sulting dissociation of the internal receptor sites induces the pH-sensitive conformational transitions of the membrane (response).

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Thermoluminescence and NMR Studies of Segmented Poly(urethane ureas) in Relation to Phase Separation and Deformation

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ABSTRACT: Thermoluminescence (TL) and pulse NMR studies of segmented poly(urethane ureas) (SPUU) were conducted in relation to phase separation and deformation. The phase separation was controlled by changing the number-average molecular weights of poly(tetramethylene glycol) (PTMG) and the nitrogen content, and the effects of annealing and elongation on the extent of phase separation in samples having a fixed PTMG molecular weight and nitrogen content were also investigated. The TL glow curve of the original SPUU film exhibits a main peak (H) at around 430 K and a weak and broad peak (L) near 350 K. The H peak is related to the liberation of electrons trapped in the hard-segment domains, and the L peak is assigned to the molecular motions of the phase-mixed intermediate phase. The TL and NMR results show that either an increase in the PTMG molecular weight or a decrease in the 4,4′-methylenebis(phenyl isocyanate) content increased the peak intensity and shifted it to a higher temperature, thus indicating an improved phase separation. Annealing also increased the intensity of the H peak, implying that the phase separation is promoted by an increased degree of hydrogen bonding in the hard-segment domains. The changes in the TL glow due to an elongation of the SPUU films showed that the orientation, disintegration, and phase mixing of the hard-segment domains occurred in stages during elongation, and as a result, the intensity of the lower TL peak L increased considerably and the intensity of the H peak decreased accordingly in this process. The above TL results were strongly supported by the pulse NMR experiments.

Introduction

Many studies have been made of the synthesis, morphology, and properties of segmented poly(urethane ureas) (SPUU), and it is well-known that the spherulite texture organized with phase-separated domains is the most important morphological feature of the material, as revealed by small and wide X-ray diffraction,[1] small-angle light scattering,[2] small-angle neutron scattering,[3] IR spectroscopy,[4] DSC,[5] IR dichroism,[6] and NMR.[7]

Concerning NMR, particularly pulsed NMR, mention must be made of the work by Assink and Wilkes[7] on the domain structure of a series of linear and cross-linked polyurethanes. Assink and Wilkes showed that the difference between segmental mobilities of the hard and soft phases decreases with cross-linking, that the fraction of rigid segments decreases in two distinct steps as the temperature increases before cross-linking, and that the change is continuous after cross-linking. Their studies also showed that the sensitivity of the NMR method is high enough to follow changes of the segmental mobilities of different domains and phases.

In parallel with these investigations, considerable efforts have been made to gain an understanding of the phase separation, deformation mechanism, and mechanical properties of the material. Factors influencing the phase separation of SPUU include the polarity of the segments, the length of segments, the crystallinity of either segment, intra- and intersegment interactions such as hydrogen bonding, the overall composition, and the molecular weight. It is also known that phase separation can be promoted by annealing and destroyed by elongation.[8]

Over the past decades, thermoluminescence (TL) has become widely used as an approach for polymer characterization. This approach is even more sensitive than other techniques for the detection of molecular motions and structural changes in some polymers,[9] and a number of papers on the TL of polymers, both theoretical and experimental, have been published recently. The first theoretical approach to TL was made by Randal et al.[10,11] in 1939, dealing with the first-order process, and this was later developed and modified by Garlick and Gibson[12] and Pender and Fleming,[13] on the second-order process. Detailed experimental TL investigations of polymers were initiated by Nikol'skii and Buben[14] and Charlesby and Partridge[15,16] in the early 1960's, and these pioneering studies indicated a close correlation between TL and

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Table I
Number-Average Molecular Weight and Corresponding Percentage Fraction of Soft Segment of PTMG

sample	MW of PTMG	soft-seg fractn
SPUU-1	850	59.7%
SPUU-3	1325	69.8%
SPUU-5	1980	77.5%

Table II
Percentage Fraction of Nitrogen in SPUU

sample	% nitrogen	sample	% nitrogen
SPUU-6	2.4%	SPUU-8	3.7%
SPUU-7	3.0%		

molecular motions and provided evidence of the usefulness of this method of studying the molecular motions and structural changes in polymers.

In a previous paper[17] we found that TL was sensitive to changes in the superstructure of poly(ethylene terephthalate) (PET) caused by annealing and drawing and that the TL intensity increased considerably with advance of fatigue.[18] This work encouraged us to extend this application of TL to other polymers. In the present work, TL is applied to characterize the structure of segmented poly(urethane ureas) (SPUU) in which the extent of phase separation is controlled chemically by either increasing the molecular weight of the PTMG (soft segment) or reducing the nitrogen content (hard segment) and further is controlled physically by annealing, static elongation, and cyclic straining. The results are discussed in comparison with the pulsed NMR data. This paper presents the results of TL and NMR on the effects of (a) the PTMG molecular weight and nitrogen content (hard segment fraction), (b) annealing, and (c) elongation at room temperature on the phase separation of SPUU. The fatigue of SPUU under cyclic extension, the second part of this work, will be reported in a future paper.[19]

Experimental Section

Samples. The two series of segmented poly(urethane ureas) (SPUU) used in this study were supplied by Nishinbo Co. Ltd. and Toyobo Co. Ltd. Both of the series of SPUU films were prepared by a prepolymer method. The soft segment consisted of poly(tetramethylene glycol) (PTMG) with chain extender 1,4-butanediol (BDO) for series II and 1,2-propylenediamine (PDA) for series I. The hard segment was composed of 4,4′-methylenebis(phenyl isocyanate) (MDI) and PDA for the series I and BDO and MDI for the series II. The number-average molecular weight of PTMG for series I changed from 850 to 2000, as shown in Table I. For the series II, the percent nitrogen content in the hard segment changed from 2.4% to 3.7%, as shown in Table II. The sample used for the annealing and elongation was a commercial as-molded SPU film supplied by Nishinbo Co. Ltd. and having a number-average molecular weight of PTMG of about 2000. The molar ratio of the MDI, BDO, and PTMG was 3:2:1.

Annealed samples of series I and II were prepared in a vacuum flask placed in a silicone oil bath at 150 °C for 24 h and 48 h, respectively. The elongation experiments were carried out at room temperature by using a manually operated extender. The thickness of all samples was 0.2 mm.

TL Measurement. TL measurements generally include (a) the irradiation by high energy rays and (b) the measurement of a TL glow intensity above the irradiation temperature. In this study the irradiation was carried out by using an X-ray generated by a copper tube operated at 35 KV and 20 mA. A detailed description of the TL apparatus and experimental procedures can be found in previous papers.[17,18]

The prepared SPUU samples were cut into rectangles measuring 20 × 20 mm and then attached to a copper sample holder, the surface of which was coated with a silver paste to obtain a uniform heating of the samples during the TL measurements. The sample after irradiation was then fixed in a vacuum cryostat at a pressure of 10^{-3} torr for the subsequent TL glow measurement. The heating rate was 6 K/min.

NMR Measurement. The NMR measurements were performed on a Nihon Bruker PC-20 spectrometer operating at 20 MHz in the diode mode. The pulse sequence of a solid echo method was used to measure the spin–spin relaxation time (T_2), and for each measurement, 1024 points were collected and averaged with a cumulative number of 100 and an attenuation of 30 and analyzed by an NEC PC-9801 computer. All NMR measurements were carried out at both 40 and 80 °C.

Mechanical Measurements. Dynamic mechanical measurements were carried out on a Rheolograph Piezo supplied by Toyoseiki Co. Ltd., with a frequency of 10 Hz at a heating rate of 3 °C/min for original SPUU films.

Analysis Methods

TL Glow Curve Analyses. The integrated intensity of a TL glow curve is proportional to the number of electron traps in a polymer, and therefore, the intensity (the number of electron traps) is used as an important parameter when characterizing the TL of the sample. From the maximum temperature T_m, lower and higher half-maximum temperatures T_l and T_h of a glow curve, the number of the electron traps n, the activation energy E, and the frequency factor S can be obtained according to the Chen method.[20] From these parameters a simulation can be provided on the multipeak glow curve of the SPUU and the peaks separated by an NEC PC 9801 computer.

NMR FID Analyses. The spin–spin relaxation time T_2 was estimated from the free induction decay of the echo signal. The free induction decay (FID) can be generally expressed as an exponential function by eq 1.[21] The

$$M(t) = M(0)\exp(-t/T_2) \qquad (1)$$

logarithmic form (2) usually yields a linear relationship

$$\ln M(t) = \ln M(0) - t/T_2 \qquad (2)$$

between the amplitude of magnetization M and the decay time t, where $M(0)$ is the initial FID amplitude. In the case of polymers, the FID is usually a combination of several components. Assink and Wilkes found two components in linear and cross-linked polyurethanes, corresponding to the relaxations of protons in the hard- and soft-segment domains, respectively. In this study, three components, having an FID which can be shown by the following equation, were clearly observed:

$$M(t) = M(\mathrm{s})\exp(-t/T_2(\mathrm{s}))^{\mu(\mathrm{s})} + M(\mathrm{i})\exp(-t/T_2(\mathrm{i}))^{\mu(\mathrm{i})} + M(\mathrm{h})\exp(-t/T_2(\mathrm{h}))^{\mu(\mathrm{h})} \qquad (3)$$

where s, i, and h express the soft phase, intermediate phase, and hard phase, respectively, and μ represents the Wiber coefficient, which was found to be about 1, 2, and 2.5 for $\mu(\mathrm{s})$, $\mu(\mathrm{i})$, and $\mu(\mathrm{h})$ respectively. The $M(\mathrm{s})$, $M(\mathrm{i})$, and $M(\mathrm{h})$ are obtained from each intersection in the semilog plot of FID's, and the fraction of each phase can be calculated according to the following equations:

$$X(\mathrm{s}) = M(\mathrm{s})/(M(\mathrm{s}) + M(\mathrm{i}) + M(\mathrm{h}))$$

$$X(\mathrm{i}) = M(\mathrm{i})/(M(\mathrm{s}) + M(\mathrm{i}) + M(\mathrm{h}))$$

$$X(\mathrm{h}) = M(\mathrm{h})/(M(\mathrm{s}) + M(\mathrm{i}) + M(\mathrm{h})) \qquad (4)$$

Results and Discussions

Effects of Molecular Weight of PTMG on Phase Separation. Figure 1 shows an example of the FID of an original SPUU and the three components which have been subtracted from the preceding logarithm plot by a least-squares method. These components can be reasonably assigned to the soft-segment phase, intermediate phase, and hard-segment phase, according to the values of the T_2

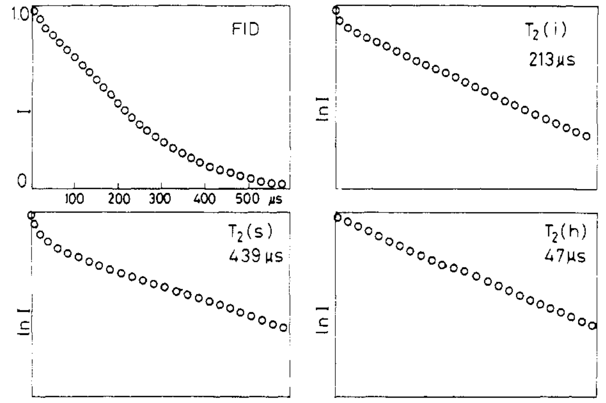

Figure 1. FID of as-molded SPUU film and the logarithm plots of the respective phases obtained from pulse NMR measured at 40 °C: T_2(s), spin-spin relaxation time of soft segment phase; T_2(i), for intermediate phase; T_2(h), for hard-segment phase.

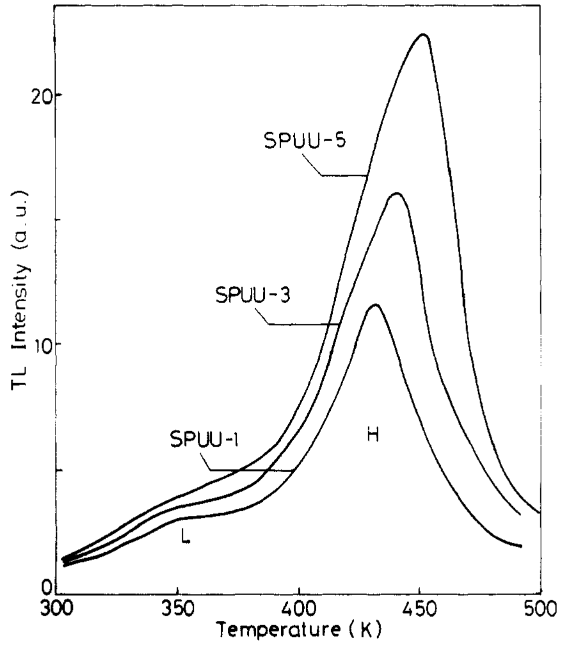

Figure 2. TL glow curves of as-cast SPUU films with different PTMG molecular weights.

relaxation times shown in Figure 1. The T_2 of the hard-segment phase is 10 times large than that of the soft-segment phase. It must also be noted that the Wiber coefficient μ(h) observed in this study was not simply 2 or 1, indicating that the FID of the hard-segment domains does not follow a simple exponential or Gaussian function, as has been shown for linear and cross-linked polyurethanes. The most important feature is the existence of the intermediate phase, even in the as-molded films, and this study will focus on the changes thereof caused by thermal and mechanical treatments.

Figure 2 shows the TL glow curves of as-molded SPUU films of series I for various number-average molecular weights of the PTMG. Each of the glow curves exhibits a main peak (marked H) at around 430 K and a weak and broad peak at about 350 K (marked L). A dynamic loss modulus versus temperature curve of the as-molded SPUU film is shown in Figure 3, in which a peak near 203 K is related to the glass transition of PTMG,[22] and an asymmetric peak near 430 K is related to the melting of hard-segment domains. No recognizable dispersion peak corresponding to the TL peak at 350 K appears in Figure 3. Comparing Figure 2 to Figure 3, it can be seen that the TL main peak near 430 K is due to the liberation of electrons caused by the melting of the hard-segment domains. It is difficult to relate the TL peak at 350 K to any mechanical dispersion, but it cannot be due to the liberation of electrons trapped in the soft-segment domains since the glass transition, as indicated in Figure 3, is located at a much lower temperature (about 203 K). The identification of this TL peak will be made by NMR later. It can be seen from Figure 2 that the intensity of the main peak H increases rapidly and its maximum temperature shifts to a higher temperature as the molecular weight of PTMG increases. Accordingly, because the intensity of the main TL peak H is proportional to the electron traps in the hard-segment domains, it can be deduced that an increase in the molecular weight of PTMG leads to an increase in the TL trap concentration in the hard-segment domains. Nevertheless, the fractional volume of the hard segment domains, as indicated in Figure 5, decreases as the PTMG molecular weight increases. Therefore, if an uniform trap site distribution is assumed, the increase in the TL trap density in the hard-segment domains could be considered a reason for the higher and larger TL peak H. This implies a higher electron density $\langle\rho^2\rangle$ and, therefore, a better phase separation, as indicated by SAXS.[23]

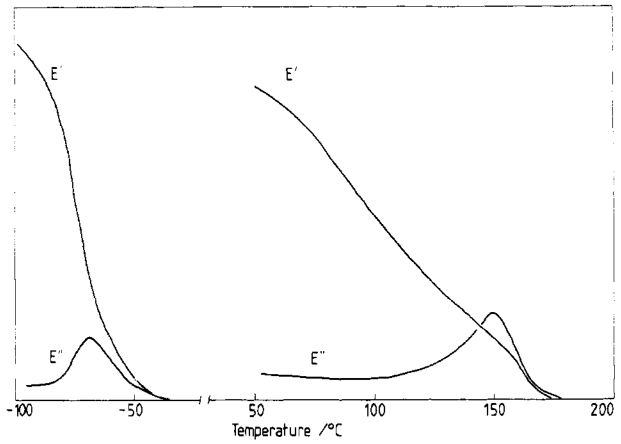

Figure 3. Loss modulus versus temperature curve of as-molded SPU film with a resonance frequency of 10 Hz and a heating rate of 3 °C/min. The Y axis was not scaled.

In Figure 4 the spin-spin relaxation times T_2 of each phase are plotted against the molecular weight of PTMG. No noticeable change in the relaxation time itself was observed when the molecular weight of PTMG was increased. Figure 5, however, shows that the fractions of phases corresponding to the soft and hard segments vary notably with an increase in the molecular weight of PTMG; i.e., the fraction of soft segment increases and that of hard segment decreases accordingly. Particular notice should be taken that, as shown in Figure 5, there is a decrease in the fraction of the intermediate phase as the PTMG molecular weight increases. It is reasonable to assume that this decrease in the intermediate phase is the result of a promoted phase separation. These considerations are also consistent with data of IR and dynamic mechanical experiments by Takahara et al.[24]

Effects of Nitrogen Content on Phase Separation. Figure 6 gives the TL glow curves of as-molded SPU films with various nitrogen contents (hard segment fraction). Here, in contrast to Figure 2, it can be seen that the intensity undergoes a considerable decrease with an increase in the hard-segment content, accompanied by a shift of the maximum temperature to lower values. This suggests that the increase in MDI is the cause of the decrease in the TL trap density and, therefore, in the electron density.

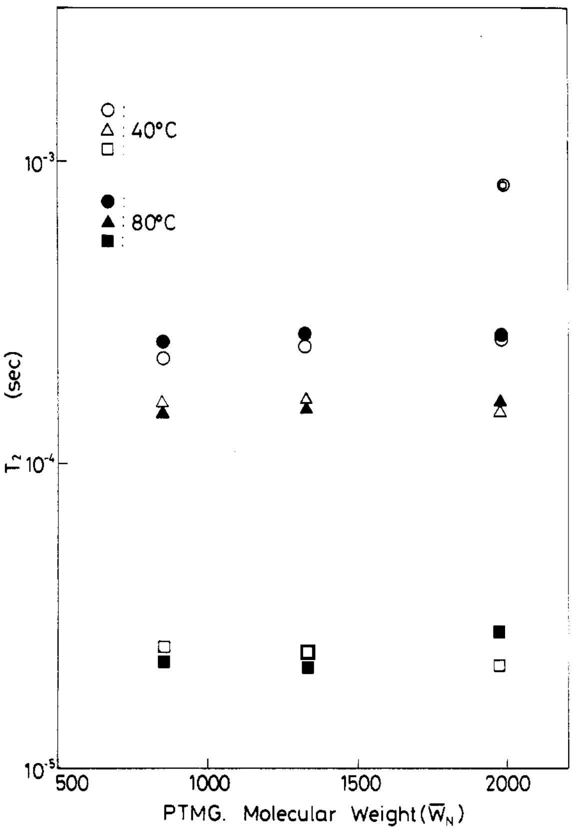

Figure 4. Spin–spin relaxation times (T_2) of the respective phases of as-cast SPUU film versus PTMG molecular weight measured at 40 °C (open) and 80 °C (solid) by NMR: (○, ●) soft-segment phase; (△, ▲) intermediate phase; (□, ■) hard-segment phase.

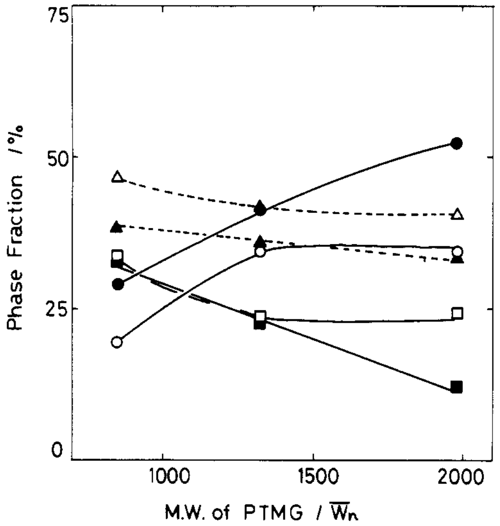

Figure 5. Phase fractions of the respective phases of as-cast SPUU versus PTMG molecular weight measured at 40 °C (open) and 80 °C (solid) by NMR. Notations are the same as in Figure 4.

A possible explanation for this change is that the increasing MDI leads to a lower degree of hydrogen bonding between the hard segments and causes some of the hard segments to leave the hard-segment domain and mix with the soft-segment matrix. This is in agreement with our prediction and the results of Seymour et al.[25-27] obtained during an IR dichroism study of MDI/BD/PTMO-1000 (1000 MW PTMO) polyurethane, in which they found that an increase in the hard-segment content from 24 to 28 wt % MDI changed the isolated hard-segment domain structure to an interconnected structure. A similar tendency was also found by Van Bogart et al.[28] from their FTIR investigations. It must be noted that, in Figure 6, the glow curve of SPU with 3% nitrogen and that with 3.7% nitrogen showed no noticeable differences, despite large changes in the nitrogen content. This may be due to the fact that an increase in the MDI content does not induce a strictly equivalent decrease in the soft-segment fraction, because the nitrogen is also included in the soft segments.

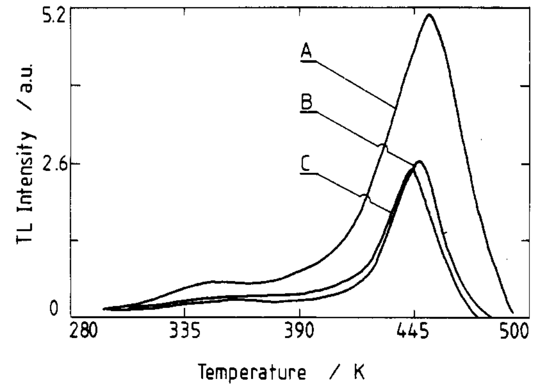

Figure 6. TL glow curves of as-molded SPU films with different nitrogen contents: (A) 2.4%; (B) 3.0%; (C) 3.7%.

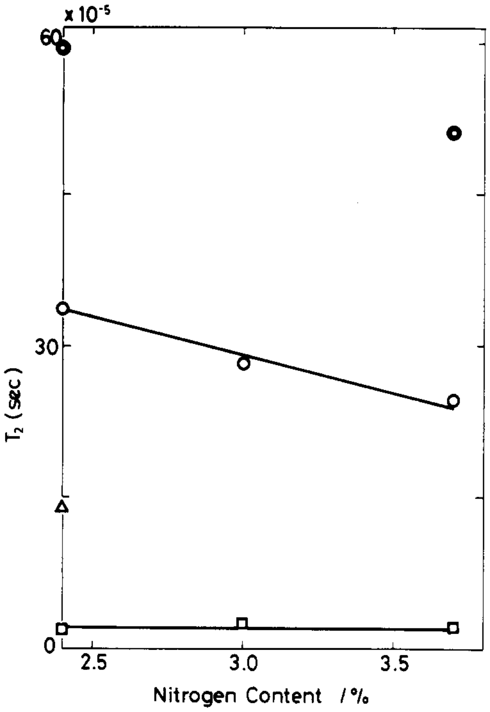

Figure 7. Spin–spin relaxation times (T_2) of the respective phases of as-molded SPUU film versus percent nitrogen content. Notations are the same as in Figure 4.

NMR data corresponding to Figure 6 are shown in Figures 7 and 8. Figure 7 shows a slight shortening in the spin–spin relaxation time of soft-segment phase, indicating a denser packing in the domain of soft segment due to phase mixing. Two components were observed in the hard-segment phase of the sample with 2.4% nitrogen, and two components were observed in the soft phase of the sample with 3.7% nitrogen. Only two phases, i.e., soft- and hard-segment phases, were observed when the nitrogen content was 3.0%, indicating that the phase separation reached an optimum state. Figure 8 shows the changes in the fractions of the phases, indicating that at a nitrogen content of 3.0%, the fractions of the soft- and hard-segment phase reach the maximum and minimum value, respectively.

Effects of Annealing on Phase Separation. Figure 9 shows the effect of annealing on the TL glow of SPU

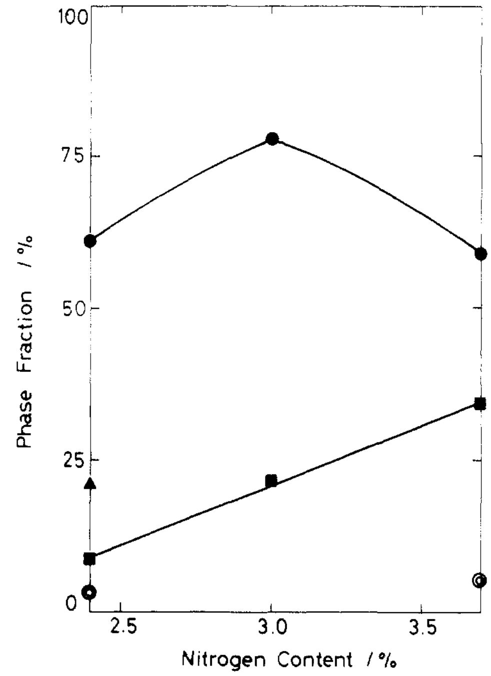

Figure 8. Percent nitrogen content dependence of the phase fraction: (⊙) phase softer than the normal soft segment phase; the other notations are the same as in Figure 4.

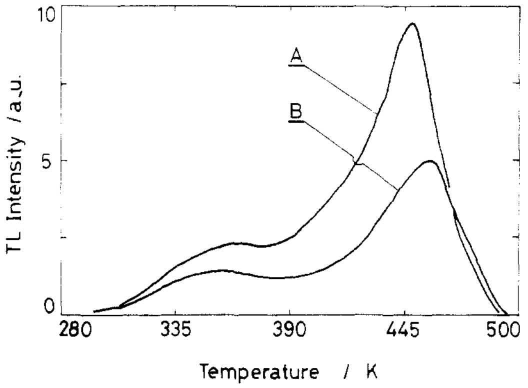

Figure 9. TL glow curves of as-molded SPU films before (B) and after annealing (A) at 150 °C in vacuum for 48 h.

film: B represents the state before and A the state after annealing in vacuum at 150 °C for 48 h. It can be seen that a remarkable increase in the intensity occurs after annealing. At the same time, the subpeak at lower temperature (L) shifted to a slightly higher temperature, and as a result, the two peaks become closer after annealing. This also indicates a noticeable increase in the extent of hydrogen bonding, and thus in the electron density of the hard-segment domains, and implies a better phase separation, as is the case of an increase in the molecular weight of PTMG. Regarding the annealing-induced phase separation, Kwei et al.[29] argued that annealing at a temperature higher than 80 °C excluded some very long hard segments from the soft-segment phase. Nevertheless, the large increase in the higher TL peak after annealing suggests that, in this case, these excluded long hard segments might rather be from hard-segment domains. As a result, the phase separation was promoted, since the narrower hard-segment length distribution should induce a better phase separation, as suggested by Miller's findings.[30] The sharpening and the small lowering of the TL maximum temperature after annealing may be explained by the above arguments because this exclusion effect makes less interconnected hard–soft domains, indicating more flexible hard-segment domains.

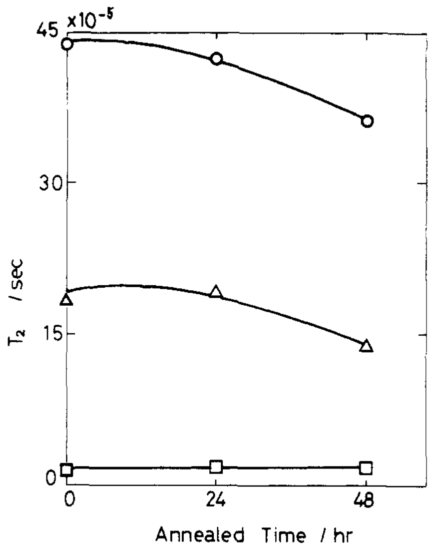

Figure 10. Annealing time dependence of spin–spin relaxation times: (○) soft-segment phase; (△) intermediate phase; (□) hard phase, measured at 40 °C.

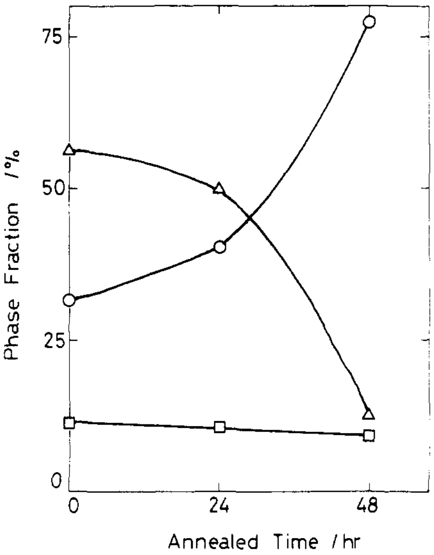

Figure 11. Annealing time (hour) dependence of the fractions of the phases in Figure 10: (○) soft-segment phase; (△) intermediate phase; (□) hard-segment phase, measured at 40 °C.

Figure 10 shows the changes in the NMR relaxation times T_2 versus the annealing time. As is easily seen, the relaxation times of both soft-segment and intermediate phases become shorter as the annealing proceeds, but the T_2 of the hard-segment phase remains almost unchanged. This is consistent with the closer maxima of the TL peaks L and H shown in Figure 9, except for the change in the T_2 of hard phase. The change in the T_2 of the hard phase could be considered as a competing effect of a decreased interconnectd structure and denser hard domains. Figure 11 plots the fractions of the phases, estimated from Figure 10, against the annealing time. The fraction of the itermediate phase, indicated by triangles in Figure 11, decreased drastically with annealing, but that of the hard-segment phase remained almost unchanged. This suggests that a majority of the decreased intermediate phase fraction, particularly the soft segments in it, was transferred to the soft-segment phase during annealing, leading to shorter relaxation times (T_2) in both phases, and as a result, a better phase separation between hard- and soft-segment domains was obtained. The fraction of the intermediate phase, actually the phase-mixed phase, as will be shown later, which amounts to almost 50% of the total

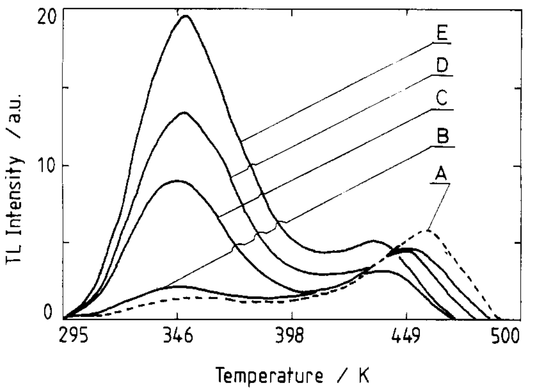

Figure 12. TL glow curves of as-molded commercial SPUU films with different elongation ratios. Broken line (A) indicates the glow curve of as-molded film: (B) 25%; (C) 100%; (D) 200%; (E) 300%.

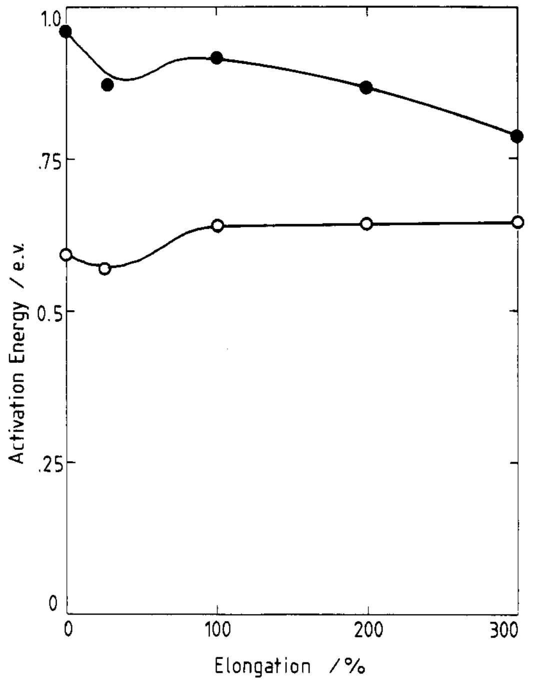

Figure 13. Elongation ratio dependence of the TL activation energy: (○) lower peak (L peak); (●) higher peak (H peak).

material, seems unbelievable, but it must be remembered that the term "phase" as used in this paper is defined based on the relaxation times T_2 obtained from NMR measurements, which obviously gives no structural information in a sense of spatial arrangement. Therefore, the values of the defined NMR fractions are not necessarily consistent with those obtained from the X-ray and other methods. The results indicate that at least no appreciable phase separation (good phase mixing) occurs in the as-molded SPU film.

Effects of Elongation on Phase Separation of SPUU. Figure 12 gives the TL glow curves of commercial SPUU films (Nishinbo) with different elongation ratios. It can be seen that the broad peak L near 350 K, which was indistinct before elongation, becomes much sharper whereas the intensity of the peak H decreases and the maximum temperature shifts to a lower value as the elongation ratio becomes larger. The activation energies, estimated from the TL glow curves and plotted against the elongation ratio in Figure 13, exhibit a slight decrease in the activation energy of both the H and L peaks. At an elongation of about 30%, which is the elastic limit in the stress–strain curve of SPU, the activation energies of both peaks indicate a minimum value. This may reflect the distinct domain orientation of SPUU at this region and corresponds very well to the results of Kimura et al.[2] The changes in the concentration of TL electron traps against elongation ratio are shown in Figure 14. The trap concentration of peak L increases linearly, but that of the peak H first decreases and then saturates with an increase in the elongation ratio. The continuing increase in the TL intensity of the intermediate phase in the later proces of the elongation can only be contributed by an increase in the soft segments. This suggests a close correlation among the soft-segment domains, elongation-induced intermediate phase, and the hard-segment domains in the process of elongation, i.e., at an early stage of elongation, some of the hard segments are disintegrated from the hard-segment domains due to domain orientation, and as elongation proceeds, these disintegrated hard segments are mixed with soft segments to form a phase-mixed zone. Therefore it is reasonable to consider the newly increased L peak as a phase-mixed "intermediate" phase. The above results also strongly support the results of Kimura et al.[2] in which a three-stage orientation process for elongation, i.e., domain orientation, phase mixing, and segment orientation, were proposed.

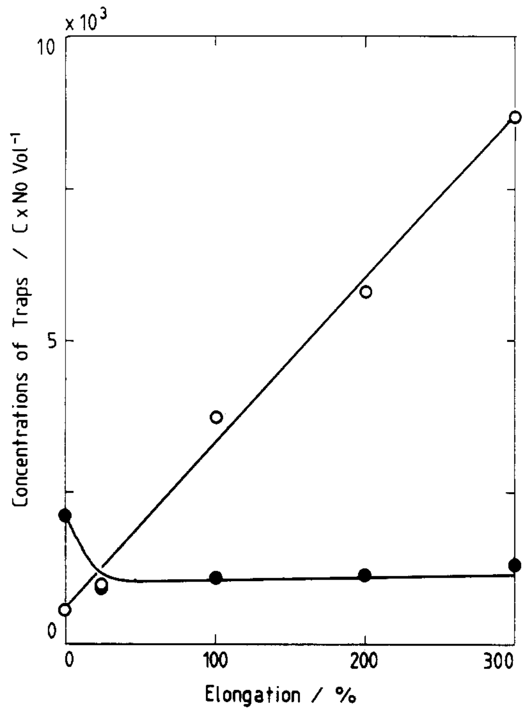

Figure 14. Changes in the concentration of TL electron traps with elongation ratios: (○) lower peak (L peak); (●) higher peak (H peak).

Conclusions

Thermoluminescence and pulse NMR studies of segmented poly(urethane ureas) (SPUU) were conducted in relation to the phase separation and deformation. The extent of phase separation was controlled by changing the number-average molecular weight of PTMG and the nitrogen content. The effects of annealing and elongation on phase separation for a sample having fixed PTMG MW and nitrogen content were also investigated. The TL glow curve of as-molded SPUU film exhibited a main peak (H) at around 430 K, which was related to the melting of the hard-segment domains, and a weak and broad peak near 350 K, which was assigned to the motions of the phase-mixed intermediate phase. The results of TL and NMR demonstrated that increasing PTMG molecular weight or decreasing MDI content led to a better phase separation.

Annealing also promoted the phase separation by increasing the degree of hydrogen bonding, and therefore TL trap concentration (intensity), in the hard-segment domains. The TL results of the elongation of SPUU showed that the orientation, disintegration, and phase mixing of the hard-segment domains occurred in stages during elongation, and as a result, the intensity of the lower TL peak L increased considerably and the intensity of the higher peak H decreased accordingly in this process. The above TL results were well supported by those of the pulsed NMR measurements. In summary, the results reported in this paper show that TL promises to provide much detailed information about the phase separation in polyurethanes and other phase-separated polymers.

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Registry No. (PTMG)(BDO)(MDI) (block copolymer), 107678-92-2; (PTMG)(MDI)(PDA) (block copolymer), 111634-02-7.

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Studies of the Antenna Effect in Polymer Molecules. 11. Photochemical Reactions of 2-Undecanone Solubilized in an Aqueous Solution of Poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene)

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ABSTRACT: Photochemical reactions of 2-undecanone solubilized in a water solution of poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS-VN) were studied by using monochromatic light at $\lambda = 280$ nm and solar-simulated radiation. Photoreactions of 2-undecanone were found to be photosensitized by the pendant naphthalene chromophores in the copolymer. Experimental evidence supports a mechanism in which singlet–singlet energy transfer occurs from the naphthalene groups to 2-undecanone by a diffusion-controlled collisional mechanism. The process was found to be efficient because of the high local concentration of ketone solubilized in the polymer microdomains. The photolysis of 2-undecanone solubilized in the copolymer occurs according to the Norrish type II process. Norrish type I reaction products were not formed in detectable amounts.

Introduction

Study of the photophysical phenomenon known as the "antenna effect" in synthetic polymers is important from both a scientific and practical point of view. The natural "antenna pigments", such as chlorophyll in green plants, have been found to act as photocatalysts in photosynthesis. The solar energy absorbed by the chlorophyll pigment is transferred via singlet energy migration to the active center where it is used in the primary steps of photosynthesis.[1] This process is also referred to as "photon harvesting". An

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