

Study of phase separation in polyurethanes using paramagnetic labels: effect of soft-segment molecular weight and temperature

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The objective of this study is to assess the effect of temperature and molecular weight of the soft segment on the degree of mixing between the hard and soft segments in segmented polyurethanes. The method of study consists of measuring electron spin resonance (e.s.r.) spectra of a nitroxide spin label in a series of segmented polyether polyurethanes (PU), in the temperature range 100–450 K. The PU are based on 4,4'-diphenylmethane diisocyanate (MDI), poly(tetramethylene oxide) glycol (PTMO) and 1,4-butane diol (BD) as the chain extender. The polymers were prepared from four molecular weights (MW) of PTMO: 650, 1000, 2000 and 2900. The hard-segment content is constant in all polymers prepared (38 wt%). The nitroxide probe 4-hydroxy-2,2',6,6'-piperidine-1-oxyl (TEMPOL) was attached to the polymer chains by reaction with an $-NCO$ group of MDI. The nitroxide label is therefore located at a chain end. Two sites for the label, differing in their dynamical properties, were detected in all polymers around 300 K and most likely represent the hard and soft domains of the PU. Analysis of the e.s.r. spectra indicates that at ambient temperature (300 K) the increase in the MW of PTMO decreases the degree of mixing between the two segments in the PU. At 400 K the trend is reversed, and the PU containing the soft segment with the largest molecular weight has the highest degree of phase mixing. The lineshapes detected at 400 K can be interpreted in terms of a distribution of label sites, characterized by widths δg and δA of the g_{iso} and A_{iso} (from ^{14}N) values, respectively, and reflecting the polarity profile in the polymers.

(Keywords: paramagnetic probes; electron spin resonance; polyurethane)

INTRODUCTION

Segmented polyurethanes (PU) are block copolymers consisting of alternating soft and hard units. The soft unit consists in many cases of an isocyanate-capped macroglycol or macroester; the hard unit is a diisocyanate that has reacted with a chain extender, usually a diol or diamine of low molecular weight. In segmented polyurethanes separation into domains rich in the soft and the hard segments, respectively, is due to incompatibility between the two basic structural units of the block polymer. Microphase separation is often incomplete and results in the formation of an interphase, which is the least understood part of the morphology. The main factors that affect the degree of phase separation, and therefore the composition of the domains, are the structure and length of the hard and soft segments and of the chain extender, the structure of the isocyanate, the hard-segment content and the thermal history of the sample¹.

The domain morphology in segmented PU has been extensively studied, in order to understand the molecular basis of the polymer properties and to control polymer performance^{2–5}. The domain size can be studied by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM); these are *average* methods. Infra-red (i.r.) and nuclear magnetic resonance (n.m.r.) spectroscopies are important *probe* methods for the study

of the polymers on a molecular scale. Measurements of glass transition temperatures and of crystallization processes by differential scanning calorimetry (d.s.c.) are also very useful for polymer characterization.

The effect of hard-segment content on the phase separation in PU based on 4,4'-diphenylmethane diisocyanate (MDI) and polyisobutylene was studied by measuring the glass transition temperature T_g of the soft segment; a constant T_g was taken as an indication of significant phase separation⁶.

The effect of an increase in the hard-segment length has been studied by preparing segmented PU in two different ways: by a one-step polymerization, and by a multistep reaction⁷. It was shown that the single-step polymers have fewer hard segments containing one MDI unit than the polymers prepared in a multistep process, and they exhibit less phase mixing. The study was done by i.r. spectroscopy, d.s.c., SAXS and dynamical mechanical analysis (d.m.a.).

The effect of the soft-segment length has also been studied. Polyurethanes based on 2,4-toluene diisocyanate (TDI) and ethylenediamine as the chain extender, for two molecular weights ($MW=1000$ and 2000) of the poly(tetramethylene oxide) glycol (PTMO), have been studied by i.r. and mechanical relaxation⁸. At ambient temperature more phase segregation and better mechanical properties have been detected in polymers containing the soft segment of higher molecular weight. In a series of PU based on PTMO and TDI studied by d.s.c. and d.m.a. measurements it was deduced that an increase in

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the *MW* of the macroglycol can be correlated with a higher degree of phase separation⁹. A similar conclusion was reached in PU based on MDI and polycaprolactone, with fixed hard-segment length, studied by various techniques¹⁰, and in poly(urethaneureas) based on DMI and various polyols¹¹.

The effect of the molecular weight of the soft segment on polymer morphology seems to be a fundamental question of considerable practical importance; we decided to approach this problem in a novel way, by using paramagnetic reporter molecules. The objective of this study is to vary the *MW* of the soft segment and to study the extent of phase separation as a function of temperature.

The polyurethanes studied are based on 4,4'-diphenylmethane diisocyanate (MDI), poly(tetramethylene oxide) glycol (PTMO) and 1,4-butane diol (BD) as the chain extender. The method of study consists of labelling the polymer at a specific position with a stable nitroxide radical as a reporter molecule and measuring the electron spin resonance (e.s.r.) spectra from the label. This method has been extensively used for the study of motional processes in polymers, copolymers and polymer blends¹²⁻¹⁶, and recently in interpenetrating polymer networks (IPN)^{17,18}. The change in the principal values of the molecular *g*-tensor and of the electron-nuclear hyperfine interaction tensor of the ¹⁴N nucleus (*I*=1) are detected in the e.s.r. spectra of the label as a function of temperature; these changes depend on the dynamics in the medium that is studied. At low temperature (100 K), the separation between the outermost signals $2A'_{zz}$ ('extreme separation') is 65–70 G. The temperature at which $2A'_{zz}$ is reduced by dynamical effects to 50 G, or $T_{50\text{G}}$, has been correlated with the glass transition temperature T_g . The difference between the values of $T_{50\text{G}}$ and T_g seems to depend on whether the reporter molecule is mixed with the polymer (a 'probe') or covalently linked to the polymer (a 'label').

In some cases e.s.r. spectra of the nitroxide label can also reflect different environments in a given sample, with different motional characteristics; 'fast' and 'slow' components are detected, and refer to the appearance of isotropic spectra due to fast motion and of anisotropic spectra for immobilized labels. The partition of the label into two or more environments, and the detection of composite e.s.r. spectra, indicate a heterogeneous medium and therefore phase separation^{12,13}. The detection of phase separation is based on the analysis of probe partition in domains with different dynamics.

The literature on spin labels in PU is limited; data obtained indicate that the e.s.r. lineshapes are sensitive to the composition of the polymer, its degree of crystallinity as well as to the label location. In a PU prepared from MDI and PTMO the label was located on the curing agent (trimethylolpropane)¹⁹; a $T_{50\text{G}}$ value of 330 K was measured. For a high content of the hard segment in PU prepared from MDI, ethylene glycol and glycerol as a curing agent, no evidence for motional averaging of the label was observed up to 410 K, the highest measurement temperature. In a more recent paper²⁰ a diol nitroxide spin label was inserted in the hard segment: two components were observed in the e.s.r. spectra, with $T_{50\text{G}}$ values of 410 K and 450 K.

The present study was undertaken in order to measure the extent of phase mixing for different lengths of the soft segment, as a function of the polymer temperature. An

additional goal in these studies has been to test the degree of sensitivity of the method used, for a study of the complex morphology in the segmented PU.

E.s.r. spectra of PU containing nitroxide labels located at chain ends were measured in the temperature range 100–450 K. Because of the labelling method, the nitroxide is expected to be located in the hard segment, at the interphase between the hard and soft segments or even close to the soft segment, and to reflect a range of localities in the segmented PU. Molecular weights of 650, 1000, 2000 and 2900 of the macroglycol were used in polymers that contained a fixed content of the hard segment, 38 wt%. The results indicate that the lineshapes of e.s.r. spectra are extremely sensitive to the length of the soft segment. At ambient temperature (300 K) the degree of phase mixing decreases with increase of the molecular weight of the soft segment. At 400 K, however, the trend is reversed and the polymer containing the largest length of the soft segment has the most homogeneous phase structure. The lineshapes detected at 400 K can be interpreted in terms of a distribution of label sites, characterized by widths δg and δA of the g_{iso} and A_{iso} (from ¹⁴N) values respectively, and reflecting the variation in the local polarity in the polymers.

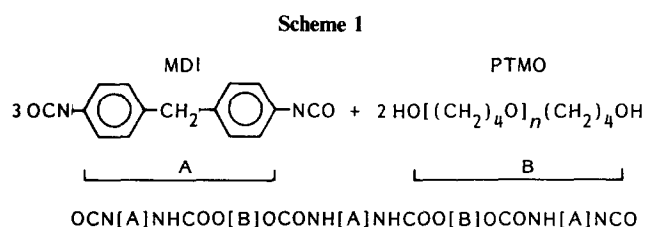
EXPERIMENTAL

Materials

The macroglycols (*MW*=650, 1000, 2000 and 2900), supplied by DuPont, were dried overnight at 343 K at a pressure of 5 torr. MDI (Mobay) was used as received. BD (DuPont) was purified by vacuum distillation, discarding the first 5% and last 5% of the distillate. The isocyanate content of MDI and of the prepolymer were determined by titration with di-*n*-butylamine.

The PU polymers were obtained in a two-step reaction. The prepolymer was obtained first by reacting MDI and the polyol; the prepolymer was then reacted with the chain extender BD, to an NCO/OH ratio of 1.05 (the 'isocyanate index' is 105).

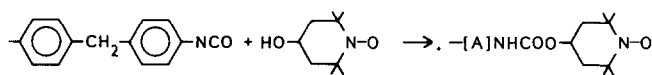
For PTMO of *MW* 650, 1000, 2000 and 2900 the prepolymer was prepared from molar ratios MDI/PTMO of 3/2, 2/1, 4/1 and 11/2, respectively. For macroglycols of *MW* 2000 and 2900 the prepolymers formed contain free MDI ('quasi-prepolymers'). The formation of the prepolymer from PTMO of *MW* 650 is shown in Scheme 1.



Methods

In order to prepare the spin-labelled prepolymer, the desired amounts of MDI and PTMO to give 38 wt% of the hard-segment content were reacted at 353 K under nitrogen. The nitroxide probe, 4-hydroxy-2,2',6,6'-piperidine-1-oxyl (TEMPOL, from Aldrich), in the amount of 10^{-4} – 10^{-5} g per gram of prepolymer, was added to the reaction mixture when the required isocyanate index was obtained, and the reaction was

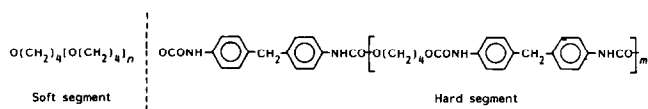
Scheme 2



continued for 1.5 h, to ensure reaction with the spin probe. The reaction is shown in **Scheme 2**.

To prepare the elastomer, the prepolymer and the chain extender were kept at 343 K. A tin catalyst, dibutyltin dilaurate (Air Products), was used to accelerate the curing reaction. The mixture was then poured into a preheated mould, which was placed on a heating press. The elastomer was cured for 20 h at 363 K. The structure of the polymers is given schematically in **Scheme 3**. The notation used for the PU samples prepared is PU650, PU1000, PU2000 and PU2900.

Scheme 3



For comparison with the spin-labelled polymer, samples containing the TEMPOL spin probe *mixed* in polyols of molecular weights 650, 2000 and 2900 were prepared; the notation for these samples is 650SP, 2000SP and 2900SP. In addition, a sample containing a spin-labelled hard segment only was prepared, using the method outlined above for preparation of the spin-labelled prepolymer; the notation is MDI-BD.

E.s.r. spectra at X-band were measured with a Bruker 200D SRC spectrometer operating at 9.7 GHz (empty cavity at ambient temperature), using 100 kHz modulation. Data acquisition and manipulation is based on an IBM PC, using the software EPRDAS (Mega Systems Solutions Inc., Rochester, NY, USA). Spectra were measured in the temperature range 100–425 K using the Bruker variable-temperature unit ER 4111 VT. E.s.r. spectra for MDI-BD were measured up to 460 K. Spectra at 77 K were taken in a liquid-nitrogen Dewar inserted in the e.s.r. cavity. The absolute value of the magnetic field was measured using the Bruker ER 035 n.m.r. gaussmeter. The microwave frequency was measured with a Hewlett-Packard 5342 A frequency counter. Calibration of g -values was based on 2,2-diphenyl-1-picrylhydrazyl (DPPH) ($g=2.0036$) and Cr^{3+} in MgO ($g=1.9796$).

Spectra were simulated by a Burroughs 6800 mainframe computer at the University of Detroit and plotted with an IBM PC and a Hewlett-Packard 7440A digital plotter.

RESULTS AND DISCUSSION

General trends and label sensitivity

E.s.r. spectra of PU2900 at X-band in the temperature range 120–420 K are shown in **Figure 1**. The extreme separation, shown in some spectra as the distance between vertical bars, decreases with increasing temperature; this is expected, because of averaging of the g -tensor and the hyperfine tensor components from ^{14}N , as a result of dynamical processes. The presence of two components is clearly seen at 280 K. At this temperature the more rigid, or 'slow', component has an extreme

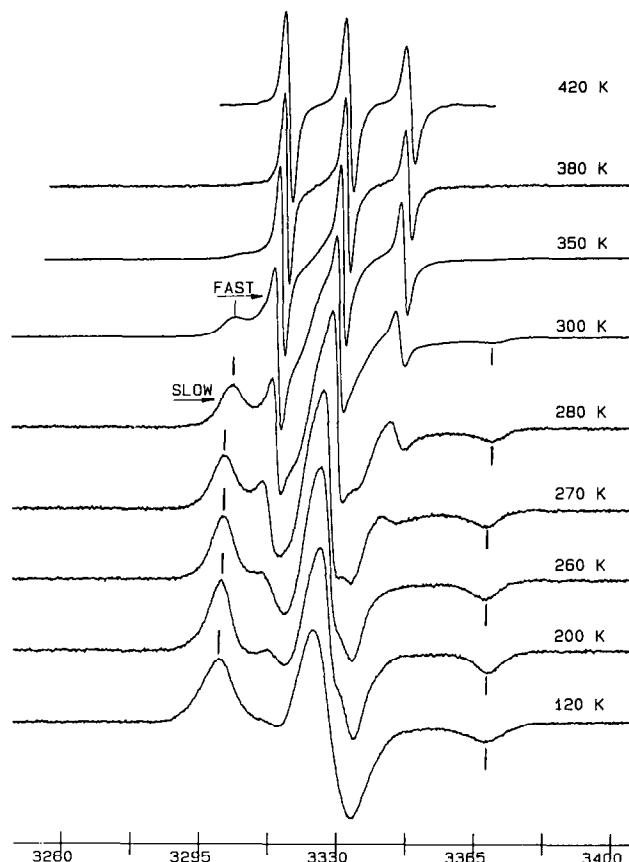


Figure 1 X-band e.s.r. spectra of spin-labelled PU2900 in the temperature range 120–420 K. Vertical bars in some spectra indicate the values of the extreme separation $2A_{zz}$. 'Fast' and 'slow' low-field signals are indicated

separation of 66.0 G, not significantly lower than the value of 68.9 G at 100 K; this spectral component most likely represents the e.s.r. signals from the nitroxide label situated in the polymer hard domains. The 'fast' component is isotropic, with $A_{iso}=15.3$ G, and clearly represents a label site in the polymer soft domains. In the temperature range 270–350 K both components are detected. The extreme separation of the slow component at 350 K is still large, 62.4 G, indicating a rigid environment. Above 350 K the slow component is not detected. Around this temperature two changes occur in the isotropic spectra from the fast component: the linewidth of the isotropic triplet increases, and the ^{14}N isotropic splitting increases to 15.6 G. Usually the linewidths of the isotropic signals in nitroxide free radicals in solids decrease with increasing temperature; the opposite trend detected in this study, and the change in A_{iso} , are due to changes in morphology, and will be discussed in more detail below.

E.s.r. spectra of PU650 at X-band, in the temperature range 100–420 K, are shown in **Figure 2**. The two spectral components, fast and slow, are detected in a narrower temperature range, 300–330 K. The temperature corresponding to the appearance of a significant contribution from the isotropic spectrum ('fast' component) is higher than for PU2900, 310 K vs. 280 K. At 320 K the extreme separation of the hard component is 60.6 G, significantly lower than the value of 69.5 G measured at 100 K. Above 330 K the slow component is not detected. It is important to notice that a broad high-field shoulder is observed in the range 370–400 K, and is indicated by an arrow in **Figure 2**, for the spectrum at 380 K.

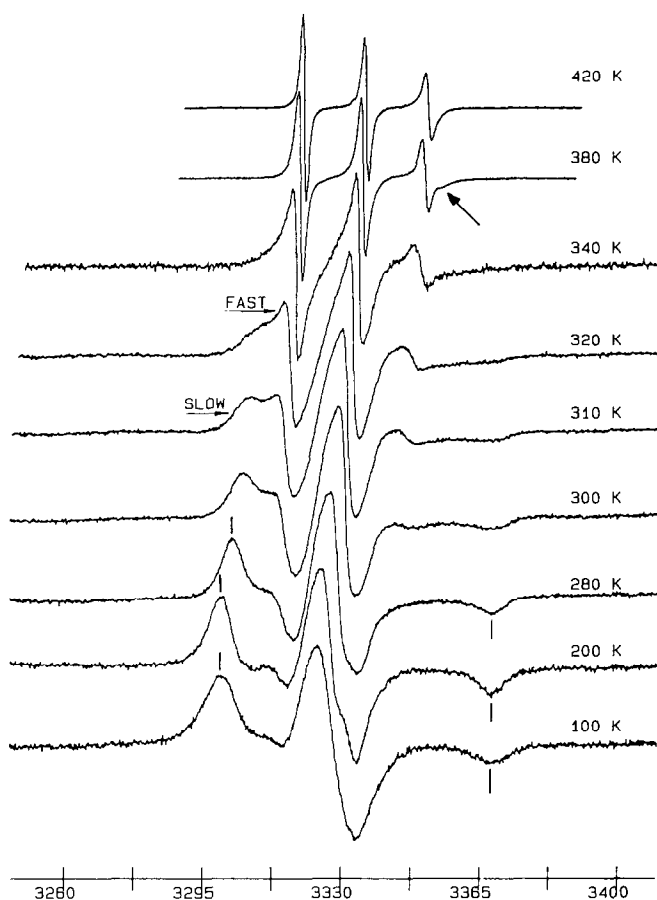


Figure 2 X-band e.s.r. spectra of spin-labelled PU650 in the temperature range 120–420 K. Vertical bars in some spectra indicate the values of the extreme separation $2A'_{zz}$. 'Fast' and 'slow' low-field signals are indicated. The arrow for the spectrum at 380 K indicates the signal from the separated hard domain

A superposition of two components has been detected in all PU prepared. For PU650, PU1000 and PU2000 this occurs in the range 300–330 K. The temperature corresponding to the appearance of the 'fast' component is higher for lower MW of the polyol: 280 K for PU2900, 300 K for PU2000, and 310 K for PU1000 and PU650. Qualitatively this indicates that a larger part of the hard segments is incorporated in the soft domains, for lower MW of the polyol. In parallel, the extreme separation of the slow component at a given temperature increases with increase in the MW of the polyol, indicating that the hard domain is progressively richer in MDI, for the PU with higher polyol MW .

The extreme separation of the 'slow' component, representing the hard domains, as a function of the temperature is shown in Figure 3. For simplicity, only data for PU650 and PU2900 are given, in the entire temperature range; the temperature dependences of the extreme separation for PU1000 and PU2000 are similar to that of PU650 and PU2900, respectively. Data for MDI-BD are given in the range 300–400 K. Also given in Figure 3 is the lowest temperature at which the isotropic component is observed for PU650 and PU2900.

The temperature corresponding to an extreme separation of 50 G, T_{50G} , is 337 ± 2 K for PU650 and PU1000. This value can be compared with the T_{50G} values of 425 K for the spin-labelled hard segment (MDI-BD), and with the value of 265 K for PTMO of MW 650 and 2000 containing TEMPOL as a

paramagnetic probe (650SP and 2000SP). Assuming that the Fox equation holds, we can deduce that the hard domains contain ~ 42 wt% polyol.

It was not possible to measure the T_{50G} values for PU2000 and PU2900. For PU2000, $2A'_{zz}$ at 340 K is about 67 G; above this temperature the signal from the hard segment simply disappears. For PU2900 an extreme separation of 64 G can be measured at 340 K; the signal is not detected above 350 K. These values of $2A'_{zz}$ are close to that for MDI-BD at 340 K, which is 68.9 G. It is not reasonable to expect that the disappearance of the slow component of PU2000 and PU2900 at ~ 350 K is due to a sudden onset of dynamical averaging. In polymers the decrease in the extreme separation is gradual and occurs in a temperature range of at least 50 K; this can be seen from the data for PU650 given in Figure 3. It appears more reasonable to suggest that the disappearance of the slow component in this case is due to changes in the morphology of the samples in the 300–400 K range.

The most relevant results are summarized in Table 1.

Morphology changes in the 300–400 K range

The specific effect of the MW of the polyol on the polymer morphology becomes evident in Figures 4 and 5, where e.s.r. spectra for the PU at 300 and 400 K, respectively, are presented. The inset in Figure 4 is the e.s.r. spectrum of the TEMPOL probe in PTMO (MW 2900) at 293 K. It is clear that an isotropic signal only is detected in the polyol; e.s.r. spectra of TEMPOL in the polyols of MW 650 are basically the same as in the inset, and are not shown. In Figure 4 it is seen that increasing the polyol MW leads to two components with larger differences in their spectral parameters. This is seen in the extreme separation of the slow component, which is larger for larger MW of the polyol; and in the linewidths of the fast component, which are smaller for high- MW polyols. The difference in the field positions of the low-field components, from the hard segment (point #1 in Figure 4) and from the soft segment (point #2 in Figure 4), increases with the MW of the polyol and is 10.1, 10.0, 10.4 and 10.7 G for PU650, PU1000, PU2000 and PU2900. The values for the two lower MW are within the experimental error. It seems that the morphology is

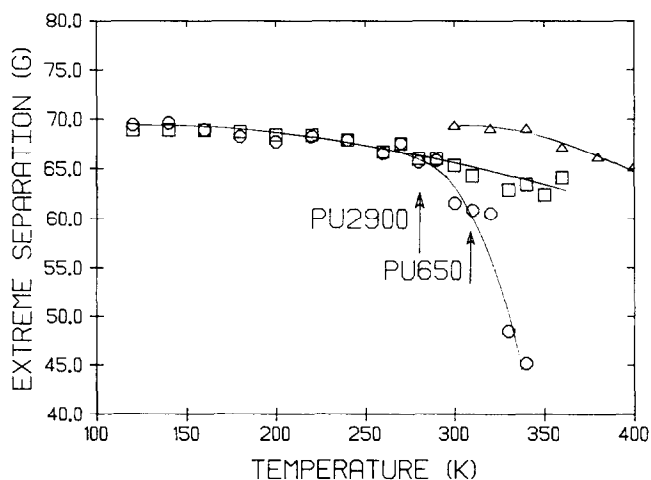


Figure 3 The extreme separation $2A'_{zz}$ for PU650 (○), PU2900 (□) and for spin-labelled MDI-BD (△), as a function of temperature. Arrows indicate the lowest temperature at which the isotropic component is observed, for PU650 and PU2900

Table 1 Spectral parameters for PU and model compounds

Samples	$T_{50\text{G}}$ (K) ^a	T_{iso} (K) ^b	$2A_{zz}$ (100 K)	A_{iso} ^c	$h(0)/h(+)$ ^d	$h(0)/h(-)$ ^d
2000SP	262	–	67.5	15.3		
MDI-BD	425	–	70.8	17.3		
PU650	370 ^c	310	69.5	15.7	0.76	0.37
PU1000	337 ^c	310	68.8	15.7	0.70	0.23
PU2000	not detected	300	69.8	15.6	0.78 (0.78)	0.36 (0.41)
PU2900	not detected	280	68.9	15.7	0.89 (0.84)	0.56 (0.54)

^a Corresponds to the slow component in a composite spectrum. The accuracy is ± 3 K

^b This is the lowest temperature corresponding to the appearance of a motionally averaged 'fast' component in a composite spectrum. The accuracy is ± 5 K

^c Measured at 400 K

^d The heights of the low-field, centre-field and high-field signals in an isotropic spectrum are $h(+)$, $h(0)$ and $h(-)$. The ratios given are measured at 400 K. For PU2000 and PU2900 the numbers in parentheses are values from the calculated spectra given in Figure 7

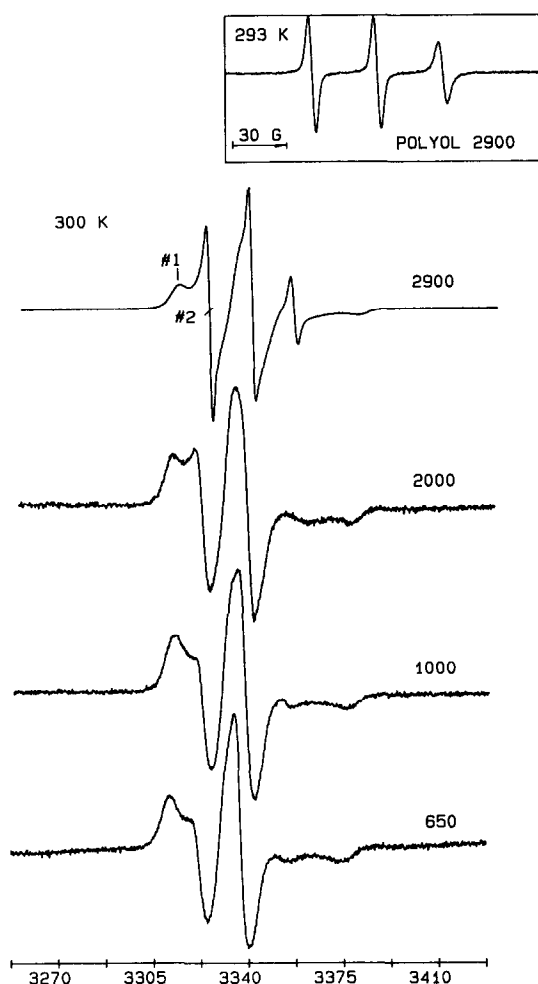


Figure 4 E.s.r. spectra for the PU at 300 K. The *MW* of the polyol is indicated. Successive spectra have been displaced horizontally, for clarity. The inset is the e.s.r. spectrum of TEMPOL as a probe in the polyol of *MW* 2900, at 293 K. The low-field signals for the slow and fast components are indicated as points #1 and #2, respectively, for the e.s.r. spectrum of PU2900

not affected by variation of polyol *MW* from 650 to 1000, or that the label cannot detect the small morphology differences between the two samples.

The inset in Figure 5 represents the e.s.r. spectrum of spin-labelled MDI-BD at 400 K; only a rigid spectrum is detected, and $2A_{zz}$ is 65.0 G, compared with 70.8 G at 100 K. The e.s.r. spectra of the model compounds, the polyol as the major component of the soft domain, and MDI-BD as the hard domain, are in marked contrast with the spectra from the PU at the same temperatures.

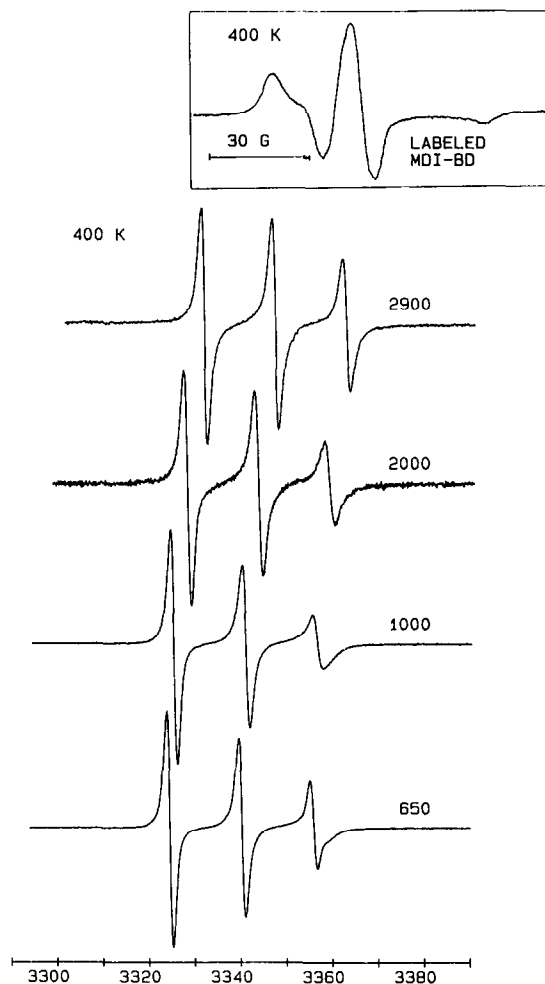


Figure 5 E.s.r. spectra for the PU at 400 K. The *MW* of the polyol is indicated. Successive spectra have been displaced horizontally, for clarity. The inset is the e.s.r. spectrum of spin-labelled MDI-BD at 400 K

The effect of increasing the temperature above 300 K is seen in Figure 6; spectra for PU1000 are given at 350, 370 and 390 K. The gradual blending of the slow component into the isotropic fast component is clearly shown by the shift to lower field of the shoulder seen in Figure 6. Even at 400 K, however, the high-field signal for PU1000 (Figure 5) is not symmetrical, indicating heterogeneity in the phase structure. For PU650 the shoulder at the high-field side is more prominent than for PU1000, indicating even less mixing. For PU2000 and PU2900 the high-field signal is symmetrical, indicating a much smaller difference in the spectral

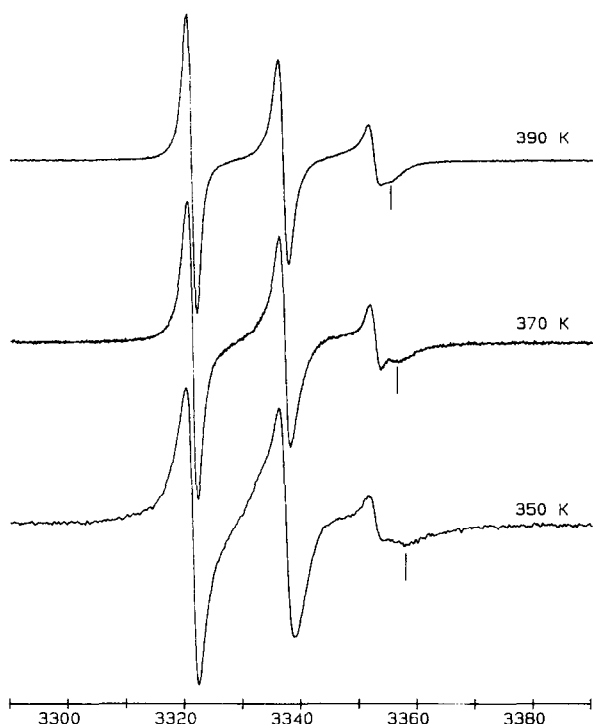


Figure 6 E.s.r. spectra for PU1000 at indicated temperatures. Vertical bars indicate the shift to lower field of the signal from the label sited in the hard separated domains, as the temperature increases

parameters of the two major spectral components. *Figures 4–6* indicate clearly that the degree of mixing is most pronounced above 350 K for PU containing the polyol of higher *MW*. This is in marked contrast to the situation at 300 K, where most phase separation has been detected for the higher-*MW* polyols. It is likely that above 300 K the hydrogen bonds that connect the hard segments begin to break²¹, leading to intercalation of the soft segments into the hard domains. It seems that this process is more pronounced in polymers containing the longer and more flexible soft segments. The process of intercalation is also likely to reduce the polarity of the hard segments, and is supported by the linewidth analysis given in the next section.

Polarity profile from linewidth analysis

In all PU prepared, in the limit of high temperature, the linewidth increases from low to high field, creating a pattern with decreasing heights of the three lines as the magnetic field increases. Similar lineshapes have been detected in our studies of spin-labelled interpenetrating polymer networks (IPN) based on polyurethanes, and have been interpreted by assuming a distribution in the values of g_{iso} and A_{iso} . In this study the implication of such a distribution is that the paramagnetic label samples regions of varying polarities. It is well known that the local polarity strongly affects the values of A_{iso} , because a higher polarity stabilizes a more ionic structure of the NO group and a greater localization of the unpaired electron on the nitrogen nucleus²². Larger values of A_{iso} are accompanied by smaller values of g_{iso} .

The width due to the distribution, δH , can be calculated by using an expression that specifically includes the effect of the m_l value and of the microwave frequency, in addition to distribution widths δg and δA ,

as shown below²³:

$$(\delta H)^2 = (m_l \delta A)^2 + \left(\frac{h\nu}{g_{\text{iso}}^2 \beta} \delta g \right)^2 - \frac{2\epsilon m_l h\nu}{g_{\text{iso}}^2 \beta} \delta g \delta A \quad (1)$$

In equation (1) ν is the microwave frequency and ϵ is a parameter that indicates the extent of correlation between δg and δA ; if $\epsilon=1$, these distributions are perfectly correlated, in the sense that all labels have the same ratio $\delta A/\delta g$. This is the assumption made in this study. The other parameters have their usual meanings.

The total linewidth at half-maximum intensity, ΔH , is composed of the residual linewidth ΔH^R and the contribution δH from the distribution widths, as shown in equation (2):

$$(\Delta H)^2 = (\Delta H^R)^2 + (\delta H)^2 \quad (2)$$

Spectra were calculated using a code based on the program of Kasai²⁴, modified in our laboratory to include the effect of the g_{iso} and A_{iso} distributions, as described in a previous publication¹⁷. In *Figure 7* we present calculated spectra that simulate well the spectra of PU2000 and PU2900 at 400 K, as seen by comparison with the experimental spectra given in *Figure 5*. The distribution widths δg used to simulate the spectra are 0.0010 and 0.0008, for PU2000 and PU2900, respectively; the distribution widths δA are 2 G for PU2000 and 1.5 G for PU2900. The other parameters are $g_{\text{iso}}=2.0059$, $A_{\text{iso}}=15.7$ G. The calculated heights are within 5% of the experimental values. The calculated linewidths for the $m_l=0, 1$ signals are within 5% of the experimental values; the calculated widths for the high-field line ($m_l=-1$) are larger than measured, 2.81 G vs. 2.35 G for PU2000 and 2.35 G vs. 2.05 G for PU2900. The reason for this discrepancy might be that the lineshapes are intermediate between Gaussian and Lorentzian, and not purely Lorentzian, as assumed in the calculated spectra. The values of δA indicate that the label explores sites of very high and very low polarities. A value of 1.5–2.0 G for δA is logical in view of the difference between the

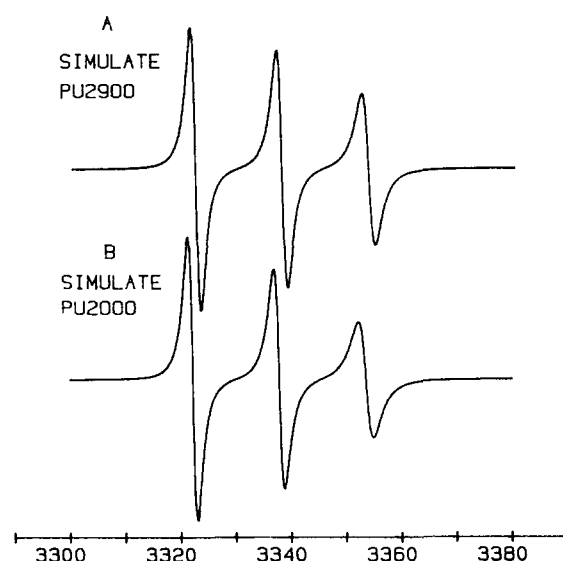


Figure 7 Calculated spectra, with $A_{\text{iso}}=15.7$ G, $g_{\text{iso}}=2.0059$. A, Simulation of the e.s.r. spectrum of PU2900 at 400 K, with $\Delta H^R=1.75$ G, $\delta g=0.0008$, $\delta A=1.5$ G. B, Simulation of the e.s.r. spectrum of PU2000 at 400 K, with $\Delta H^R=1.75$ G, $\delta g=0.0010$, $\delta A=2.0$ G

values of A_{iso} : 15.3 G for the polyols and 17.3 G for labelled MDI-BD, as seen in Table 1. The larger value for A_{iso} needed to simulate e.s.r. spectra from PU2000 at 400 K, compared with PU2900, might indicate that blending between the two phases destroys the very polar regions which can be identified with the strongly hydrogen-bonded hard segments.

We have also attempted to simulate e.s.r. spectra for PU650 and PU1000 at 400 K; for $\delta g = 0.0008$, $\delta A = 1.5$ G and $\Delta H^R = 1.5$ G the relative heights of the spectra were simulated but the linewidths do not agree with the experimental values measured. This discrepancy might be due to the presence of a separated hard domain, in addition to a continuous range of label sites, in PU650 and PU1000 at 400 K.

The relative weights of the soft and hard domains in all polymers can, in principle, be deduced by superposition of spectral components based on pure PTMO and MDI-BD. The procedure is complicated because the linewidths and lineshapes must be accurately known in order to obtain meaningful results. A careful study of the lineshapes, possibly in deuterated labels, and deconvolution of the experimental lineshapes into Gaussian and Lorentzian components are needed, and are planned in the future.

CONCLUSIONS

A nitroxide paramagnetic label has been attached to a terminal isocyanate group in segmented polyurethanes (PU) based on MDI, PTMO and BD as chain extender. The degree of mixing between the hard and soft segments has been studied by measuring the e.s.r. spectra of the label as a function of temperature for PU containing polyols of molecular weights 650, 1000, 2000 and 2900, at a constant content of the hard segment, 38 wt%.

E.s.r. spectra from the label are very sensitive to the polymer composition and to variations in the temperature.

Around 300 K two spectral components differing in their mobility have been detected in all polymers. The rigid component represents the hard domain; its anisotropy depends on the polyol MW and was compared with the anisotropy of the spin label in a model polymer composed of hard segments only. The fast component represents the soft domain and was compared with e.s.r. spectra of a spin probe mixed in the polyols.

At 300 K the degree of mixing increases with decrease in the MW of the polyol; at 400 K the opposite trend has been observed. The gradual incorporation of the hard segment into the soft domain is clearly seen for PU1000 in the temperature range 350–390 K.

The lineshapes measured around 400 K are interpreted in terms of a range of sites for the paramagnetic label, differing in their g_{iso} and A_{iso} values. Spectra can be simulated by assuming distribution widths δg and δA , arising from a range in the local polarities. The polarity profile can be expressed by the values of the distribution widths.

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