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MULTIPHASE STRUCTURE OF A SEGMENTED POLYURETHANE: EFFECTS OF TEMPERATURE AND ANNEALING

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ABSTRACT

The multiphase structure and related relaxations of a segmented polyurethane were characterized by using a combination of differential scanning calorimetry (DSC), dynamical mechanical analysis (DMA), stress-strain test, thermally stimulated discharge current (TSDC), and synchrotron small-angle X-ray scattering (SAXS). The polymers studied consisted of 4,4'-diphenylmethane diisocyanate (MDI), 1,4'-butanediol (BD) hard segments with soft segments comprised of PTMO end-capped with PPO at a 70/30 PTMO/PPO weight ratio. The results showed a soft segment glass transition temperature ($T_{g,s}$) which is significantly higher than the $T_{g,s}$ (-84°C) of the corresponding pure soft segment, suggesting an incomplete phase separation behavior for the soft segments. The specimen lost its mechanical strength at above 200°C while DSC indicated an endotherm ca. 195°C due to the hard segment domain consisting of dissolution into the soft segment matrix. TSDC showed interfacial polarization due to the multiphase characteristics. Synchrotron SAXS scanning from 26°C to 250°C indicated that the sample structure remained stable with increasing temperature. A small change around 75°C was attributed to the glass transition of the amorphous hard segment domain. Phase mixing took place when the temperature was above 190°C, in agreement with the DSC and DMA results. Synchrotron SAXS was also used to study the post-annealing effects on the segmented polyurethane with a well-defined thermal history. The structural changes were irreversible upon annealing. Thermal post-annealing did not have a significant effect on the multiphase structure once the structure development had reached equilibration and interactions among the hard segments had reached a certain degree of strength. However, post-annealing could promote perfection inside the hard segment domain or further phase separation of some hard segments inside the soft segment matrix. The structures from the samples which have not reached equilibration or have very weak interactions among the hard segments could be changed dramatically by post-annealing. The only way to change the existing structure entirely is to melt the sample. Although the phase separation process in the segmented polyurethane was very slow, the phase mixing at high temperatures was extremely fast. Based upon the Koberstein-Stein coiling/folding hard segment model, a temperature- and interaction-dependent coiled hard segment model could be used to interpret our observations. The mobility of the hard segement and the viscosity of the system are two key factors which control the structure in segmented polyurethanes.

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EXPERIMENTAL SECTION

INTRODUCTION

Segmented polyurethanes are a class of thermoplastic elastomers which form multiphase structures owing to the thermodynamic incompatibility between the hard and soft segments.[1] The hard segment usually consists of aromatic diisocyanate such as 4,4'-diphenylmethane diisocyanate (MDI) extended by either a low molecular weight diol, such as 1,4'-butanediol (BD), or a low molecular weight diamine. The soft segment usually consists of either a polyether or a polyester macroglycol with molecular weight between 600 to 3000. The hard segments, which act as crosslinking points are in a crystalline state or an amorphous glass state; the soft segments are in a rubbery state at room temperature which gives the elasticity. The combination of hard and soft segments gives this class of materials very unique properties which can be changed by adjusting the chemical structure of the polymers, and equally importantly, by controlling the multiphase structure and the morphology of the polymers during processing and other post-polymerization treatments. This is part of the reason why the structure-properties relationships have drawn so much attention since the suggestion by Cooper and Tobolsky[2] that segmented polyurethanes consisted of multiphase structures.

The polymerization of segmented polyurethanes usually generates macromolecules which are polydispersed and have chemical compositional heterogeneity including hard segment length distributions. All of these structure characteristics are functions of polymerization conditions, and the multiphase structures are generally believed to be formed from nonequilibrium phase separations. Consequently, the structure and properties of segmented polyurethanes depend strongly upon the thermal history and processing conditions. It is very important from both basic and applied viewpoints to find out how the structures could be controlled via synthesis, thermal history, and processing conditions in order to get the expected mechanical properties.

In this report, we are interested in the following:

- The phase structure of the segmented polyurethane after polymerization
- The temperature dependence of the structure
- How the structure can be affected by post-annealing

The multiphase structure and related relaxation of segmented polyurethanes have been studied by a variety of techniques such as differential scanning calorimetry (DSC) and dynamic mechanical anaylsis (DMA), and have been reviewed by Gibson, et al.[1] Basically, a soft segment had a glass transition temperature at around -50°C to -20°C and the dissolution of the hard segment domain occurs at ca. 200°C. The phase structure depends upon many factors such as the hard segment content, the soft segment length, and annealing and processing conditions. It is desirable to carry out a detailed characterization of the structure and properties of the segmented polyurethane samples since the structure of the samples is a function of so many factors. Except for the stress-strain test, all the techniques were used to investigate the temperature dependent behavior revealed by the structures from different viewpoints.

The post-annealing effects on the structure of segmented polyurethanes have been studied by several groups. DSC studies by Seymour and Cooper[3] using compression molded sheets of both polyester and polyetherurethanes having MDI-BD hard segments showed

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[1] GIBSON, P. E., VALLENCE, M. A. and COOPER, S. L. *Development in Block Copolymers*. I. Goodman, ed., Appl. Sci. Ser., Elsevier, London, England, 1982, p. 217.

[2] COOPER, S. L., and TOBOLSKY, A. V. J. Appl. Polym. Sci., v. 10, 1966, p. 1837.

[3] SEYMOUR, R. W., and COOPER, S. L. J. Polym. Sci. Polym. Lett. Ed., v. 9, 1971, p. 689.

three endothermic peaks; region 1 peaked at ca. 70°C, region 2 at 160°C, and region 3 at 185°C. Post-annealing of the compression molded sheets at 80°C shifted peak 1 to a higher temperature with peaks 2 and 3 unchanged. Further treatment continued this movement until the original peaks in regions 1 and 2 merged to form a single peak at the high temperature side of the original peak 2. Post-annealing at 150°C moved both peaks 1 and 2 into peak 3. Also, a sharp wide angle X-ray diffraction (WAXD) ring was attributed to the formation of crystalline hard segment structure. Further studies by Samuels and Wilkes,[4] and by Seymour and Cooper[5] using samples without hydrogen bonding ability showed similar phenomena, indicating that the multiendothermic phenomena were not due to the dissociation of hydrogen bonds. Instead, Seymour and Cooper proposed that all three peaks were morphological in origin. Peaks 1 and 2 represented the disordering of hard segments with a relatively short-range order that could be improved continuously by post-annealing. Peak 3 was assigned to a relatively well-ordered microcrystalline structure by the hard segments. Jacques[6] studied the effects of post-annealing at high temperatures (150°C to 250°C) on injection molded samples. By using DSC, WAXD, infrared spectroscopy (IR) and DMA, his results showed that post-annealing below 200°C resulted in only long-range ordered hard segment domains, while post-annealing at 200°C and above resulted in the crystallization of hard segment domains. Later, in a series of studies on the post-annealing effects by the Cooper group, Hesketh, et al.[7] concentrated on post-annealing-induced ordering at high temperatures (120°C to 190°C), and Van Bogart, et al.[8] concentrated on post-annealing between -10°C and 120°C. Basically, these studies reconfirmed the existence of three endothermic peaks. It should be noted that in their experiments, the samples were held at 250°C for five minutes and then cooled at a rate of 10°C/min (not quenching at a rapid rate) to the desired annealing temperatures. Recently, Leung and Koberstein[9] studied the multiple endothermic and phase separation behavior in segmented polyurethanes by using DSC. Three regions of annealing temperature for segmented polyurethanes with high MDI-BD segment contents were observed. Annealing at or below 140°C (defined as region 1) showed no significant crystallization. Annealing at 140°C to 190°C (region 2) gave rise to hard segment crystallization. Annealing at and above ca. 200°C showed phase mixing of noncrystalline hard segments and soft segments. It should be noted that in their annealing experiments, specimens were held at 240°C for one minute and then cooled at 10°C/min (again, not quenching at a rapid rate) to the desired annealing temperatures. Koberstein and Russell[10] used simultaneous SAXS/DSC to study the phase structure changes and the multiple endothermic behavior in segmented polyurethanes. The results showed that the intermediate endotherm was associated with the onset of partial phase mixing. In their experiment, the specimens were heated at 10°C/min to 250°C then cooled to (once more, not quenching at a rapid rate) the selected annealing temperatures and annealed for 40 minutes. Galambos, et al.[11] used the same technique to study the phase separation, crystallization, and multiple endothermic behavior. The observations were essentially similar. Gibson, et al.[12] performed SAXS experiments to investigate the multiphase structural changes of segmented polyurethanes upon post-annealing. They found that annealing generally improved the degree of phase separation and increased the hard segment domain size. Thicker interfacial regions were also observed in the annealed materials.

[4] SAMUELS, S. L., and WILKES, G. L. J. Polym. Sci. Polym. Lett. Ed., v. 11, 1973, p. 807.

[5] SEYMOUR, R. W., and COOPER, S. L. Maromolecules, v. 6, 1973, p. 48.

[6] JACQUES, C. H. M. *Polymer Alloys: Blends, Blocks, Grafts, and Interpenetrating Networks.* D. Klempner, K. Frisch, eds., Polymer Science and Technology, Plenum Press, New York, NY, v. 10, 1977, p. 287.

[7] HESKETH, T. R., VAN BOGART, J. W. C., and COOPER, S. L. Polym. Eng. Sci., v. 20, 1980, p. 190.

[8] VAN BOGART, J. W. C., BLUEMKE, D. A., and COOPER, S. L. Polymer, v. 22, 1981, p. 1428.

[9] LEUNG, L. M., and KOBERSTEIN, J. T. Macromolecules v. 19, 1986, p. 706.

[10] KOBERSTEIN, J. T., and RUSSELL, T. P. Macromolecules. v. 19, 1986, p. 714.

[11] GALAMBOS, A. F., RUSSELL, T. P., and KOBERSTEIN, J. T. Polym. Mater. Sci., Eng., Proc. of Am. Chem. Soc., Div. Polym. Mater. Sci. Eng., v. 61, 1989, p. 359.

[12] GIBSON, P. E., VAN BOGART, J. W. C., and COOPER, S. L. J. Polym. Sci. Polym. Phys. Ed., v. 24, 1986, p. 885.

The studies mentioned above used either compression molded specimens *without* indicating the thermal history of the specimens, or specimens which were *slowly cooled* to the desired annealing temperatures, instead of quenching. It could be possible that the samples before post-annealing might not be in an equilibrium state since the thermal history was not specified clearly. It is believed that the effects of post-annealing could depend upon the starting original structure. The slow cooling during the sample preparation represents a nonequilibrium kinetics which could produce different structures in response to the changing temperatures as well as the cooling rate based upon the original structure. Therefore, it is not clear how the post-annealing will affect the phase structure of segmented polyurethanes if we do not know what the original structure is. A sample with a well-defined thermal history could be used to find out the post-annealing effects in a more decisive way. It is also necessary to know whether the original structure was achieved under equilibrium conditions. This requirement becomes even more obvious from one of our recent studies. In a previous paper[13] the phase separation kinetics of a segmented polyurethane was investigated after the melt was quenched to the desired annealing temperatures. It was found that the phase separation process was very slow and could be accomplished in hours, depending upon the annealing temperature. Therefore, a well designed experiment must carefully consider whether the time-dependent data are obtained from a system starting in some well-defined equilibrium state. It is desirable to investigate the reversibility of structural changes upon annealing using a sample with a well-defined thermal history. The results in this report indicate that the structural changes upon annealing are irreversible. Thermal post-annealing does not change the phase structure significantly, although ordering inside the hard segment domain or further phase separation of some hard segments from the soft segment matrix are possible. Therefore, all the experiments involving thermal history, thermal transition, or thermal characterization need to be carefully designed and interpreted; i.e., the thermal history of the sample is a dominant factor in the structural studies of segmented polyurethanes. It is equally important to undersand the equilibration rate in connection with time-dependent studies.

EXPERIMENTAL SECTION

Material

The segmented polyurethane used in this study was prepared by a two-step bulk reaction process. The soft segment was poly(tetramethylene oxide) (PTMO) end-capped with poly(propylene oxide) (PPO) having wt% PTMO:PPO = 70:30 and an average molecular weight of about 1000 g/mole (PPO-PTMO). The hard segment was MDI extended with BD. The hard segment content was 50 wt%. The polymerization route was as follows: At 80°C, MDI was added to vacuum dehydrated PPO-PTMO and prepolymerized for half an hour. Then BD was added and well mixed. After one minute the reaction mixture was poured into a Teflon mold and heated in an oven at 140°C for three hours and then at 80°C for 12 hours in order to complete the polymerization process. The sample was stored in a desiccator for more than three months before any experiment was performed. The sample, denoted as PPO-PTMO-PU-50, was characterized by elementary analysis, gel permeation chromotography (GPC), IR, and nuclear magnetic resonance (NMR).[14] The sample without any further treatment is known as the as-reacted sample. All annealing experiments were carried out in vacuum.

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[13] LI, Y., GAO, T., and CHU, B. Submitted to Macromolecules.

[14] LI, Y., M. S. Thesis, Henan Inst. of Chem., P. R. China, 1985.

Instrumentation

DCS measurements were carried out by using a Perkin-Elmer Model DSC-2C instrument operated at a 20°C/min heating rate; a sample weight of about 10 mg was used for DSC experiments.

DMA measurements were performed by using a Rheovibron DDV-III dynamic viscoelastometer. The heating rate was 2°C/min and the test frequencies were 110 Hz, 35 Hz, 11 Hz, and 3.5 Hz.

Stress-strain testing at room temperature (20°C) was performed by using a stress-strain testing apparatus manufactured by Changchun No. 2 materials testing factory (P. R. China) with a stretching rate of 100 mm/min.

Thermally stimulated depolarization current (TSDC) experiments were performed on a model KH-1 TSDC apparatus manufactured by the Institute of Chemistry, Academia Sinica operating at the temperature of polarization of 100°C, the time of polarization of 10 minutes, and the polarization electric field of 5 kV/cm. The heating rate was 5°C/min.

Synchrotron SAXS experiments were carried out at the SUNY X3A2 beamline, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). Details about the setup can be found in References 15 and 16. A modified Kratky camera along with a Braun position-sensitive detector was used at an X-ray wavelength of 0.154 nm. The sample-to-detector distance was 1330 (± 5) mm. The beam size at the same position was ca. 0.2 x 2 mm^2. The synchrotron beam was focused onto the beam stop which was ca. 40 mm in front of the Braun detector having a receiving window width of ca. 2 mm. Therefore, smearing effects on the SAXS patterns was negligible. Time-dependent experiments were performed by using a double cell high temperature jumper which had been described elsewhere.[13] The temperature precision was ± 0.5°C. Preliminary experiments were performed at the SAXS facility, SUNY, Stone Brook, NY. Routine correction procedures, except for the absolute intensity calibration, were performed on SAXS data.

RESULTS AND DISCUSSION

Figure 1 shows the DSC thermogram of the as-reacted specimen of the segmented polyurethane. The baseline shift at -21°C indicates the soft segment glass transition. The glass transition temperature of pure PPO-PTMO ($T_{g,s,o}$) can be estimated by using the copolymer equation[17]

$$1/T_{g,s,o} = w_{PPO}/T_{g,PPO} + w_{PTMO}/T_{g,PTMO} \qquad (1)$$

where $T_{g,PPO}$ and $T_{g,PTMO}$ are, respectively, the glass transition temperature of pure PPO (-75°C)[18] and PTMO (-88°C).[19] The weight fraction of PPO and PTMO are w_{PPO} and w_{PTMO}, respectively. The calculated $T_{g,s,o}$ is -84°C. Therefore, the glass transition

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[15] CHU, B., WU, D., and WU, C. Rev. Sci. Instrum, v. 58, 1987 p. 1158.

[16] WU, D., Ph. D. Thesis, SUNY at Stony Brook, NY, 1990.

[17] FOX, T. G. Bull. AM. Phys. Soc., v. 1, 1956, p. 123.

[18] BEAUMONT, R. H., CLEGG, B., GEE G., HERBERT, J. B. M., MARKS, D. J., ROBERT, R. C., and SIMS, D. Polymer, v. 7, 1966, p. 401.

[19] CLEGG, G. A., GEE, D. R., MELIA, T. P., and TYSON, A. Polymer, v. 9, 1968, p. 501.

temperature of the soft segment matrix $T_{g,s}$ is about $T_{g,s,o}$ by 63°C. The reason is twofold: First, the hard segment domains act as crosslinking points which restrict the movements of the soft segments, thus increasing the $T_{g,s}$. Second, some hard segments are mixed inside the soft segment matrix, resulting in an increase in the $T_{g,s}$ value. The endotherm around 195°C represents a dissolution of hard segment domains. Careful evaluation at around 70°C reveals an endotherm along with a baseline shift. This behavior might be interpreted as a glass transition of the amorphous hard segment along with a dissolution of short-range ordered hard segments. It is noted that the glass transition of the amorphous hard segment domains has not been observed in most of the DSC investigations. The discrepancy could be due to the difference in the thermal history of the samples.

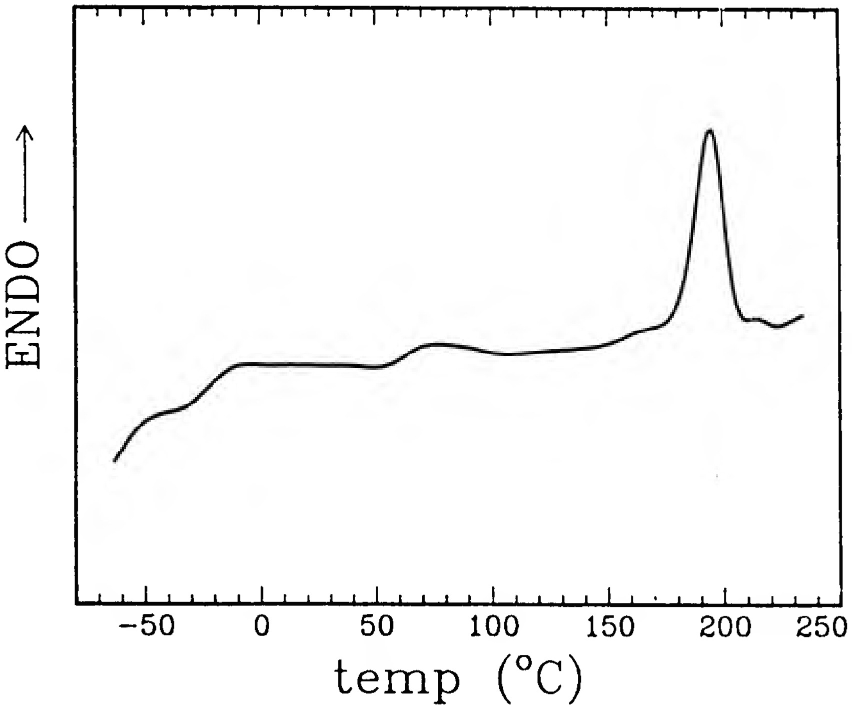

Figure 1. DSC thermogram of PPO-PTMO-PU-50 as-reacted sample.

Figure 2 shows the dynamical properties; i.e., storage modulus and tan $\delta = E''/E'$ with E' and E'' being, respectively, the storage modulus and the loss modulus. Measurements at different frequencies (110 Hz, 35 Hz, 11 Hz, and 3.5 Hz) were performed in order to determine the apparent activation energy (ΔH^*) of the relaxation processes in the sample by using the equation

$$\Delta H^* = 2.303Rd(\log f) / [d(1/T_{peak})] \qquad (2)$$

where f is the frequency at the tan δ peak and R is the gas constant. The relaxation at -3°C with an apparant activation energy of 47.6 kcal/mol represents the glass transition of the soft segment matrix. During the transition, the storage modulus (E') drops approximately two orders of magnitude. The material changes from a hard plastic to a thermoplastic elastomer. The value of the apparent activation energy (47.6 kcal/mol) is very close to that obtained by Huh and Cooper[20] using PTMO as the soft segment (45.7 kcal/mol).

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[20] HUH, D. S., and COOPER, S. L. Polym. Eng. Sci., v. 11, 1971, p. 369.

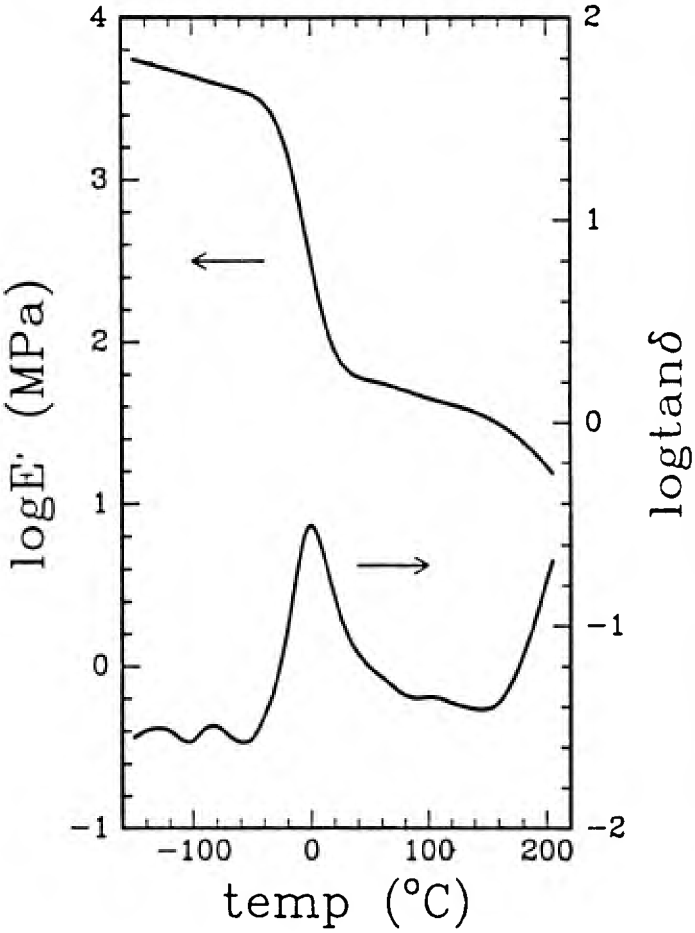

Figure 2. Storage modulus E' and tan δ of PPO-PTMO-PU-50 as-reacted sample measured at 110 Hz.

A secondary loss peak was observed at ca. -25°C. It is generally believed that this peak is due to the motion involving amorphous -CH_2 sequences in the soft segment matrix. The apparent activation energy of 6 kcal/mol is lower than Schatzki's prediction of ca. 13 kcal/mol for the crankshaft-like motion of methylene sequences.[21] The relaxation with the same apparent activation energy of 6 kcal/mol was also observed in our sample using PPO as the soft segment.[14] Therefore, the relaxation at ca. -125°C is probably not a simple Schatzki motion. According to Huh and Cooper,[20] it may be assigned to a local motion of the methylene sequences in the soft segment and in the diol portion of the hard segment.

The secondary relaxation at ca. -85°C, according to Huh and Cooper, is attributed to the motion of NH and C = O groups to which water molecules are attached by hydrogen bonding.

A loss peak at approximately 100°C also observed. In combination with the DSC result, this peak represents the glass transition of the amorphous hard segment domain. The glass transition temperature of pure MDI-BD hard segments has been found by MacKnight, et al.[22] to be 109°C. The difference between the two values is due to the low molecular weight of the hard segments in our segmented polyurethanes sample.

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[21] SCHATZKI, T. F. J. Polym. Sci., v. 57, 1962, p. 496, Polym. Prepr., v. 6, 1965, p. 646.

[22] MACKNIGHT, W. J., YANG, M., and KAJIYAMA, T. Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem., v. 9, 1968, p. 860.

When the temperature is raised to ca. 200°C, the material loses its mechanical strength due to the dissolution of the hard segment domains which act as fillers and crosslinking points.

Figure 3 shows a stress-strain test of the as-reacted sample. The curve shows the behavior of an elastomer. The ultimate elongation is 480% and the tensile strength at break is 28.9 MPa. The mechanical properties can be changed by controlling the hard segment content.[14]

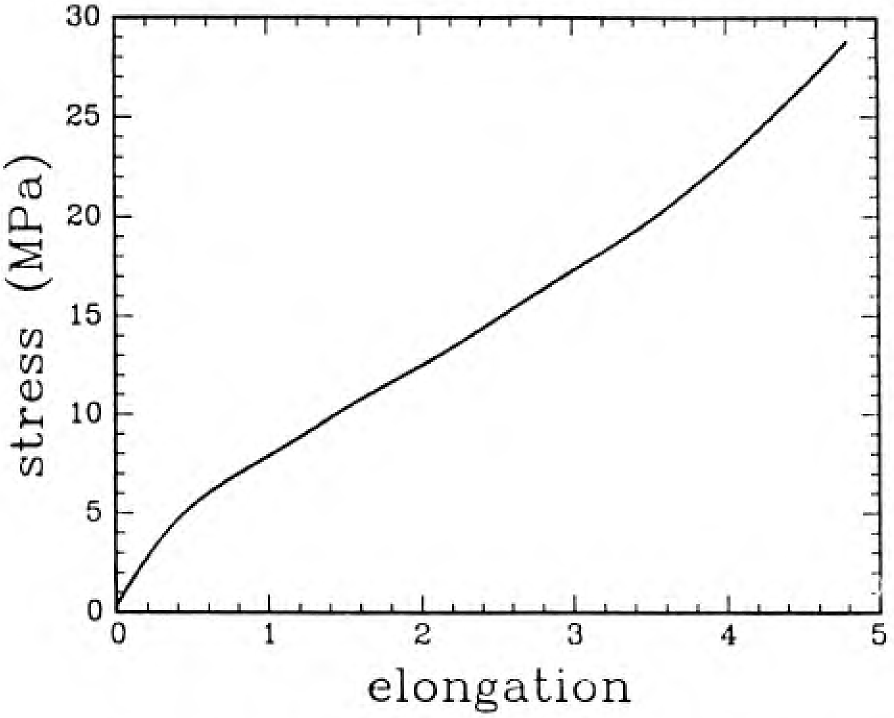

Figure 3. Stress-strain curve of PPO-PTMO-PU-50 as-reacted sample.

The glass transition temperature of the soft segment matrix was also observed by TSDC at around -7°C, as shown in Figure 4. In addition, another peak which cannot be related to DSC and DMA results was observed at 37°C. This peak is attributed to the interfacial polarization (MWS polarization) due to the difference in electrical conductivities of hard and soft segment phases.[23,24] The upturn at above 60°C cannot be correlated with the DSC and DMA results. After the temperature scanning was finished, the sample was once again cooled to -130°C but without polarization electric field. A repeat of the temperature scanning still showed the upturn but the peaks at -7°C and 37°C disappeared. Thus, the upturn could be due to the motion of space charges.

The high flux of a synchrotron radiation source along with the position-sensitive detectors provides a possibility of investigating the time dependence of structural changes of segmented polyurethanes as a function of temperature. Before the synchrotron SAXS results are presented, a brief review of the appropriate SAXS theory will facilitate the discussion of the SAXS experimental results.

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[23] VAN TURNHOUT, J. *Thermally Stimulated Discharge of Polymer Electrets*. Elsevier, Amsterdam, Holland 1975.

[24] VANDERSCHUEREN, J., and GASIOT, J. *Thermally Stimulated Relaxation in Solids*. P. Braunlich, ed., Top. Appl. Phys., Springer-Verlag, Berlin, Germany v. 37, 1979, p. 135.

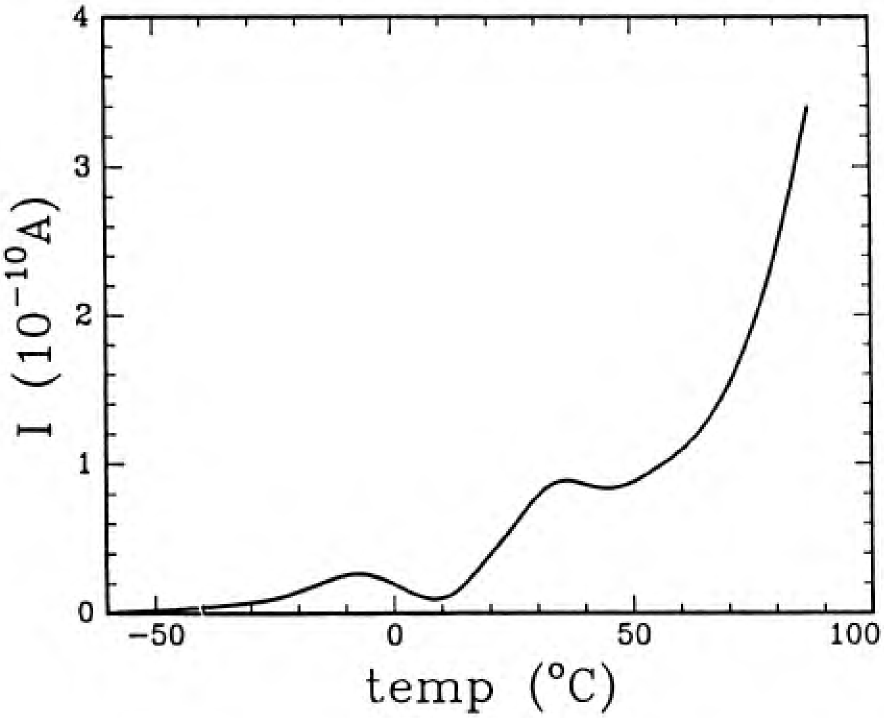

Figure 4. TSDC pattern of PPO-PTMO-PU-50 as-reacted sample.

For a system with spherical symmetry, the scattered intensity of X-rays is related to the so-called three-dimensional normalized correlation function by[25]

$$\gamma_3(r) = (1/Q)\int_0^{\infty} q^2 I(q)[\sin(qr)/(qr)]\,dq \tag{3}$$

where $\gamma_3(r) = <\eta(r_1)\eta(r_2)>/<\eta^2>$, with $r = |r_1 - r_2|$ and $\eta(r)$ being the local electron density fluctuations at postion r; q is the magnitude of the scattering vector, and $q = (4\pi/\lambda)\sin(\theta/2)$ with λ and θ being, respectively, the wavelength and the scattering angle; Q, the so-called invariant, is defined by

$$Q = \int_0^{\infty} q^2 I(q)dq\ . \tag{4}$$

For an ideal two-phase system with a sharp interface, Q can be written as

$$Q = c\phi_1\,\phi_2\,(\rho_1 - \rho_2)^2 \tag{5}$$

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[25] *Small Angle X-Ray Scattering*. O. Glatter, and O. Kratky, eds., Academic Press, London, England, 1983.

where ϕ_i and ρ_i are the volume fraction and electron density of the *i*th phase and c is a constant related to the instrument setup and the primary beam intensity. The physical importance of Q is that it is directly related to the mean square fluctuations of the electron density and is, therefore, related to the *degree of phase separation*, irrespective of the nature of the phase structure.

The assumption of spherical symmetry is not valid for many cases. For example, systems with lamella structure obviously show local anisotropy. In such cases, a one-dimensional correlation function can be used[26,27]

$$\gamma_1(x) = (1/Q)\int_0^{\infty} q^2 I(q)\cos(qr)dq \ . \qquad (6)$$

In principle, the correlation functions contain all the information pertaining to the shape and the spatial distribution of the phases. As the scattered intensity is related to the correlation functions via a Fourier transform, they should contain the same amount of information. The difference is simply that the scattered intensity is expressed in reciprocal space while the correlation function is expressed in real space; therefore, an analysis of the correlation function should give a more direct view of the phase structure. However, it must be noted that the experimental results are obtained over a finite range of the reciprocal space; i.e., due to instrumental limitations, the SAXS pattern cannot cover the whole q space. In addition, the SAXS pattern has limited precision at very low q values, often because of parasitic scattering, and at very high q values, because of low scattered intensity. This finite q-range limitation means that the Fourier transform of a SAXS pattern in reciprocal space to the correlation function in r space is ill-conditioned; i.e., a Fourier transform of the SAXS pattern will give rise to a correlation function whose form can cover a range of specifications. Therefore, in making a comparison of experimental results with theory, one should consider both SAXS pattern and its Fourier transform, the correlation function.

The high frequency fluctuations in a SAXS pattern can be filtered out by smoothing the experimental data. In the smoothing process, it should be noted that smoothing does not distort the desired information. One way is to change the degree of smoothing and to see whether different conclusions can be reached as a result of smoothing. The truncated scattering curves can be extended at both ends by applying existing theories. At the low q end, either the Guinier law of the Debye-Bueche theory could be considered, taking into account the physics of the system. The Guinier law reads[27]

$$I(q) = I(0)\exp(-q^2 R_g^2/3) \qquad (7)$$

where I(q) and (0) are the scattered intensity at q and the scattered intensity extrapolated to $q = 0$, respectively. R_g is the radius of gyration.

For a system with completely random distribution of domain sizes and shapes, the Debye-Bueche theory has the form[28]

$$\gamma(r) = \exp(-r/l_p) \qquad (8)$$

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26. FEIGIN, L. A., SVERGUN, D. I. *Structure Analysis by Small-Angle X-Ray and Neutron Scattering.* Plenum Press, New York, NY, 1987.
27. GUINIER, A., and FOURNET, G. *Small Angle Scattering of X-Rays.* Wiley & Sons, New York, NY, 1955.
28. DEBYE, P., and BUECHE, A. M. J. Appl. Phys., v. 20, 1949, p. 518.

where l_p is a correlation (inhomogeneity) length.

In reciprocal space, Equation 8 takes the form

$$I(q) = 8\pi < \eta^2 > l_p^3 / [1 + l_p^2 q^2]^2 . \tag{9}$$

Based upon structural considerations, Equations 7 and 8 can be used to fit the low angle data; then the equation can be used to generate extended data points to make up the low angle region.

It seems that the Guinier law works well for dilute particulate systems while the Debye-Bueche theory can generally be used to take into account long range local inhomogeneities of the system. However, if the SAXS low angle resolution is around 1 mrad, corresponding to a q value of 0.04 nm^{-1}, the selection of one form or another becomes less important for data treatment in segmented polyurethanes. In our experiments, the lowest q value was around 1 mrad to 1.5 mrad. It was noted that the two models were insensitive to the q variations in the low angle SAXS range.

An extension of the high scattering angle data can be achieved by using the Porod-Ruland theory.[26,27]

For an ideal two-phase system with a sharp interphase, the Porod theory gives the following relation:[26,27]

$$\lim_{q \to \infty} [I(q)] = K_p / q^4 \tag{10}$$

where K_p is a constant related to the surface-to-volume ratio of the phases.

If the system contains diffuse phase boundaries, the scattered intensity decays more quickly and the corresponding relation becomes

$$\lim_{q \to \infty} [I(q)] = K_p H^2(q) / q^4 \tag{11}$$

where $H^2(q)$ is the Fourier transform of a smoothing function and represents the effects due to diffuse phase boundaries.

The thermal density fluctuations inside a phase also contributes to the scattered intensity; therefore, the corresponding equation for the scattered intensity becomes

$$\lim_{q \to \infty} [I(q)] = K_p H^2(q) / q^4 + I_B \tag{12}$$

where I_B is the scattered intensity due to thermal fluctuations inside a phase.

Different models have been proposed and corresponding expressions for $H^2(q)$ and I_B have been reviewd by Koberstein, et al.[29] It was noted in the experiments the sigmoidal model for the diffuse phase boundaries and a constant I_B worked reasonably well; i.e.,

[29] KOBERSTEIN, J. T., MORRA, B., and STEIN, R. S. J. Appl. Crys., v. 13, 1980, p. 34.

$$\lim_{q\to\infty} [I(q)] = K_p/q^4 \exp(-\sigma^2 q^2) + I_B \tag{13}$$

where I_B is a constant and σ is related to the thickness of the interface E by the relation

$$E \approx (12)^{1/2}\,\sigma. \tag{14}$$

Therefore, the high angle experimental data can be used to fit Equation 14 to get K_p, σ and I_B, and then the parameters can be put into Equation 13 to generate extended data points for the high angle region.

The interdomain spacing d can be estimated from the position of the primary maximum of the correlation function if the one dimension geometry is applicable. The other method is to use the Bragg equation

$$nd = 2\pi/q_m \tag{15}$$

where n is the order of reflections and q_m is the q value at the position of a maximum in the scattering curve. However, if the system contains randomly oriented lamella structures, the random arrangement of the one-dimensional repeating structure has to be corrected by perfoming the so-called Lorentz correction; i.e., by multiplying the scattered intensity with q^2. Then the peak position is determined from $I(q)q^2$ versus q, instead of I(q) versus q.

For a synchrotron SAXS experiment involving temperature change, the difference between the thermal expansion coefficient of the two phases could give rise to a change in $(\rho_1 - \rho_2)$ which influences the Q value, according to Equation 5. In segmented polyurethanes, the hard segment domain has a lower thermal expansion coefficient than the soft segment matrix. As the temperature is raised, the density of both phases is decreased. Therefore, the difference $(\rho_1 - \rho_2)$ is increased. This increase will result in an increase in the invariant (Q). In order to obtain the structural parameters, this effect has to be corrected.

Following Fisher, et al.[30,31] and Gehrke, et al.[32] the thermal expansion coefficient is defined as

$$\alpha = d\rho/dT. \tag{16}$$

If the volume fractions ϕ_1 and ϕ_2 remain unchanged, a combination of Equations 5 and 16 yields

$$[Q(T)/Q(T_O)]^{1/2} = 1 + [(\alpha_1 - \alpha_2)/\,|\rho_1(T_O) - \rho_2(T_O)|\,](T - T_O) \tag{17}$$

where T_O is any reference temperature; α_1 and α_2 are the thermal expansion coefficient of phase 1 and 2, respectively. From Equation 17, a plot of $[Q(T)/Q(T_O)]^{1/2}$ versus $(T - T_O)$ should give a straight line if the structural changes other than thermal expansion do not take place in the system. A structural change would usually cause a change in $(\alpha_1 - \alpha_2)$ and, therefore, a corresponding slope change.

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30. FISHER, E. W., KLOOS, F., and LIESER, G. J. Polym. Sci. Polym. Lett. Ed., v. 7, 1969, p. 845.
31. FISHER, E. W. Pure Appl. Chem., v. 26, 1971, p. 385.
32. GEHRKE, R., RIEKEL, C., ZACHMENN, H. G. Polymer, v. 30, 1989, p. 1582.

Figure 5 shows the synchrotron SAXS profiles of the as-reacted segmented polyurethane sample at different temperatures. The temperature precision was controlled to within 1°C. The entire scan took about 100 minutes. Each step took about four to five minutes. The measurement time for each pattern was 200 seconds. With increasing temperature, the scattering peak gradually shifted toward lower q values. The scattered intensity first increased and then decreased at above 90°C. Figure 6 shows that the invariant Q increased first with increasing temperature. Based upon Equation 17, $[Q / Q_{26^{o}C}]^{1/2}$ should be linearly proportional to T if there were no structural changes except the thermal expansion. The result shows that there was a small structural change around 70°C to 90°C in agreement with the DSC result (see Figure 1). The small bump in Figure 6 could possibly be due to the glass transition of the amorphous hard segment domain along with breakage of the short-range ordered structure. The overall tendency of the curve from 26°C to 180°C was close to a straight line indicating that during the temperature scan in this region the structural changes were very small. The increase in Q due to thermal expansion should not generally be considered as a structural change. When the temperature was above ca. 185°C the Q value started to drop dramatically. We could attribute this drop to the phase mixing of the hard segments with the soft segments. DSC and DMA results also showed the same transition temperature. The mixing process finished at ca. 220°C. Figure 7 shows that the interdomain spacing d (calculated from Equation 15) increased with increasing temperature. A small structural change was observed around 70°C to 90°C. The d values showed an overall slow shift upwards due to the thermal expansion of the two phases and could be distinguished from other more abrupt structural changes. The d values started to increase sharply when the temperature was above ca. 200°C, again confirming the presence of phase mixing. Koberstein and Russell[10] observed this transition at ca. 160°C, about 30°C lower than that in the present study. The difference could probably be attributed to the difference in the thermal history of the samples.

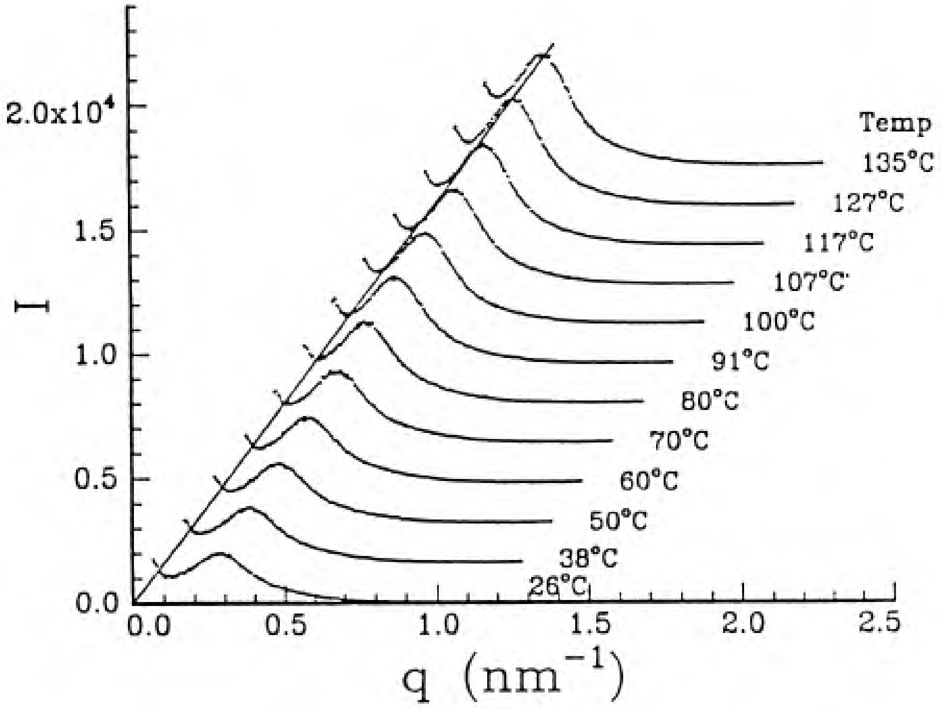

Figure 5a. SAXS patterns of PPO-PTMO-PU-50 as-reacted sample as a function of temperature.

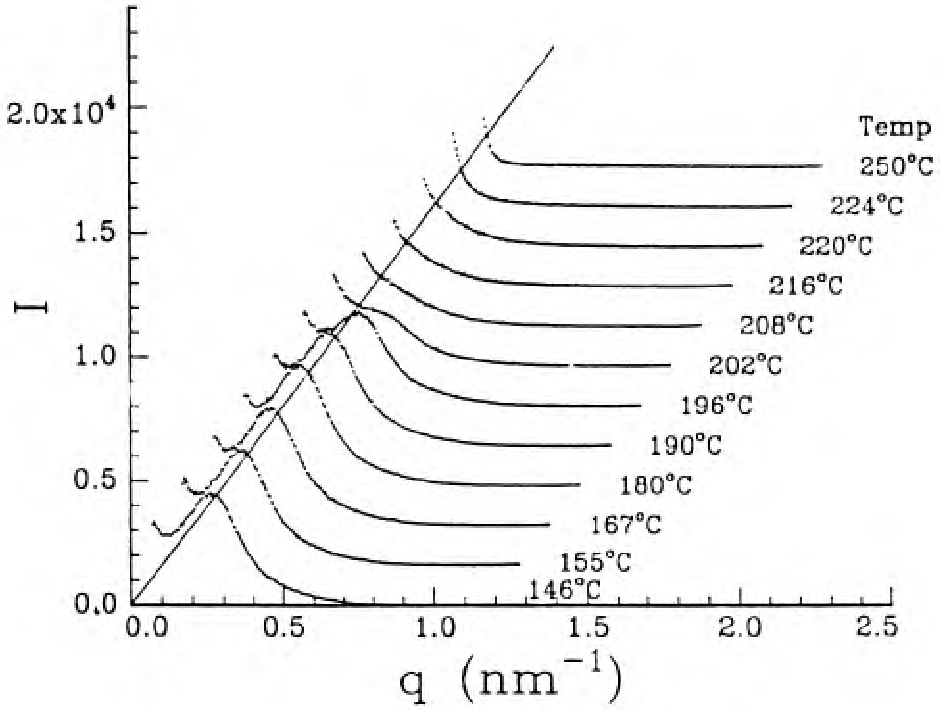

Figure 5b. SAXS patterns of PPO-PTMO-PU-50 as-reacted sample as a function of temperature.

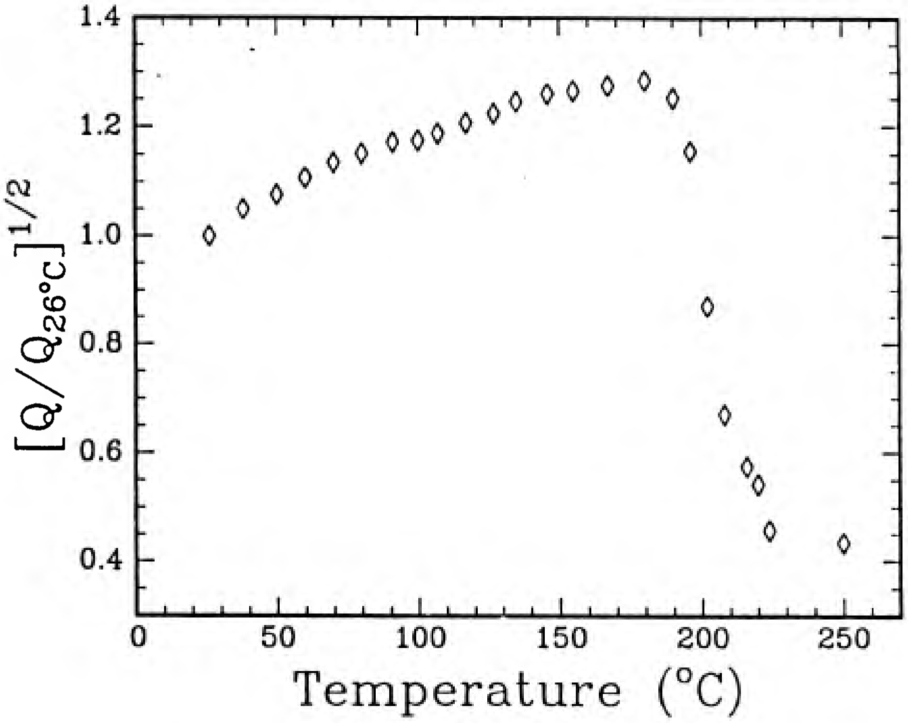

Figure 6. Square root of integrated scattered intensity of PPO-PTMO-PU-50 as-reacted sample as a function of temperature.

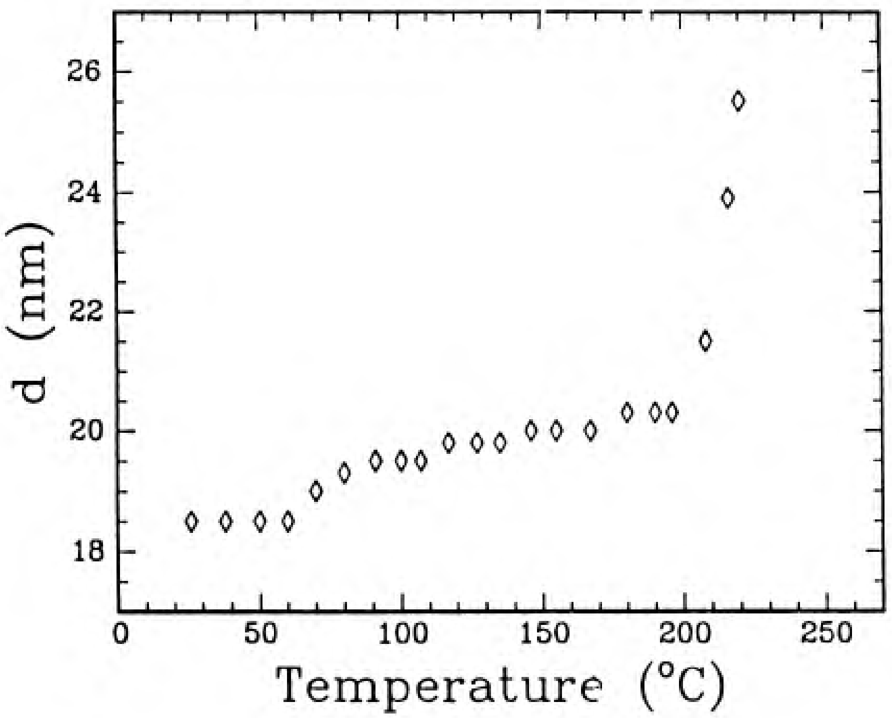

Figure 7. Interdomain spacing d (calculated from Equation 15) of PPO-PTMO-PU-50 as-reacted sample as a function of temperature.

Correlation function analysis was employed to investigate the phase structure of the segmented polyurethane. The Debye-Bueche theory was used to extend the low q region and the Porod-Ruland theory for the high q limit. Without the extensions of the data points the correlation function $\gamma(r)$ would show many ripples due to the finite accessible experimental q range. After the extension, the ripples disappeared. The correlation function was not sensitive to the models used in the low angle region, partially because our data were already fairly close to the zero scattering angle; i.e., our SAXS patterns could already reach small values of q. The results from SAXS curves with different degree of smoothing were also compared with each other. The degree of smoothing did not affect the results in any observable way, unless the SAXS curves were severely over-smoothed. With the high flux of the synchrotron X-ray source, ca. 300 seconds of data accumulation could reach an adequate precision for the correlation function analysis. Both one- and three-dimensional correlation functions were computed. Figures 8 and 9 show the corresponding results for the as-reacted sample. If the system were totally random the three-dimensional correlation function should be equal to $\exp(r / l_p)$, the Debye-Bueche behavior. As shown in Figure 8, the system did not follow this relation. The position of the first maximum gave the interdomain spacing. However, the three-dimensional correlation function shows a very broad peak which makes the determination of the peak position difficult ($d \approx 24.2$ nm). The one-dimensional correlation function in Figure 9 shows a typical two-phase structure. The interdomain spacing calculated from the one-dimensional correlation function was 19.0 nm, considerably smaller than that from the three-dimensional correlation function. The interdomain spacing calculated from the Lorentz-corrected SAXS pattern was 18.5 nm, in good agreement with the one-dimensional correlation function analysis. The phase structure in segmented polyurethanes is believed to be close to lamella, at least on a local scale. Our recent investigation[33] indicated that spherulite structures could be formed if the segmented polyurethane melt was quickly quenched to annealing temperatures above 120°C. Therefore, an analysis based upon the one-dimensional correlation function should be more appropriate and will be used in the following discussions.

[33] LI, Y., LIU, J., YANG, H., MA, D., and CHU, B. Submitted to J. Polym. Sci. Polym. Phys. Ed.

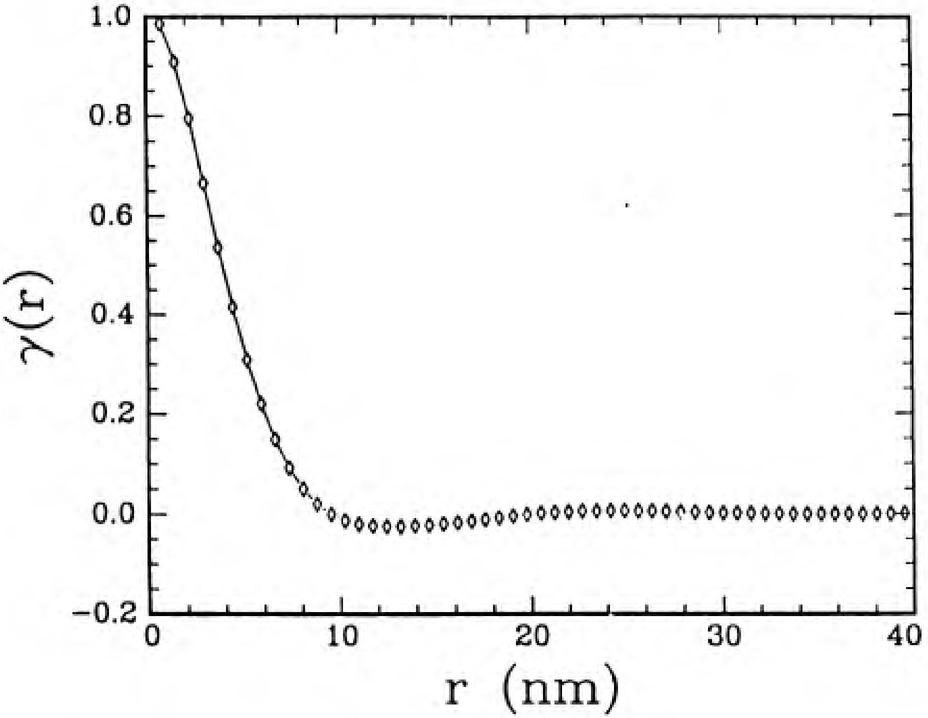

Figure 8. Three-dimensional correlation function of PPO-PTMO-PU-50 as-reacted sample at 26°C.

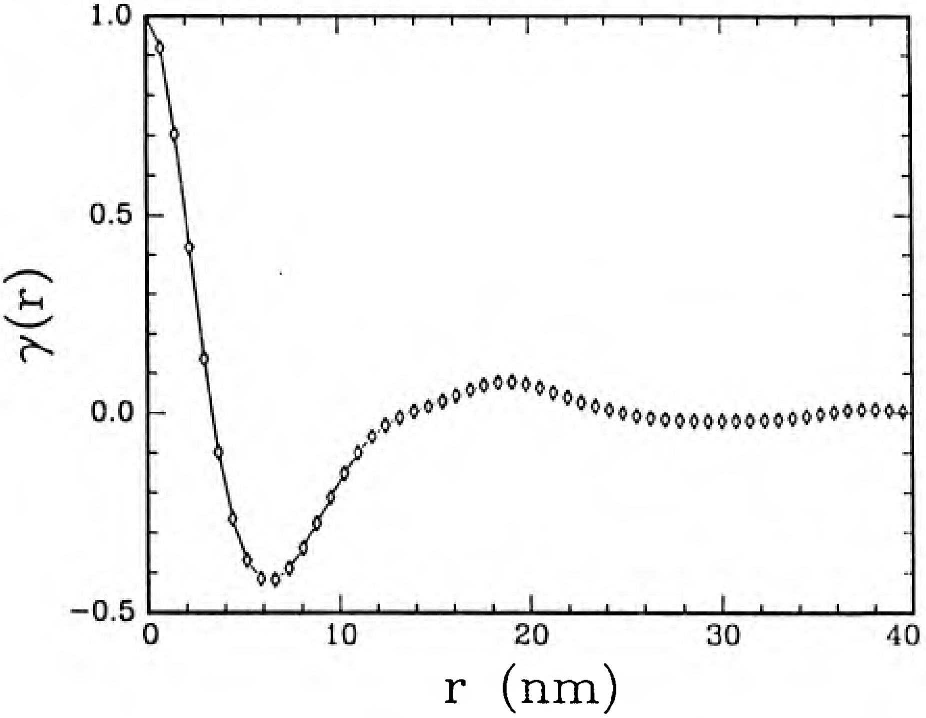

Figure 9. One-dimensional correclation function of PPO-PTMO-PU-50 as-reacted sample at 26°C.

The one-dimensional correlation function of the sample as a function of temperature is shown in Figure 10. The phase structure did not show significant changes except that the first maximum shifted to greater value indicating that the interdomain spacing increased with temperature. The phase contrast increased slightly due to the difference in the thermal expansion coefficient of the two phases. It is interesting to note that there was a shoulder at r ca. 11.5 nm. A similar shoulder was observed by Koberstein and Stein.[34] The exact nature of this shoulder is not yet clear, although it could be due to the fact that the thermal history involved two different polymerization temperatures; i.e., 140°C (three hours) and 80°C (12 hours). At temperatures above ca. 200°C, the one-dimensional correlation functions again showed some ripples. On the other hand, the three-dimensional correlation function changed closer to an exponential decay, as shown in Figure 11. This behavior could imply that when substantial phase mixing took place the system could become more and more random.

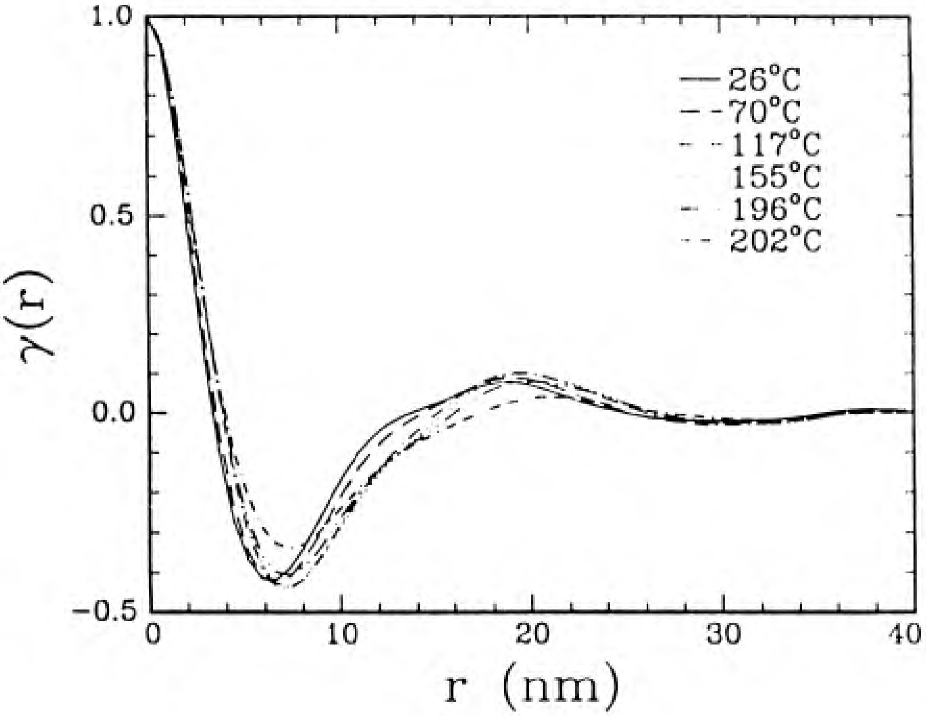

Figure 10. One-dimensional correlation function of PPO-PTMO-PU-50 as-reacted sample as a function of temperature.

After the phase structure and related relaxations of the segmented polyurethane were characterized, it became interesting to see how post-annealing will affect the phase structure of the segmented polyurethane after the samples were thermally annealed at certain temperatures for 48 hours. The as-reacted sample was not used for this purpose because the as-reacted sample used two polymerization temperatures. In order to start from a sample with a well-defined thermal history, the as-reacted samples were melted at 221°C and then quenched to the desired annealing temperatures. The samples were annealed at the annealing temperatures for 48 hours, then part of the samples were further annealed at different temperatures

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[34] KOBERSTEIN, J. T., and STEIN, R. S. J. Polym. Sci. Polym. Phys. Ed., v. 21, 1983, p. 1439.

(post-annealing) in order to investigate the post-annealing effects. First of all, the as-reacted samples had to be melted and to become homogeneous after the annealing at 221°C for three to four minutes. Obviously, if a sample were not completely melted, the residual structure would definitely affect the conclusions on the annealing effects. In the study by Leung and Koberstein,[9] a copolymer equation was used to check whether the starting samples were homogeneous. We used a SAXS experiment to check the short annealing time at 221°C. Figure 12 shows SAXS profiles of the as-reacted sample after it was jumped from room temperature (25°C) to 221°C. The scattered intensity increased first as the sample reached the temperature of the thermal bath (221°C). The increase was once again due to the difference in the thermal expansion coefficient of the hard and soft segment domains. When the sample reached 221°C, which was above the highest dissolution temperature of the hard segment domain from DSC, DMA, or SAXS measurements, the scattered intensity dropped very quickly. The time for the sample to reach a homogeneous state in our temperature jump apparatus was about 90 seconds. The scattering patterns remained basically unchanged for another two to three minutes before an upturn at the low scattering angle started to grow. The small upturn could probably be used as an indication of some degradation reaction. A small amount of air bubbles was found after about seven to eight minutes of annealing at 221°C. SAXS experiments on the melting process at 231°C, 241°C, 251°C, and 261°C were also performed. The behavior was similar to that observed at 221°C except that the time required for the sample to become homogeneous was reduced from about 90 seconds at 221°C to about 60 seconds at higher temperatures. A melting time of two to three minutes was used in order to insure our material to have a homogeneous state.*

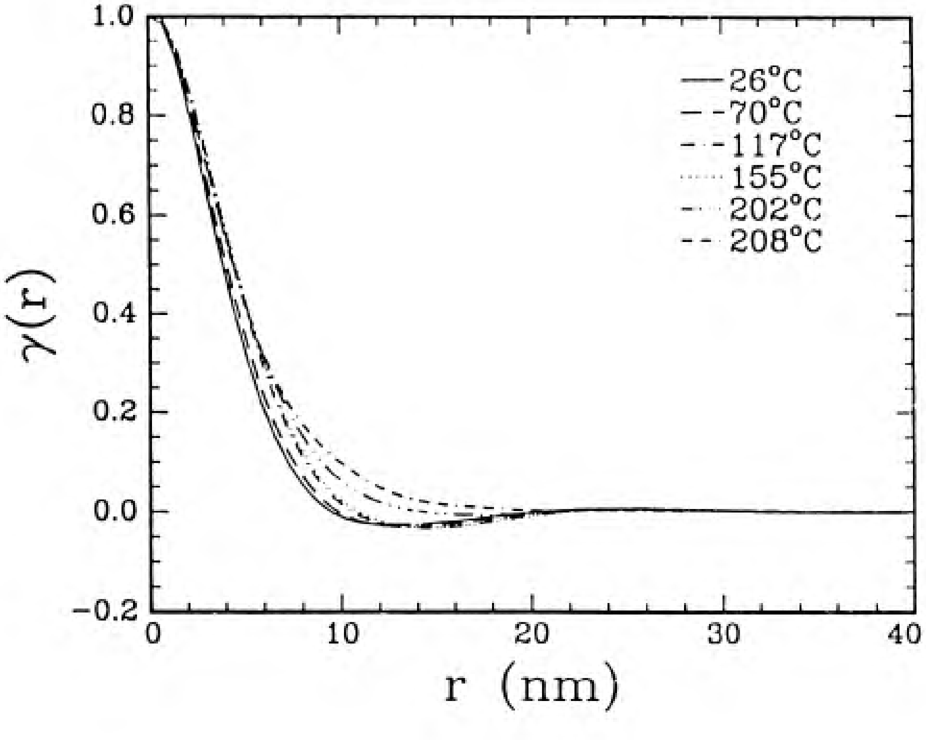

Figure 11. Three-dimensional correlation function of PPO-PTMO-PU-50 as-reacted sample as a function of temperature.

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*Here *homogeneous state* only means that the obvious two-phase structure has disappeared. In this state weak scattering could still be observed due to concentration fluctuation.

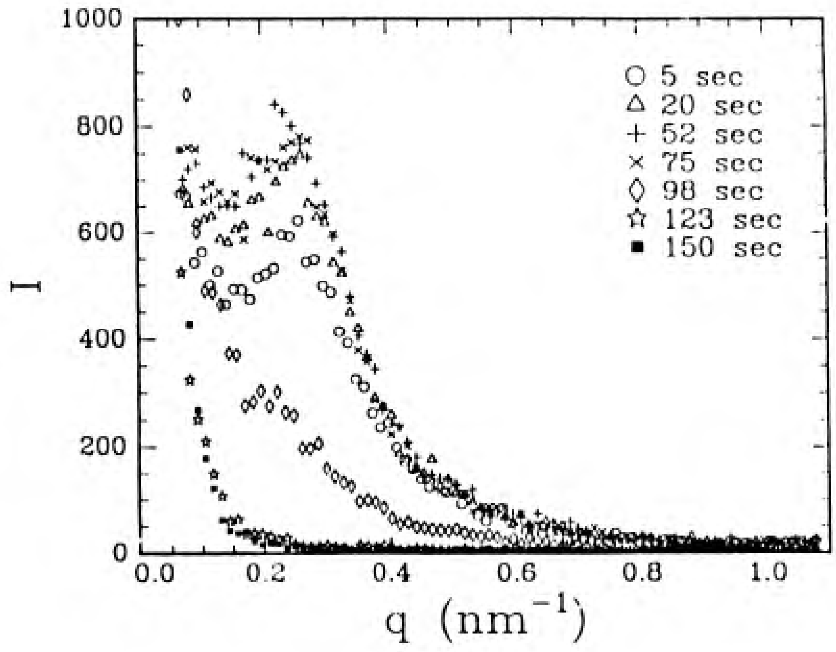

Figure 12. SAXS patterns of PPO-PTMO-PU-50 as-reacted sample after being jumped from room temperatures to 221°C.

The homogeneous melt was then quenched to different annealing temperatures. The annealing time was 48 hours to make sure that the structural development could have sufficient time to reach equilibration. Based upon the phase separation kinetics studies, the 48 hour annealing time could be shown to be enough. SAXS curves in Figures 13, 14, and 15 show the effect of post-annealing on the phase structure of the segment polyurethane, and Figures 16, 17, and 18 show the corresponding one-dimensional correlation functions. As a comparison, SAXS patterns of the sample annealed at 80°C, 135°C, and 167°C are also plotted in the three figures.

It is noted that the starting structure had very significant effects on the phase structure. As the annealing temperature was increased, the scattering peak shifted to lower scattering angles, indicating increasing interdomain spacing. The degree of phase separation first increased with annealing temperature and later decreased slowly as the annealing temperature was raised to 167°C, in agreement with the observations of our earlier reports.[33,35]

From Figure 13, the post-annealing at 135°C of the 80°C annealed sample and post-annealing at 167°C of the 80°C annealed sample resulted in an increase in the scattered intensity. The shapes of the three scattering curves were very similar. This is obvious from the correlation functions shown in Figure 16 in which the interdomain spacing shifted slightly toward smaller values. The increase in the scattered intensity could be attributed to the ordering inside the hard segment domain. The post-annealing at 135°C or 167°C of the 80°C annealed sample generated samples which are by no means identical or close to the 135°C annealed sample or the 167°C annealed sample, respectively. Therefore, the first annealing from melt is a decisive step. The change of the phase structure is irreversible.

Figures 14 and 17 show that the post-annealing at 80°C and 167°C of the 135°C annealed sample produced very little structural change.

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35. CHU, B., and LI, Y. Submitted to Coll. Polym. Sci.

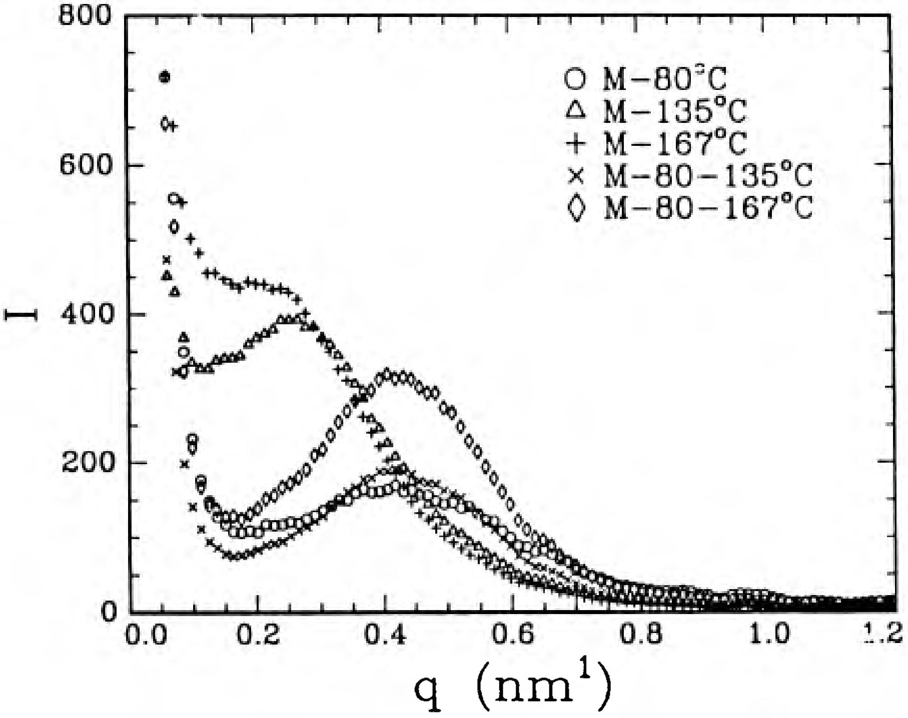

Figure 13. SAXS patterns of PPO-PTMO-PU-50 samples with different thermal treatments in order to study the effects of post-annealing on the structure of 80°C annealed samples. Samples were annealed for 48 hours at each temperature indicated in the legends; SAXS pattern was obtained at final annealing temperature.

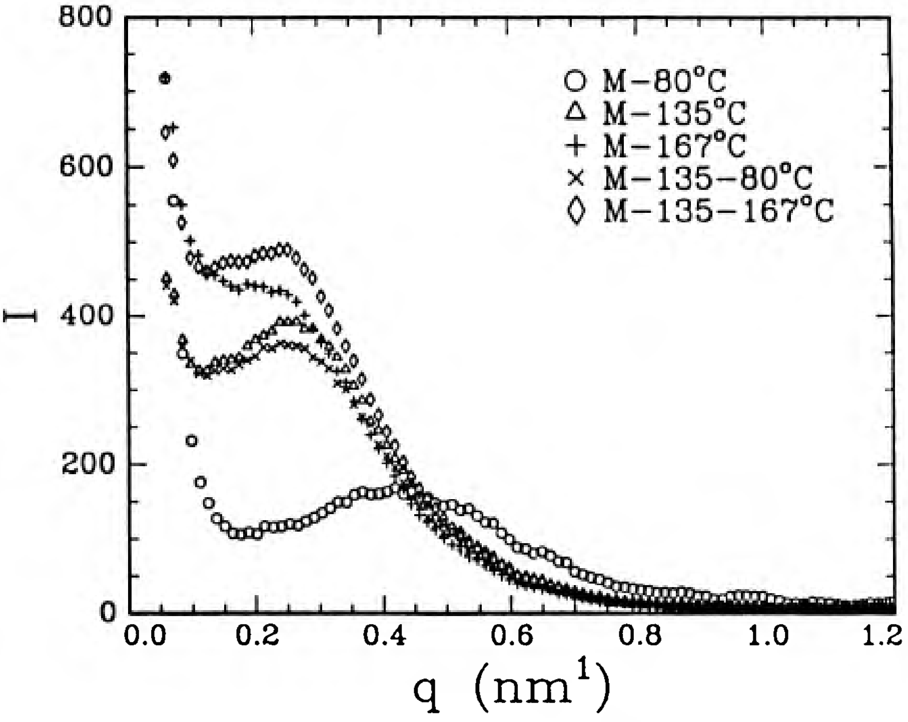

Figure 14. SAXS patterns of PPO-PTMO-PU-50 samples with different thermal treatments in order to study the effects of post-annealing on the structure of 135°C annealed samples. Samples were annealed for 48 hours at each temperature indicated in the legend; SAXS pattern was obtained at final annealing temperature.

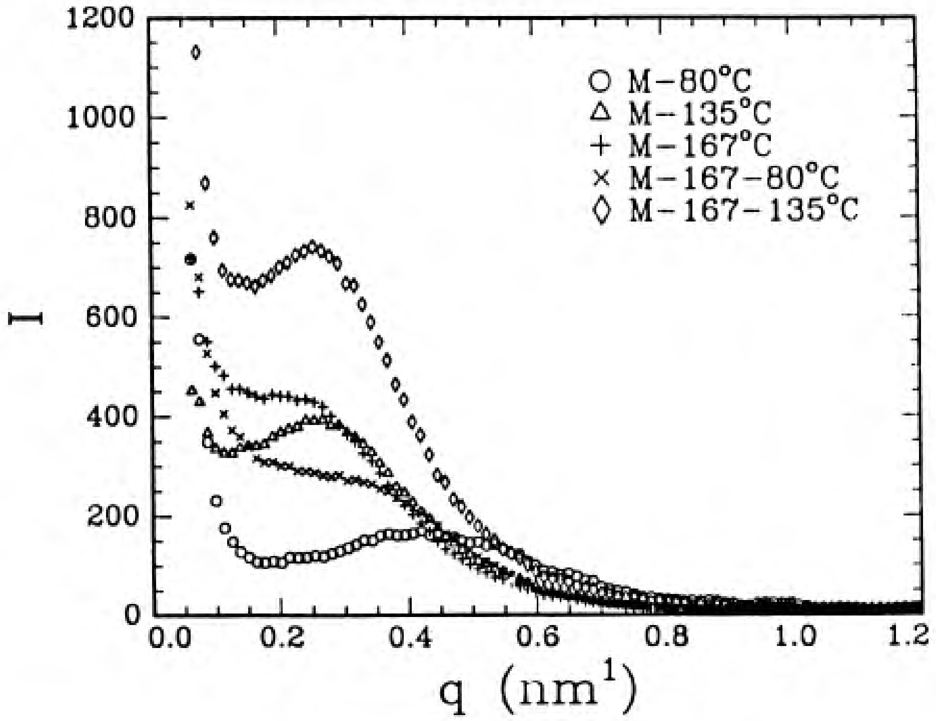

Figure 15. SAXS patterns of PPO-PTMO-PU-50 samples with different thermal treatments in order to study the effects of post annealing on th3 structure of 167°C annealed samples. Samples were annealed for 48 hours at each temperature indicated in the legend; SAXS pattern was obtained at final annealing temperature.

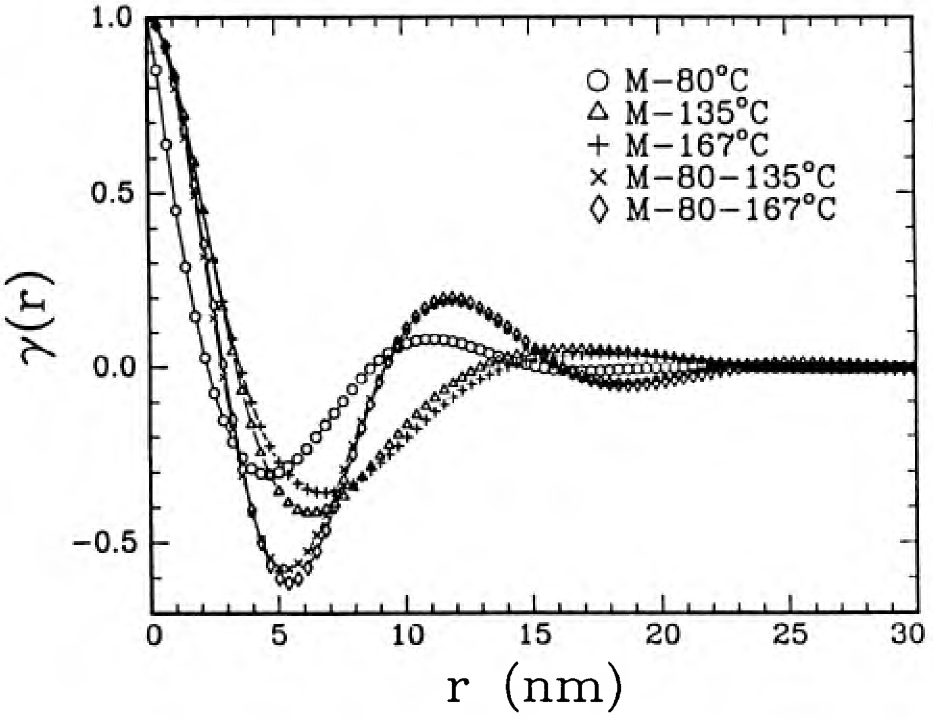

Figure 16. One-dimensional correlation function of PPO-PTMO-PU-50 samples with different thermal treatments in order to study the effects of post-annealing on the structure of 80°C annealed samples.

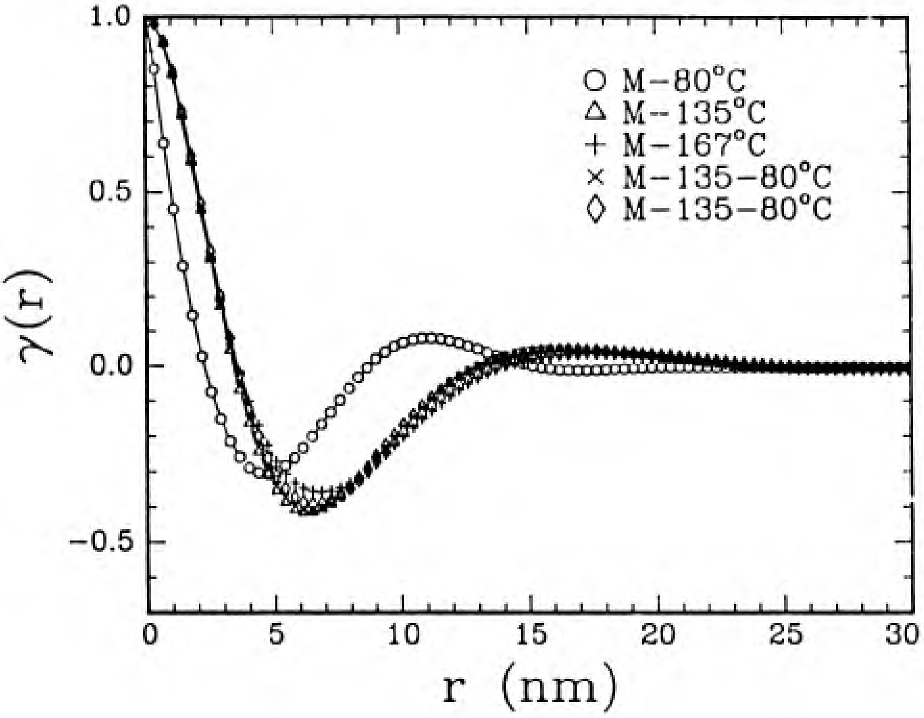

Figure 17. One-dimensional correlation function of PPO-PTMO-PU-50 samples with different thermal treatments in order to study the effects of post-annealing on the structure of 135°C annealed samples.

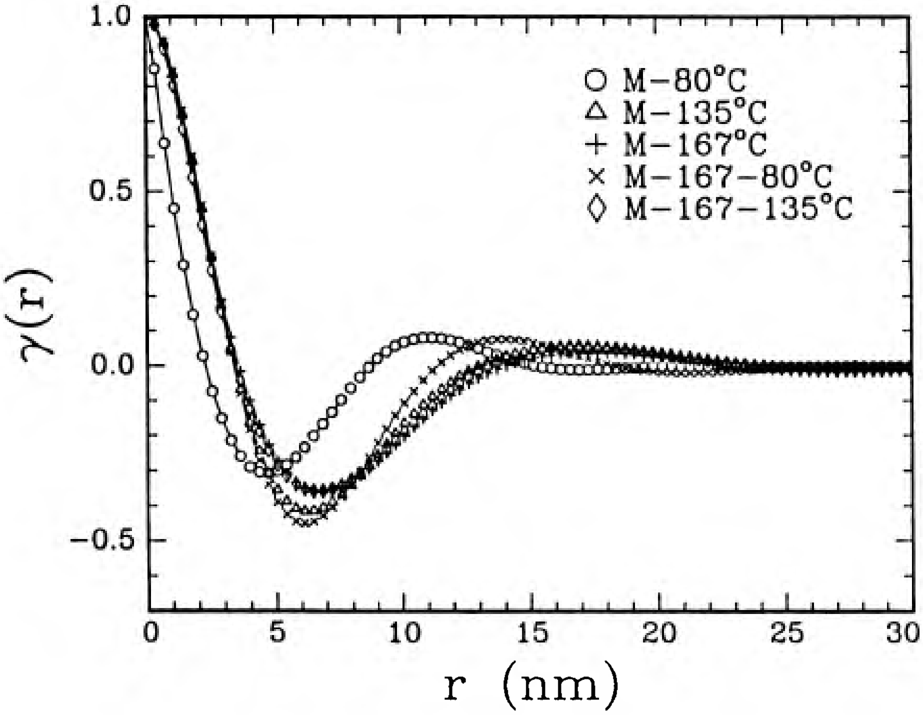

Figure 18. One-dimensional correlation function of PPO-PTMO-PU-50 samples with different thermal treatments in order to study the effects of post-annealing on the structure of 167°C annealed samples.

In Figure 15, the post-annealing at 135°C of the 167°C annealed sample again shows little change except for an increase in the Q value. The post-annealing at 80°C of the 167°C annealed sample showed a decrease in the interdomain spacing. This change can be explained in the following way. The 167°C annealed sample had more short hard segment dissolved in the soft segment matrix. During the 80°C post-annealing, these short hard segments became thermodynamically incompatible with the soft segments and would separate from the soft segment matrix and caused a decrease in the d value.

Although the post-annealing effects of those samples annealed at other elevated temperatures were very small, significant post-annealing effects were observed in those samples first annealed at a temperature below the glass transition temperature of the hard segment domain. In an earlier paper,[34] it was shown that when the samples were quenched from the melt to room temperatures (25°C) and remained at 25°C for 24 hours and then post-annealed at higher temepratures above the glass transition temperature of the hard segment domain, the structure was very close to those samples without the room temperature annealing although no spherulites were observed.

The above results show that the structure of segmented polyurethanes is largely decided by the first annealing starting from the melt. The second annealing has a very small effect. The structural changes are irreversible. Generally, if the post-annealing temperature is lower than the first annealing temperature, the hard segment domains remain basically unchanged. However, some of the hard segments may phase separate from the soft segment matrix. If the post-annealing temperature is higher than the first annealing temperature, the soft segment matrix changes very little while the hard segment domains may undergo further perfection with the overall shape of the hard segment domains basically unchanged. However, if the system has not reached an equilibration state in the first annealing, post-annealing will change the structure dramatically. Also, the change occurs mainly in those domains which have not reached an equilibration state in the first annealing. This statement can be proved in the following experiments.

The sample was melted at 221°C first and then *jumped* to 167°C. Figure 19 shows the phase separation process. After one hour of annealing the sample was jumped to 80°C. The scattered intensity at higher q values started to grow while the scattered intensity at lower q values decreased a little. The phase separation process at 80°C has been found to be much faster than that at 167°C. Figure 20 shows two different processes. It is clear that the phase separation at 80°C mainly happened in those parts where phase separation had not taken place. The portion where phase separation had taken place remained basically unchanged during the annealing. When the melt was first quenched to 80°C and annealed for 1380 seconds and then fast heated to 167°C, the scattered intensity at lower q values started to increase. The scattered intensity at higher q values decreased slightly (see Figure 21). The two different phase separation processes were once again observed, as shown in Figure 22.

The original model of the hard segment chain was proposed by Bonart[36] who stated that the hard segment chains were in an extended state. Recently Van Bogart, et al.[37] and Koberstein and Stein[34] have concluded from their experiments that the hard segment chains must be in a coiled or even folded configuration. In particular, Koberstein and Stein proposed a model which stated that the thickness of the hard segment domains were controlled by the minimum critical sequence length insoluble in the soft segment matrix. Hard segments longer than this critical length had to adopt either coiled or folded configuration in order to keep themselves inside the hard segment domain. Hard segments shorter than this critical length were mostly dissolved in the soft segment matrix.

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36. BONART, R., MORBITZER, L., and HENTZE, G. J. Macromol. Sci. Phys., v. B3(2), 1969, p. 337.
37. VAN BOGART, J. W. C., Ph. D. Thesis, University of Wisconsin, Madison, WI, 1981.

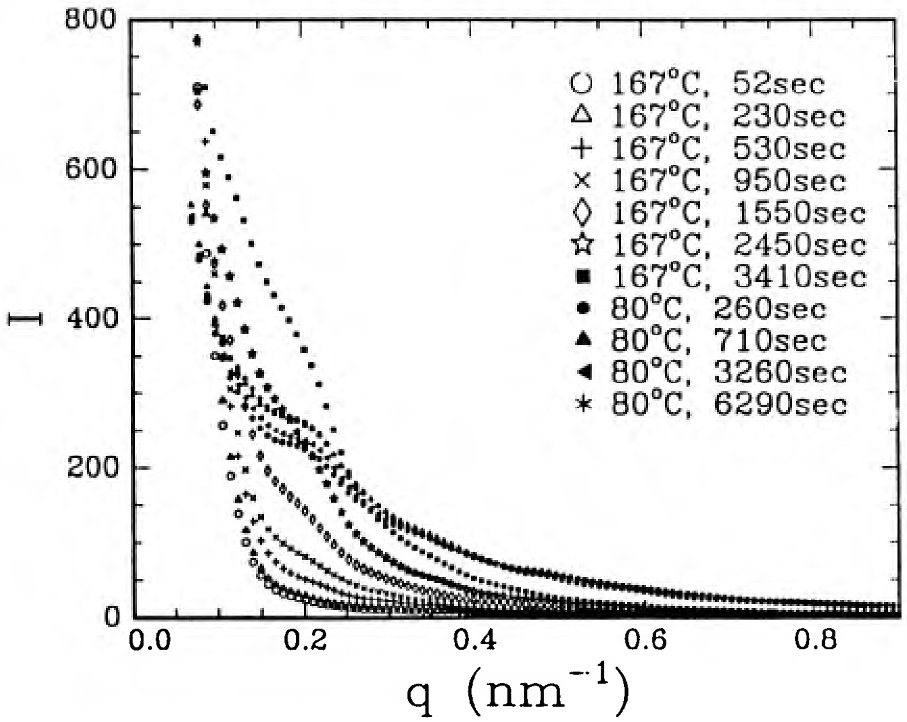

Figure 19. SAXS patterns of PPO-PTMO-PU-50 after being jumped from the melt state (221°C) to 167°C for 3600 seconds and then jumped to 80°C.

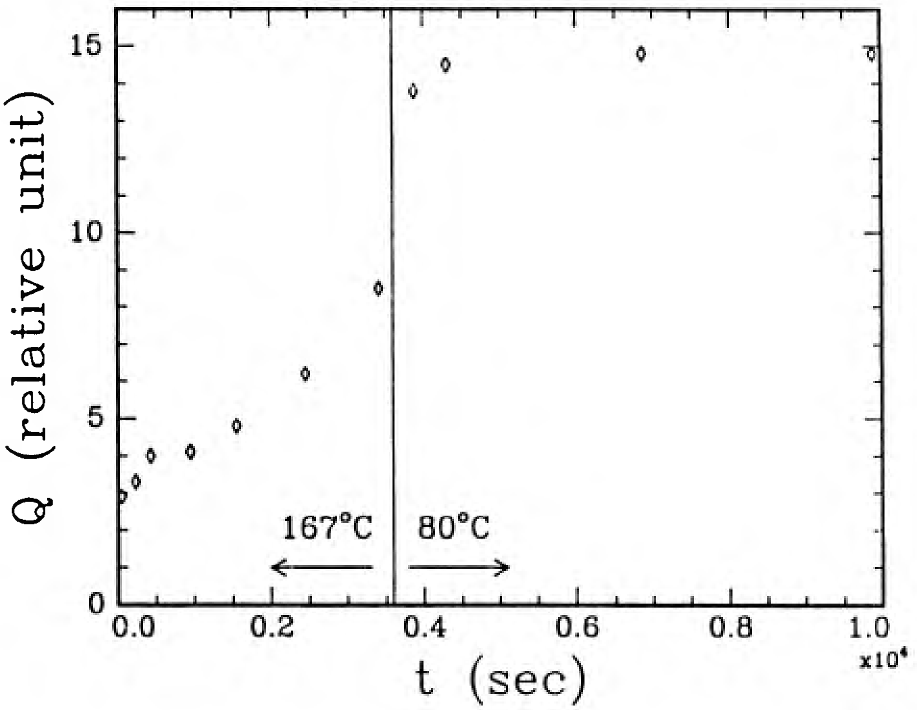

Figure 20. Integrated scattered intensity of PPO-PTMO-PU-50 under different time and temperature.

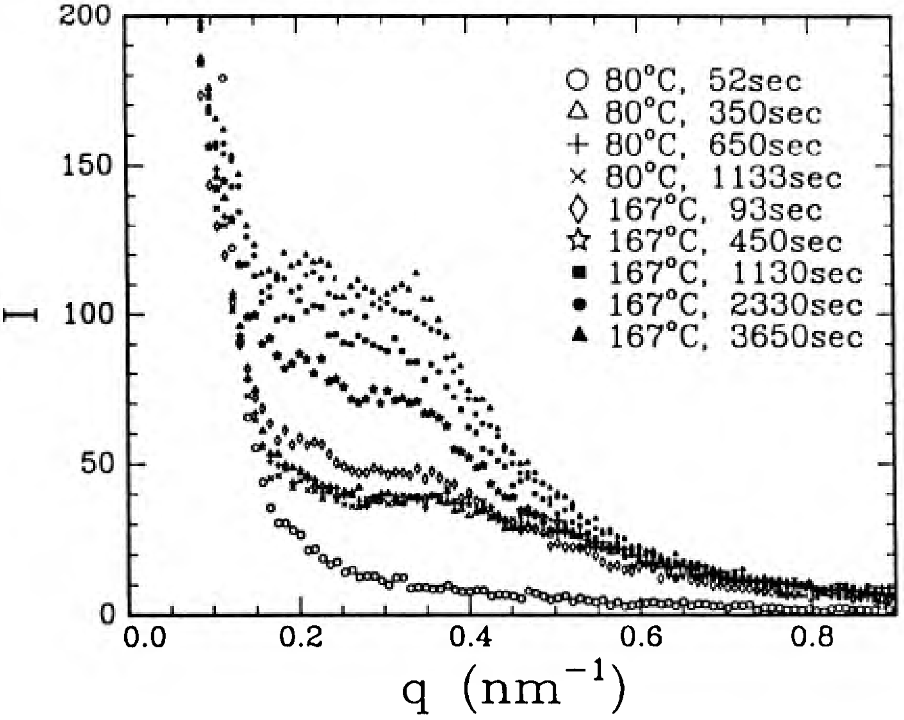

Figure 21. SAXS patterns of PPO-PTMO-PU-50 after being jumped from the melt state (221°C) to 80°C for 1380 seconds and then fast heated at a heating rate of ca. 50°C/min to 167°C.

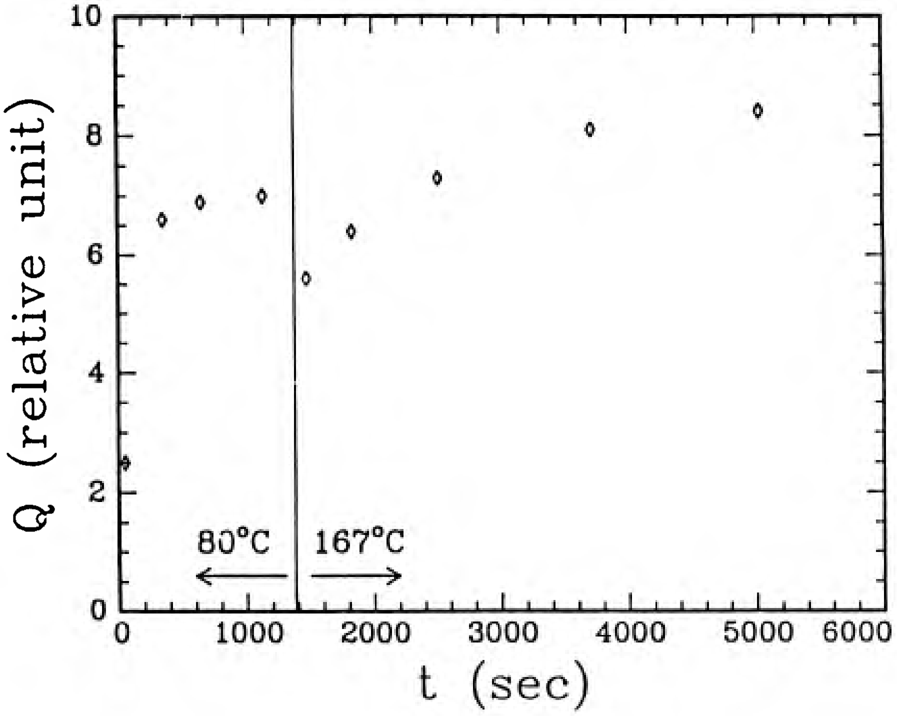

Figure 22. Integrated scattered intensity of PPO-PTMO-PU-50 under different time and temperature.

In an earlier study,[13] it was found that after the melt was quenched to different temperatures the phase separation process was very slow. It took hours to accomplish. The process could be described by an equation of relaxation suggesting that the process could be controlled by the mobility of the hard segments and the system viscosity. The above experimental results, combined with earlier kinetics studies, led to the following proposition.

- The Koberstein-Stein model could be extended to explain the annealing effects. The hard segments are essentially coiled or folded. The degree of coiling or folding is temperature-dependent. The hard segments extend gradually with increasing annealing temperature. This can explain the increase in interdomain spacing with increasing annealing temperature.

- The mobility of the hard segment and the viscosity of the system are two important factors controlling the phase separation process. When the melt is quenched to below the glass transition temperature of the hard segment domain, most of the hard segments do not have enough mobility to reach an equilibration state. When the sample is later post-annealed at higher temperature, the mobility of the hard segments is increased and the viscosity of the system is decreased. The hard segments may then be able to rearrange and to form phase separated structures.

- The interaction between the hard segments is another factor which could affect the hard segment domain stability. As the annealing temperature is increased, the hard segments extend and interact more strongly. The interaction among the hard segments in the segmented polyurethane system is usually very stong, giving rise to the good mechanical properties of the material. However, the strong interactions may not be solely due to the crystallization of the hard segments. When the samples were post-annealed at temperatures higher than the first annealing temperature, the hard segments which have not reached strong enough interactions will rearrange to a more ordered structure in order to increase their interaction level. When the sample was post-annealed at temperatures lower than the first annealing temperature, the critical length of the hard segment decreased.[10] Those hard segments longer than the new critical length would separate from the soft segment matrix. The original hard segment domain would remain unchanged because the temperature could not provide the hard segments enough energy to overcome the interaction barrier. When the sample was post-annealed at below the glass transition temperature of the hard segment domain, the system was basically frozen and no significant post-annealing effects would be observed. No observable structural changes were determined whether the measurements were performed at annealing temperatures or at room temperatures if the thermal expansion effects on the structures had been corrected.

CONCLUSION

A combination of DSC, DMA, TSDC, stress-strain test, and synchrotron SAXS has been used to characterize the multiphase structure of a segmented polyurethane. The sample showed a glass transition of soft segment matrix, a glass transition of hard segment domain, and a dissolution of the hard segment domain into the soft segment matrix. The material basically showed good temperature stability. The increase in Q and d due to thermal expansion of the two phases should not be considered as a phase structure change. The post-annealing effects on the samples with a well-defined thermal history were studied by synchrotron SAXS. The structural changes were irreversible. Once the system reached an equilibration state and a certain degree of interaction, post-annealing could only produce small effects.

Based upon the temperature-dependent coiled/folded hard segment chain model, mobility of the hard segments, viscosity of the system, and the interaction of the hard segments are responsible for the multiphase structures.

It is emphasized here that in a well designed experiment, the thermal history of the sample has to be well specified because it will dominate the annealing effects. In kinetic studies the sample should start from an equilibrium state because the time for the system to reach equilibrium could usually be very long.

The viscosity-mobility-interaction argument could be further tested by using samples with different hard segment flexibility. These samples have been synthesized by intentionally changing the chemical structure of the hard segments. The synchrotron SAXS and DSC results on these systems will be presented in a later report.

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REFERENCES

1. GIBSON, P. E., VALLENCE, M. A. and COOPER, S. L. *Development in Block Copolymers.* L Goodman, ed., Appl Sci. Ser., Elsevier, London, England, 1982, p. 217.
2. COOPER, S. L., and TOBOLSKY, A. V. J. Appl. Polym. Sci., v. 10, 1966, p. 1837.
3. SEYMOUR, R. W., and COOPER, S. L. J. Polym. Sci. Polym. Lett. Ed., v. 9, 1971, p. 689.
4. SAMUELS, S. L., and WILKES, G. L. J. Polym. Sci. Polym. Lett. Ed., v. 11, 1973, p. 807.
5. SEYMOUR, R. W., and COOPER, S. L. Maromolecules, v. 6, 1973, p. 48.
6. JACQUES, C. H. M. *Polymer Alloys: Blends, Blocks, Grafts, and Interpenetrating Networks.* D. Klempner, K. Frisch, eds., Polymer Science and Technology, Plenum Press, New York, NY, v. 10, 1977, p. 287.
7. HESKETH, T. R., VAN BOGART, J. W. C., and COOPER, S. L. Polym. Eng. Sci., v. 20, 1980, p. 190.
8. VAN BOGART, J. W. C., BLUEMKE, D. A., and COOPER, S. L. Polymer, v. 22, 1981, p. 1428.
9. LEUNG, L. M., and KOBERSTEIN, J. T. Macromolecules v. 19, 1986, p. 706.
10. KOBERSTEIN, J. T., and RUSSELL, T. P. Macromolecules. v. 19, 1986, p. 714.
11. GALAMBOS, A. F., RUSSELL, T. P., and KOBERSTEIN, J. T. Polym. Mater. Sci., Eng., Proc. of Am Chem. Soc., Div. Polym. Mater. Sci. Eng., v. 61, 1989, p. 359.
12. GIBSON, P. E., VAN BOGART, J. W. C., and COOPER, S. L. J. Polym. Sci. Polym. Phys. Ed., v. 24, 1986, p. 885.
13. LI, Y., GAO, T., and CHU, B. Submitted to Macromolecules.
14. LI, Y., M. S. Thesis, Henan Inst. of Chem., P. R. China, 1985.
15. CHU, B., WU, D., and WU, C. Rev. Sci. Instrum, v. 58, 1987 p. 1158.
16. WU, D., Ph. D. Thesis, SUNY at Stony Brook, NY, 1990.
17. FOX, T. G. Bull. AM. Phys. Soc., v. 1, 1956, p. 123.
18. BEAUMONT, R. H., CLEGG, B., GEE G., HERBERT, J. B. M., MARKS, D. J., ROBERT, R. C., and SIMS, D. Polymer, v. 7, 1966, p. 401.
19. CLEGG, G. A., GEE, D. R., MELIA, T. P., and TYSON, A. Polymer, v. 9, 1968, p. 501.
20. HUH, D. S., and COOPER, S. L. Polym. Eng. Sci., v. 11, 1971, p. 369.
21. SCHATZKI, T. F. J. Polym. Sci., v. 57, 1962, p. 496, Polym. Prepr., v. 6, 1965, p. 646.
22. MACKNIGHT, W. J., YANG, M., and KAJIYAMA, T. Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem., v. 9, 1968, p. 860.
23. VAN TURNHOUT, J. *Thermally Stimulated Discharge of Polymer Electrets.* Elsevier, Amsterdam, Holland 1975.
24. VANDERSCHUEREN, J., and GASIOT, J. *Thermally Stimulated Relaxation in Solids.* P. Braunlich, ed., Top. Appl. Phys., Springer-Verlag, Berlin, Germany v. 37, 1979, p. 135.
25. *Small Angle X-Ray Scattering.* O. Glatter, and O. Kratky, eds., Academic Press, London, England, 1983.
26. FEIGIN, L. A., SVERGUN, D. I. *Structure Analysis by Small-Angle X-Ray and Neutron Scattering.* Plenum Press, New York, NY, 1987.
27. GUINIER, A., and FOURNET, G. *Small Angle Scattering of X-Rays.* Wiley & Sons, New York, NY, 1955.
28. DEBYE, P., and BUECHE, A. M. J. Appl. Phys., v. 20, 1949, p. 518.
29. KOBERSTEIN, J. T., MORRA, B., and STEIN, R. S. J. Appl. Crys., v. 13, 1980, p. 34.
30. FISHER, E. W., KLOOS, F., and LIESER, G. J. Polym. Sci. Polym. Lett. Ed., v. 7, 1969, p. 845.
31. FISHER, E. W. Pure Appl. Chem., v. 26, 1971, p. 385.
32. GEHRKE, R., RIEKEL, C., ZACHMENN, H. G. Polymer, v. 30, 1989, p. 1582.
33. LI, Y., LIU, J., YANG, H., MA, D., and CHU, B. Submitted to J. Polym. Sci. Polym. Phys. Ed.
34. KOBERSTEIN, J. T., and STEIN, R. S. J. Polym. Sci. Polym. Phys. Ed., v. 21, 1983, p. 1439.
35. CHU, B., and LI, Y. Submitted to Coll. Polym. Sci.
36. BONART, R., MORBITZER, L., and HENTZE, G. J. Macromol. Sci. Phys., v. B3(2), 1969, p. 337.
37. VAN BOGART, J. W. C., Ph. D. Thesis, University of Wisconsin, Madison, WI, 1981.

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MULTIPHASE STRUCTURE OF A SEGMENTED
POLYURETHANE: EFFECTS OF TEMERATURE AND
ANNEALING -
Yingjie Li, Tong Gao, Jian Liu, Kung Linliu,
C. Richard Desper, and Benjamin Chu

Technical Report MTL TR 92-4, February 1992, 30 pp-
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