell. Sample size was 10.0 ± 0.1 mg, and the heating rate was 10°C/min. The procedure of annealing samples was the following. For long-term annealing, the samples were first heated to and maintained at 190°C in an oven for 15 min. They were then transferred to four other ovens maintained at 120, 90, 80, and $60 \pm 0.1^\circ C$, respectively. A fifth set of samples was cooled quickly to room temperature by placing the samples on a large metal block on a laboratory bench. A variation of the above procedure was adopted for short-term annealing, for example, several minutes in duration. The sample was heated in the calorimeter to 190°C, maintained at that temperature for 15 min, and then cooled immediately to the desired annealing temperature in the DSC cell.

Microscopy. A detailed account of optical microscopy studies will be given in a separate report by F. J. Padden, Jr. Preliminary observations were carried out with the use of a microscope at 127 times magnification.

RESULTS

A small piece of the polymer was melted between a microscope slide and a cover slip. The assembly was transferred to a Mettler hot stage attached to the microscope. When the sample was held at 130°C for 1.5 h, a high population of primary nucleating sites ($\sim 10 \mu$) was observed, but there was very little growth from each nucleus. When the same procedure was repeated at 90, 140, 150, and 160°C, results were qualitatively the same. At 160°C, only a few nucleation sites were visible after 1 h. These results are indicative of the formation of imperfectly organized domains under the experimental conditions. Whether thermal degradation is responsible, in part, for our experimental observations at temperatures above 130°C remains to be examined.

The DSC thermograms of the as-received material show variations in details from sample to sample in the same lot. A representative thermogram embodying the essential features is exhibited in Figure 1. An increase in the specific heat of the material in the region of -60 – $-30^\circ C$ is attributed to the glass transition of the soft phase. Two endotherms which represent the disordering of hard segment domains occur between 30 and 90°C and between 90 and 140°C, respectively. There is no evidence of a glass transition of the hard segments.

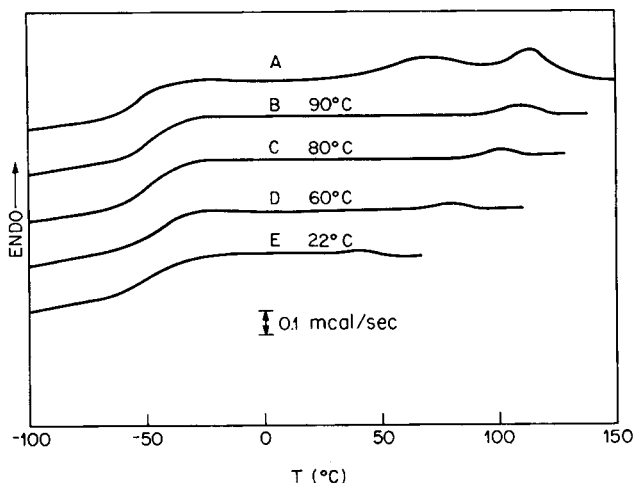


Fig. 1. DSC thermograms of polyurethanes, (A) as received (B-E) annealed for 1 h at temperatures indicated after 15 min at 190°C.

The thermograms of specimens heated at 190°C for 15 min and then annealed for 1 h at 90, 80, 60, and 22°C, respectively, are also shown in Figure 1. Each thermogram reveals a shift in the baseline in the -60°C region and an endotherm above room temperature. The exact positions of both events are dependent on the temperature and time of annealing. We have recorded four characteristics of each thermogram: the temperature of initial rise (extrapolated) in C_p as T_g of the soft phase, the temperatures of the inception, T_i , and of the end, T_f , of the endotherm, and the heat Q absorbed in the endothermic process. The reproducibilities for these measurements are: $\pm 0.5^{\circ}\text{C}$ for T_g , $\pm 1.0^{\circ}\text{C}$ for T_i or T_f , and about $\pm 10\%$ for Q . These four quantities are plotted as a function of annealing time in Figures 2-4. The Q values for samples annealed at 120°C are not included because the baselines of the endotherms are not matched properly.

Glass transition temperatures. The thermogram of a sample quenched directly in liquid nitrogen exhibits only one thermal response, a glass transition at -54°C , which can be regarded as the T_g of a "homogeneous" mixture of hard and soft segments. At each annealing temperature, the T_g values decrease at first linearly with the logarithm of the annealing times (Fig. 2). Upon extrapolation to short times, the data converge at 0.06 min to a common value of -54°C , identical to that found for the sample quenched in liquid nitrogen. The internal consistency of the experimental data is reassuring.

At long annealing times, a plateau T_g value, T_{gp} , is reached for each temperature. The plateau value is lower but the time to reach T_{gp} is longer at a lower annealing temperature.

Disordering of hard segments. At short annealing times, T_i is nearly the same as the annealing temperature. It increases slightly with time and reaches a limiting value between 20 and 200 h (Fig. 3). The limiting T_i values are 98, 89, 73, and 39°C for samples annealed at 90, 80, 60, and 22°C , respectively. The T_f values increase linearly with $\log t$ at first but also reach a limiting value for each annealing temperature after several hundred hours. The leveling off of

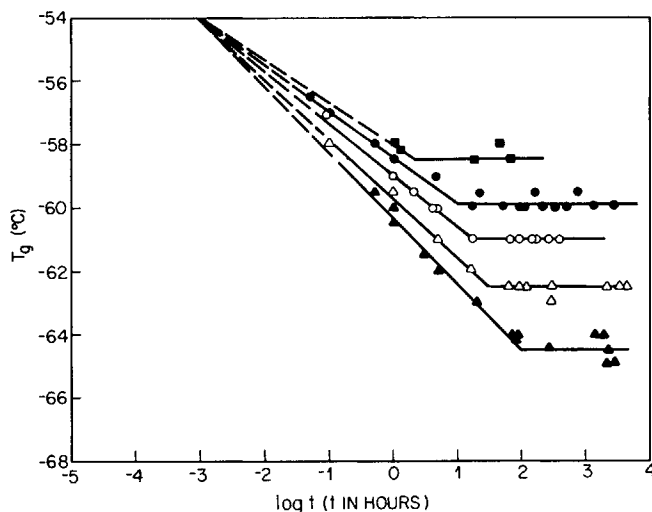


Fig. 2. Glass transition temperature ($^{\circ}\text{C}$) of the soft phase as a function of time: (■) 120; (●) 90; (○) 80; (△) 60; (▲) 22.

T_f values may not seem obvious from Figure 3 because the data collected at long times are spaced closely on the $\log t$ scale, but can be seen clearly when plotted on a linear time scale. The limiting T_f values are approximately 55°C higher than the corresponding annealing temperatures.

The enthalpy changes associated with the disordering processes are plotted against time in Figure 4. For the sake of clarity, the results at short times are shown separately in the inset in that figure. The values of Q are nearly identical for samples annealed at 80 and 90°C . After an initial rapid increase of Q with time, the absorbed heat reaches a constant magnitude of 1.3 ± 0.1 cal/g after about 600 h. The 60°C data appear to be somewhat higher than the 22°C values at short times, but the two sets of results become indistinguishable at long annealing times and have a common steady state value of 0.66 ± 0.8 cal/g.

In an additional set of experiments, samples are annealed at 80°C for 386 h and then maintained at 22°C . The thermograms of these samples exhibit two endotherms, one beginning at about 30°C and the other at about 85°C (Fig. 5). A sample annealed at 60°C for 1608 h followed by subsequent annealing at 22°C does not show the additional endotherm near room temperature.

DISCUSSION

The decrease in T_g upon annealing results from the progressive enrichment of soft segments in the soft phase. Annealing at high temperatures promotes the mixing of soft and hard segments, and, consequently, the T_g of the soft phases is higher. When the plateau T_g value, T_{gp} , is plotted against the annealing temperature, a straight line results (Fig. 6). The straight line extrapolates to a T_g value of -54°C at an annealing temperature of 185°C . It may be concluded that at the latter temperature the hard and soft segments form a single phase. Our choice of 190°C as the melt temperature before quenching or annealing is therefore appropriate.

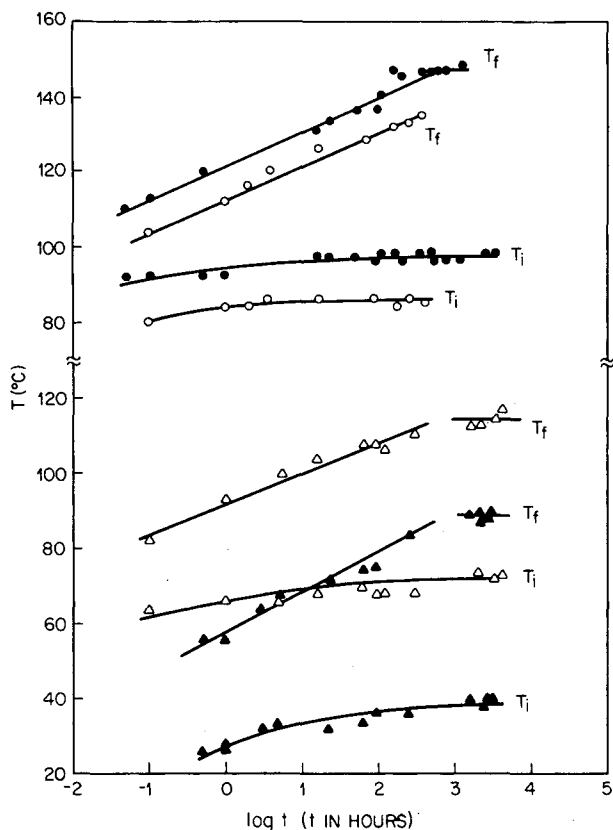


Fig. 3. The temperatures ($^{\circ}\text{C}$) of the beginning and the end of the disordering endotherm as a function of time: (●) 90; (○) 80; (Δ) 60; (\blacktriangle) 22.

The time t_p to reach the plateau T_g value is a measure of the rate of segmental segregation. When $\log t_p$ is plotted against the reciprocal of the absolute temperature, the data can be represented by two intersecting straight lines (Fig. 7). The change in slope, which occurs at 73°C , is suggestive of different mechanisms of segment segregation at temperatures below and above 73°C . A more detailed discussion of the significance of the slope change will be deferred to a later section.

A second measure of the rate of segmental segregation is the rate of decrease of T_g with time. The logarithmic decay of T_g with t shown in Figure 2 has also been reported previously.^{2,14} The rate of logarithmic decrease, $dT_g(T_{gp} - T_g)d \log t$, is smaller at low annealing temperatures although the total amount of decrease is larger. A plot of the logarithmic rate of T_g decrease vs. the reciprocal of the temperature shows an abrupt change in slope at 71°C (Fig. 7), as in the $\log t_p$ vs. $1/T$ plot.

We have mentioned earlier that T_i corresponds closely to the annealing temperature but the end of the endotherm occurs at a much higher temperature. The large temperature span between T_i and T_f is a reflection of the wide distribution of the size and the degree of perfection of the hard domains. We note that T_f continues to increase long after the T_g of the soft phase has reached a plateau value. Thus, the exclusion of the hard segments from the soft phase is

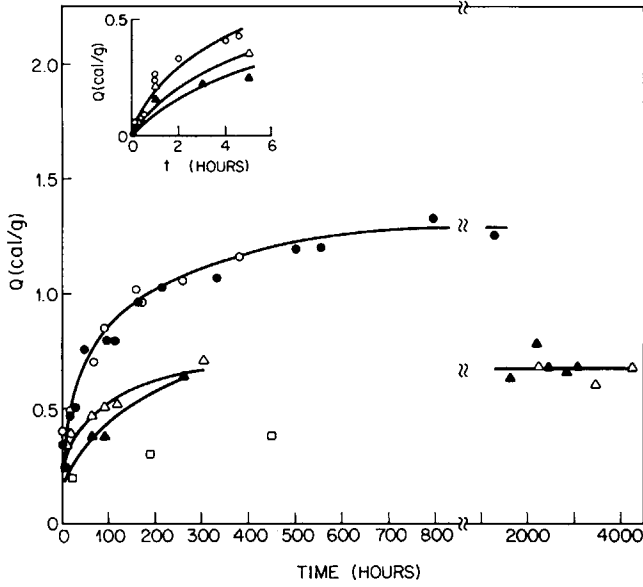


Fig. 4. Heat absorbed in the disordering process as a function of time: (●) 90°C; (○) 80°C; (△) 60°C; (▲) 22°C; (□) 80°C for 386 h + 22°C.

a relatively fast process, but the development of order in the hard domain takes a longer time to reach completion. At very long times, between 500 and 800 h, T_f arrives at a constant value for each annealing temperature. We believe that the ordering process of the hard domains has reached a steady state in that time interval. This interpretation is supported by the observation that the enthalpy changes also reach a limiting value at approximately the same time (Fig. 4).

When the values of Q are plotted against t on a log-log scale, the data can be

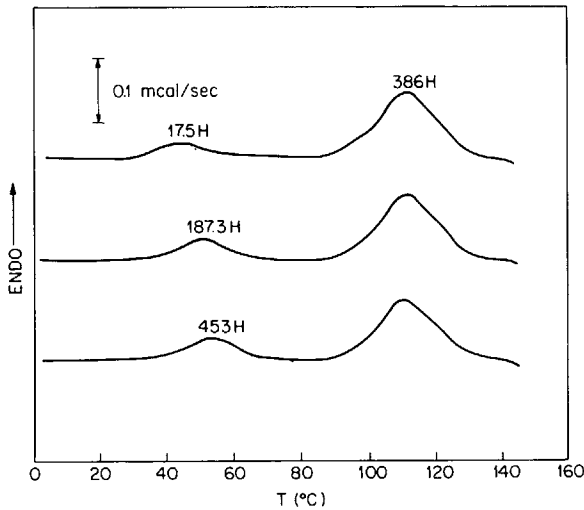


Fig. 5. DSC thermograms of samples subjected to the following thermal histories: 15 min at 190°C plus 386 h at 80°C plus 17.5, 187.3, and 453 h, respectively at 22°C.

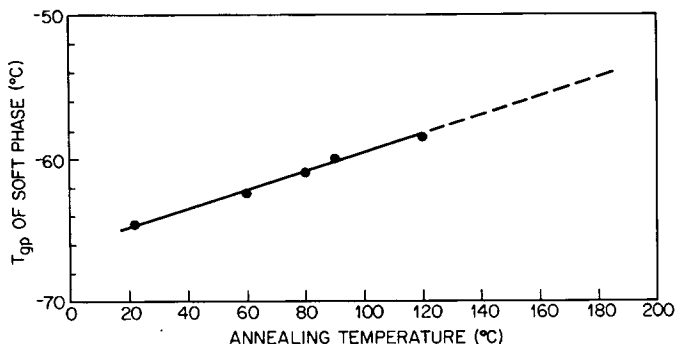


Fig. 6. Dependence of the limiting value of the T_g of soft phase on annealing temperature.

represented approximately by straight lines, but the exponent of t is less than 0.2. Therefore, the results are not compatible with a simple, diffusion-controlled mechanism. Attempts to fit the experimental data with the Avrami-type equation often used in the study of crystallization kinetics¹⁵ likewise yield exponents of t which are unreasonably small, 0.27–0.50. We have no mechanistic explanation for the time dependence of Q .

But the results of two additional sets of annealing experiments appear to have interesting implications. In the first set, samples were subjected to following thermal treatment: 190°C for 15 min plus 80°C for 386 h plus 22°C for 17.5, 187, and 453 h, respectively. The thermograms in Figure 5 show clearly that the ordering process at 22°C can still proceed, even though the magnitude of the 80°C endotherm has reached 90% of the limiting value at that temperature and exceeds the limiting Q value at 22°C. The only plausible explanation is that hard segments of different lengths are responsible for the ordering processes at 80°C and at 22°C. A similar conclusion has been proposed by Seymour and Cooper.¹ In the second set of experiments, the thermal histories were 190°C for 15 min plus 60°C for 1608 h plus 22°C for 18.5 and 23 h, respectively. In neither sample was there any evidence of an endotherm in the 22°C region. We therefore conclude that the ordering processes at 22°C and at 60°C involve the same short hard segment, although the aggregates must be larger at the latter temperature in order to have higher T_i and T_f .

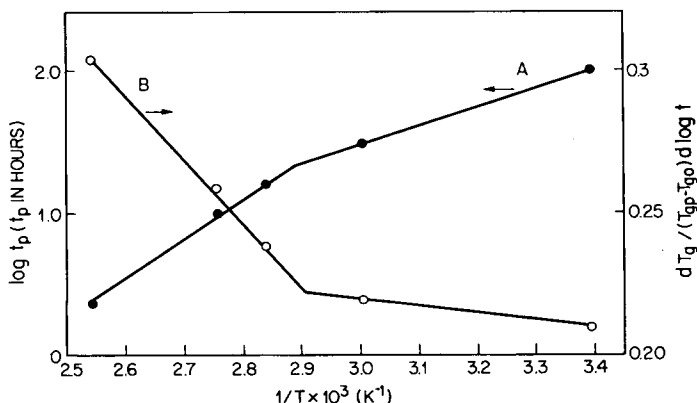


Fig. 7. Temperature dependence of (A) the time to reach limiting T_g value and (B) the rate of exponential decrease of T_g with time.

If the above explanation about hard domains is correct, the following inferences may be drawn about the character of the soft phase. At temperatures of 80°C or higher, long sequences of hard segments are excluded from the soft phase in which short hard segments are still soluble. At lower temperatures, even short hard segments are rejected by the soft phase. The difference in the mobilities of long and short hard segments to segregate themselves from the soft phase is probably responsible for the changes in slope at 71–73°C found in the plots of t_{gp} vs. $1/T$ and of $dT_g/(T_{gp} - T_g)d \log t$ vs. $1/T$ in Figure 7. This argument presupposes that there is a sharp demarcation between the lengths of short and long hard segments. It is undoubtedly an oversimplification, and we have no knowledge of the distribution of sequence lengths in the polymer. In this regard, Seymour and Cooper¹ have postulated that clusters of short hard segments, perhaps of only one MDI unit, give rise to the lower temperature endotherm. Hard segments of longer lengths are expected to have greatly decreased mobility, which inhibits their mutual alignment at low temperatures, and only short segments arrange themselves in an ordered state. Consequently, the magnitude of Q is smaller below 80°C, although the total amount of segregated hard segments is larger. The abrupt change in mobility near 80°C is also manifested in a "transition" at 75°C in the infrared NH absorbance in a similar polymer.¹ (We do not wish to imply here that by using the word endotherm in the text we understand with confidence the nature of the disordering process in this temperature region.)

CONCLUSIONS

During phase separation in a segmented polyurethane, the T_g of the soft phase decreases logarithmically with time to a limiting value at each annealing temperature. The normalized rate of decrease in T_g is lower at lower annealing temperatures, although the total decrease in T_g is larger. The exclusion of hard segments from the soft phase is a relatively fast process, but the development of order in hard domains takes a longer time to reach completion. The hard domains consist of both long and short segments when annealed at temperatures below 80°C, but the ordering process is due mainly to the alignment of short segments. Annealing at 80 or 90°C results in the segregation and ordering of longer segments.

The contributions of F. C. Schilling in C¹³ NMR analysis and of F. J. Padden Jr. in microscopy are gratefully acknowledged.

References

1. R. W. Seymour and S. L. Cooper, *Macromolecules*, **6**, 48 (1973).
2. G. L. Wilkes and J. A. Emerson, *J. Appl. Phys.*, **47**, 4261 (1976).
3. R. A. Assink and G. L. Wilkes, *Polym. Eng. Sci.*, **17**, 606 (1977).
4. R. A. Assink, *J. Polym. Sci.*, **15**, 59 (1977).
5. C. S. Paik Sung, C. B. Hu, and C. S. Wu, *Macromolecules*, **13**, 111 (1980).
6. A. Lilaonitkul and S. L. Cooper, *Rubber Chem. Technol.*, **50**, 1 (1977).
7. Z. H. Ophir and G. L. Wilkes, in *Multiphase Polymers*, Advances in Chemistry Series No. 176, S. L. Cooper and G. M. Estes, Eds., American Chemical Society, Washington, D.C., 1979, pp. 53–67.
8. G. A. Senich and W. J. MacKnight, in Ref. 7, pp. 97–127.
9. A. L. Chang and E. L. Thomas, in Ref. 7, pp. 31–52.
10. C. S. Schollenberger, in Ref. 7, pp. 83–96.

11. R. Bonart, L. Morbitzen, and G. Henze, *Macromol. Sci. Phys.*, **B3**, 337 (1969).
12. T. R. Hesketh and S. L. Cooper, *Am. Chem. Soc., Polym. Prepr.*, **37**(2), 509 (1977).
13. F. C. Schilling, private communication.
14. J. W. C. Van Bogart, A. Lilaonitkul, and S. L. Cooper, in *Multiphase Polymers*, S. L. Cooper and G. M. Estes, Eds., Advances in Chemistry Series No. 176, American Chemical Society, Washington, D.C., 1979, pp. 3-30.
15. M. Avrami, *J. Chem. Phys.*, **9**, 177 (1941).

Received September 24, 1981

Accepted January 22, 1982