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# Temperature dependence of molecular motions in the polyurethane-based membranes studied with paramagnetic spin probe

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## Abstract

This third paper in this series regarding structure and dynamics of the polyurethane-based membranes studied with TEMPO spin probe presents the results of the ESR measurements performed to characterise mobility of segments in the permeable regions of the membranes. The variations of the spin probe motions with temperature have been analysed for the series of polyurethanes (PU) differing in molecular structure and compared with the results of the DSC studies. Along with $T_{50\ \mathrm{G}}$, the other temperatures, $T_n$, $T_i$, $T_\tau$, at which the significant change in dynamics occurs have been determined and correlated with the length of the PU soft and hard segments, and then discussed with regard to the respective relationships of $T_g$. The results have demonstrated the sensitivity of the ESR method to the segmental motions, which have not been detected by the DSC technique. From the DSC and ESR data the size of the motional chain segment in various PUs has been estimated, which has been found to follow the trend that polymers with higher $T_g$ have bulkier segments. Two unusual observations have been made, concerning the deviation from the Arrhenius relation at high temperature for some PUs, and the increased mobility of the TEMPO molecules in some poly(urethane-urea)s after their thermal treatment. These results have been interpreted so far either in terms of the possible translational diffusion of the TEMPO molecules for those PUs showing lesser amount of the hard segments, or in terms of the increased free volume resulting from the temperature induced structural changes within the permeable regions of poly(urethane-urea)s.

*Keywords:* Polyurethanes; Paramagnetic spin probe; Segmental mobility

## 1. Introduction

Segmented polyurethanes (PU) [1] are $[AB]_n$ type condensation multiblock copolymers which have thermoplastic properties as a result of a two-phase microstructure due to the incompatibility of the two dissimilar segments. The degree of thermodynamic incompatibility, which depends on parameters such as interaction energy between the unlike segments or their length, has an important influence on the morphology of the bulk phase, and thereby on the final engineering properties of polyurethanes. The properties of polyurethanes used as thermoplastic elastomers, fibres or coatings have been studied extensively over the past decades. Recently, the possibility of a new application of these materials in membrane technology has been demonstrated [2–6]. The interest in the polyurethane-based materials is generated by their morphology and properties which can be controlled in a simple fashion at the synthesis stage by changing the reaction components or their composition. From our previous research [2,3], it appeared that modifications of the polyurethane molecular structure had a tremendous effect on the pervaporation properties of the resulting membranes. The further development of these materials needs, however, the correlations between structure and transport properties to be well established. This in turn requires advances in the structural characterisation of the membranes. The methods used for investigating the segmented copolymers refer to various levels of the structural heterogeneity and comprise such techniques as electron microscopy (SEM, TEM), AFM, various scattering techniques (SAXS, SANS, SALS), as

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well as DSC and DMA. The effect of the molecular structure variations in PUs on the morphology displayed by these polymers in a form of a pervaporation membrane has already been examined by us using direct methods such as AFM [7] and SAXS [8,9]. The complex relation between properties and morphology obtained as a result of these experiments, accompanied by the observations of the morphology changes due to solvent effect [10,11], has indicated that further characterisation of the investigated materials is needed. The ESR spin probe method chosen by us recently to gain more information on a polyurethane structure has proved to be particularly successful.

In the first paper of the series presenting the results of our ESR studies, we developed a method of a selective examination of the permeable domains in the polyurethane-based membranes [12]. This was achieved by incorporation of TEMPO spin probe into the ready prepared membrane via diffusion from the vapour phase. The ESR spectra obtained were found to be morphology sensitive and to display temperature and structure dependent anisotropic rotation of the spin probe. To compare the PUs studied, the simplified method of the correlation time determination was evaluated based on the Arrhenius approach. The assumption that the method adopted is able to provide adequate information on PU microstructure to correlate with transport properties of the PU-based membranes was verified in the subsequent paper [13]. The exponential and linear empirical equations were obtained for PU/cyclohexane and PU/water systems, respectively, connecting the rotation correlation time of the spin probe with the respective diffusion coefficients calculated based on the pervaporation and sorption results.

In this paper, we focus our attention on the effect of the PU chain structure on the soft segment inherent mobility in order to understand, on the molecular level, the origin of the differences in the transport properties of the PUs studied. The results of spin probe motional variations in the homologous series of PUs as a function of temperature are discussed with respect to the results of the DSC measurements.

## 2. Experimental

### 2.1. Materials

The series of segmented polyurethanes and poly (urethane-urea)s (PU) described in the previous paper [13] has been studied. The details of the synthesis procedure and characterisation have been reported previously [13]. The samples were prepared in DMF solution using poly(oxytetramethylene) diol (PTMO, $M_n$ =2000, 1000, 650), 2,4-tolylene diisocyanate (TDI), and one of the following chain extenders (ChExt): 4,4′-bis(2-hydroxyethoxy)biphenyl (BHBP), or 4,4′-diaminodiphenylmethane (PP). Three types of a sample composition were selected, for which molar ratio of TDI/ChExt/PTMO was 4/3/1, 2/1/1, and 1/0/1. The notation used for this series of polymers is PU(ChExt,*x*)-M, where ChExt represents the kind of a chain extender, *x* refers to the number of the (TDI, ChExt) repeat units in the hard segment, and *M* is the soft segment molar mass.

Table 1 lists the chemical compositions of the materials along with some of their physical characteristics.

The spin probed PUs used in this study were prepared by incorporating the spin probe, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), into the PU sample via diffusion from a vapour phase according to the method described earlier [12].

### 2.2. Measurements

The ESR spectra of the doped polymers were recorded in the temperature range of 100–450 K using a CW X-band ESR spectrometer (Radiopan, Poland) operating at 9.2 GHz with 100 kHz modulation.

The separation (in gauss) between the outermost lines of the nitroxide spectrum ($2A'_z$), as well as the line heights ($I_{+1}$, $I_0$, $I_{-1}$) and width ($\Delta H_0$), necessary for the calculation of the rotational correlation time $\tau_C$, were measured from the spectrum recorded with the following parameters: modulation amplitude 0.2 G, microwave power 10 mW, sweep width 200 G, scan time 240 s, time constant 0.3 s. The variations of the central line width ($\Delta H_0$) with temperature in the whole temperature range were obtained by measuring the peak-to-peak width of the derivative curve of the spectrum recorded at the sweep width of 40 G, 20 G, or 10 G, depending on a polymer sample.

DSC data were obtained with a Rheometric Scientific DSC Plus apparatus. The scanning was carried out at a rate of 10°/min from 123 to 523 K.

## 3. Results and discussion

ESR spectra of the TEMPO doped PUs were measured in the temperature range of 100–450 K at intervals of approximately 10 K. Typical spectra recorded for these systems are shown in Fig. 1.

At low temperature, the ESR spectrum approaches the rigid limit spectrum with the separation between the outermost extrema of about 67 G. With increasing temperature, the spectral lines narrow and the distance between the outer peaks decreases. At a certain temperature characteristic for a particular sample, the spectrum shows the relatively sharp and narrowed three-line pattern typical for the motionally narrowed ESR spectra. The similar character of the line shape changes with temperature has been observed for all PUs studied. In previous publication [12], we have shown that these spectra reflect the motion of a spin probe in one type of microenvironment.

Table 1
Characterisation of polymers

| Polymer | Molar composition TDI/ChExt/PTMO | Chain extender | *x* | Molar mass of PTMO | Soft segments content [wt %] |
|---|---|---|---|---|---|
| PU(0)-2000 | 1/0/1 | – | 0 | 2000 | 92 |
| PU(PP,1)-2000 | 2/1/1 | PP | 1 | 2000 | 78 |
| PU(PP,3)-2000 | 4/3/1 | PP | 3 | 2000 | 61 |
| PU(0)-1000 | 1/0/1 | – | 0 | 1000 | 85 |
| PU(PP,1)-1000 | 2/1/1 | PP | 1 | 1000 | 65 |
| PU(BHBP,3)-1000 | 4/3/1 | BHBP | 3 | 1000 | 40 |
| PU(PP,3)-1000 | 4/3/1 | PP | 3 | 1000 | 44 |
| PU(0)-650 | 1/0/1 | – | 0 | 650 | 79 |
| PU(BHBP,1)-650 | 2/1/1 | BHBP | 1 | 650 | 51 |
| PU(PP,1)-650 | 2/1/1 | PP | 1 | 650 | 54 |

### *3.1. PU transitions from extrema separation*

The temperature dependence of the ESR spectrum is due to the changes in the rotational rate of the nitroxide radical. One of the measures of probe mobility is the extrema separation $2A'_z$, which decreases with increasing mobility. The variations of $2A'_z$ as a function of temperature for selected PUs are shown in Fig. 2.

The sigmoidal shape of the curves with a rapid change of $2A'_z$ over a substantially narrow temperature range seems to be a characteristic feature of the systems studied. For every curve the upper limit of extreme separation is about 65–67 G at low temperatures, and the lower limit of $2A'_z$ is 33–34 G at high temperatures. The strong decrease in the $2A'_z$ values occur, however, at different temperature range depending on the PU structure. The transition is shifted to lower temperature with increasing length of the soft segment, and is analogous to the decrease of the glass transition temperature $T_g$. The literature data [14] show that temperature at which the extrema separation becomes 50 G corresponds closely to the inflection point of the $2A'_z$ vs. temperature curves for most of the polymers investigated. It means that the rate of rotation of the probe molecules undergoes the most substantial changes at this temperature. Therefore, the $T_{50\,G}$ parameter is commonly used to correlate with the glass transition temperature measured with other methods. The $T_{50\,G}$ values are generally higher than those of $T_g$, since the rotational frequency at $T_{50\,G}$ is of $10^7$ Hz for nitroxides, whereas the $T_g$ is measured at 1 Hz by calorimetric methods. According to the literature data [14], the correlation between $T_g$ and $T_{50\,G}$ is non-linear if a broad range of $T_g$s is regarded, and shows approximate linearity within narrower temperature regions. As can be seen from the data in Table 2, the nearly linear correlation of $T_{50\,G}$ with $T_g$ can also be noted for most of the PUs studied in this work. The deviation from the linear relationship has been

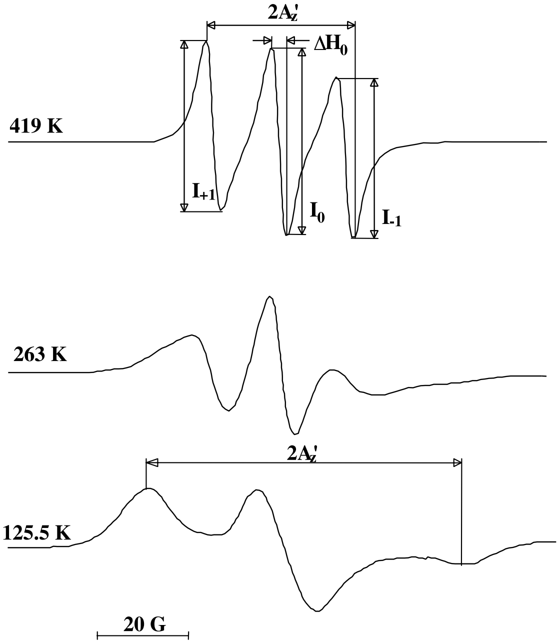

Fig. 1. ESR spectra of TEMPO probe in PU(0)-1000 at different temperatures.

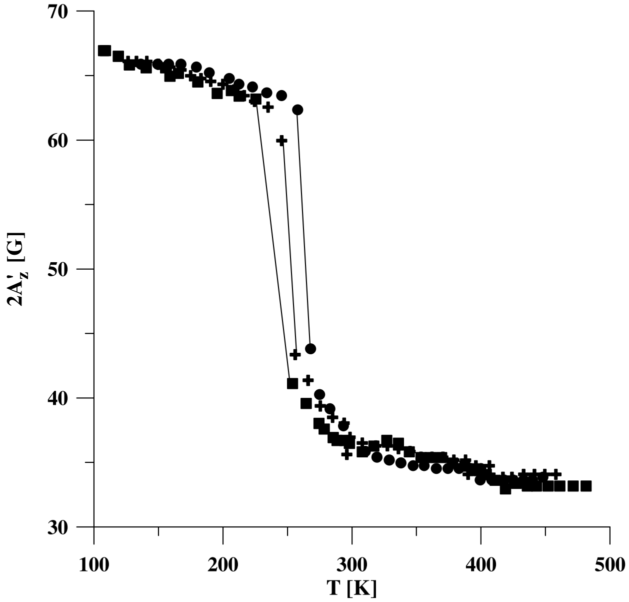

Fig. 2. Outer peak splitting $2A'_z$ as a function of temperature for TEMPO doped PUs; (■) PU(0)-2000, (+) PU(0)-1000 and (●) PU(0)-650.

Table 2
Values of $T_g$ and related transition temperatures for the series of PUs

| Polymer | $T_g$[a] [K] | $T_{50\,G}$[b] [K] | $T_n$[c] [K] | $T_i$[d] [K] | $T_\tau$[e] [K] |
|---|---|---|---|---|---|
| PU(0)-2000 | 196 | 232 | 236 | 274 | 194 |
| PU(PP,1)-2000 | 190 | 236 | 231 | 270 | 203 |
| PU(PP,3)-2000 | 190 | 242 | 245 | 304 | 188 |
| PU(0)-1000 | 221 | 251 | 245 | 285 | 223 |
| PU (PP,1)-1000 | 221 | 253 | 249 | 294 | 226 |
| PU(BHBP,3)-1000 | 217 | 255 | 258 | 330 | 258 |
| PU(PP,3)-1000 | 227 | 270 | 266 | 378 | 257 |
| PU(0)-650 | 239 | 261 | 262 | 304 | 233 |
| PU(BHBP,1)-650 | 242 | 261 | 264 | 329 | 238 |
| PU(PP,1)-650 | 241 | 265 | 265 | 334 | 245 |

[a] From DSC measurements, Ref. [13].
[b] From $2A'_z$ vs. temperature curves.
[c] From $\Delta H_0$ vs. temperature curves.
[d] Temperature at which motionally narrowed spectrum is detected.
[e] From the crossover point of the Arrhenius plots.

observed for PUs, for which the weight fraction of the soft segments is less than 50%.

Due to the linear correlation between both parameters, the same trend of $T_{50\,G}$ changes with PU molecular structure can be expected. Like for $T_g$, the straight lines have been obtained when the $T_{50\,G}$ values of PUs with varying soft segment length and fixed hard segment (PU(0) or PU(PP,1) series) were plotted against soft segment molar mass (Fig. 3). The decrease of the $T_{50\,G}$ values with the increase of the macrodiol molar mass can be explained by the decreasing influence of the TDI-based stiffening elements due to their declining concentration.

Although the $T_g$ values of PUs with lower degree of microphase separation have not been found to vary within the series of the fixed soft segment molar mass (PU-1000 series), the influence of the hard segment length can be observed in case of $T_{50\,G}$ as a linear correlation of both variables (Fig. 4). The higher value of the respective transition temperature for PUs with a higher hard segment content could generally be awaited, mainly because of the presence of the hard segments in the soft segment rich phase due to the less complete phase separation. On the other hand, there are literature data [15–16] showing that the soft segment glass transition is only nominally affected by the change in hard segment content, that is also in accordance with our DSC results. Thus, the worse defined $T_g$s of the samples with a high hard segment weight fraction, resulting presumably from the broader transition temperature region,

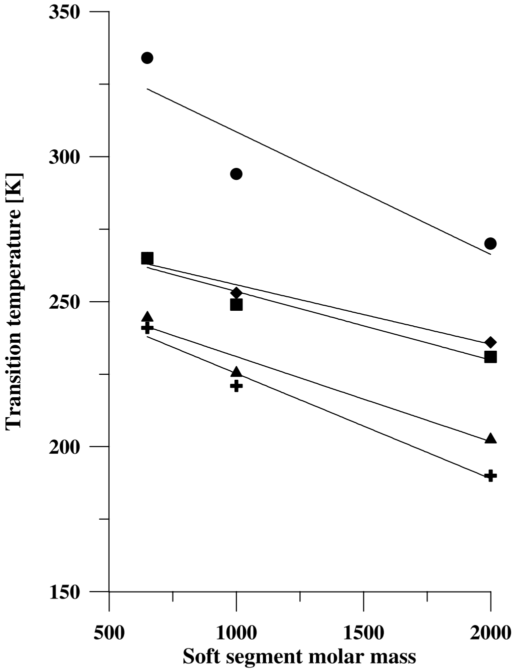

Fig. 3. Dependence of the transition temperatures on the soft segment molar mass for the PU(PP,1) series; (+) $T_g$, (◆) $T_{50\,G}$, (■) $T_n$, (●) $T_i$, (▲) $T_\tau$.

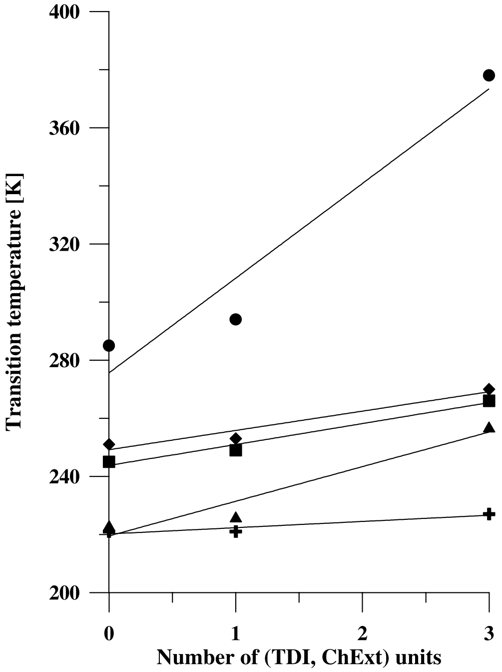

Fig. 4. Dependence of the transition temperatures on the hard segment length for the PU-1000 series; (+) $T_g$, (◆) $T_{50\,G}$, (■) $T_n$, (●) $T_i$, (▲) $T_\tau$.

accompanied by the diminished magnitude of heat capacity at the transition, can serve as an explanation for the observed discrepancies in the behaviour of both parameters, $T_g$ and $T_{50\ G}$. From Table 2, evidence can also be seen of a slightly reduced soft segments mobility expressed by the higher $T_{50G}$ values for PUs with the PP-based hard segments comparing to those with the BHBP-based ones. This can be related to the more efficient physical crosslinking of the soft segment matrix coming from a greater number of the smaller size hard domains, as observed in the AFM images of the PP-based PUs [7].

### 3.2. PU transitions from ESR central line width

For studying the molecular transitions in the series of PUs, the alternative approach based on the line width variation with temperature has been used.

The line width alteration, i.e. its dependence on the nuclear spin quantum number and the reorientation correlation time [17] is described by Freed approach [18] or Kivelson theory [19] resulting from perturbation treatments of spin relaxation. In its simplified form, as the Eq. (4), it is commonly used for the calculations of the rotational correlation time. However, for intermediate and slow rates of tumbling this treatment has to be replaced with a complete line shape calculation.

Here, the width of the central line, $\Delta H_0$, measured directly from the ESR spectra of various TEMPO doped PUs has been examined over a broad range of temperatures. Representative plots of $\Delta H_0$ vs. $T$ for some of the systems are presented in Fig. 5.

The plots show that the line width changes very little for temperatures below 200 K. Above 200 K, the line width decreases quite rapidly, and it becomes again less sensitive to temperature above a certain temperature from the temperature range of 280–340 K. The exception from this behaviour are PUs from the PU-2000 series and PUs with shorter hard segments from the PU-1000 series, for which the sharp increase in the line width above 330 and 360 K, respectively, is observed (PU(0)-1000 in Fig. 5). This phenomenon, which also marks the temperature variations of the rotational correlation times, will be discussed in the next section. Generally, the results obtained for all PUs exhibit temperature dependent line width, which is represented by a broad sigmoidal curve with a distinct inflection point. This point defines the temperature at which the line width is changing most rapidly, that in turn may allow a new experimental parameter, $T_n$, to be introduced to correlate with glass transition temperature. The values of this parameter estimated for the whole series of PUs are listed in Table 2. Inspecting the data from Table 2, it appears that the results concerning $T_n$ agree very well with the $T_{50\ G}$ values determined from the extrema separation vs. temperature plots. Using the $T_n$ values for correlation with a PU molecular structure, almost the same linear relationships between $T_n$ or $T_{50\ G}$ and the soft or hard segment length have been obtained, as illustrated by the plots in Figs. 3 and 4. The very similar linear correlation, including the same points deviating from it, has also been found for both parameters when plotted against $T_g$. It seems, therefore, that this new parameter, the determination of which is objective and does not suffer from the subjective errors likely to occur in recording the outerpeak maxima in the complex ESR spectra, can be used as an alternative to $T_{50\ G}$ parameter or as its supplement.

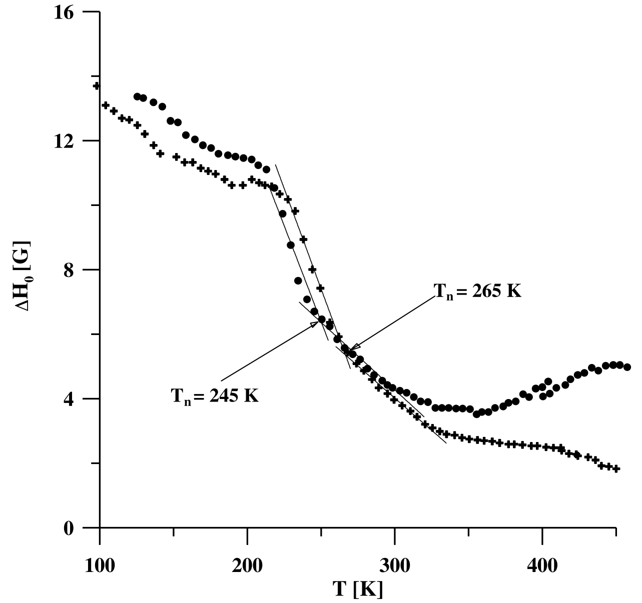

Fig. 5. Temperature dependence of the central line width for TEMPO doped PUs; (●) PU(0)-1000 and (+) PU(PP,1)-650.

### 3.3. Effective volume of PU soft segments

A correlation between $T_g$ and $T_{50\ G}$ established by Kumler et al. [14] enables an estimation of the effective volume of the polymer segment undergoing local motion at $T_g$. From the temperature shift between the high frequency and low frequency glass transition, using the Eq. (1) derived by Kusumoto et al. [20]:

$$T_{50\ G} - T_g = 52\left[2.9f\left(\ln\frac{1}{f}+1\right)-1\right] \qquad (1)$$

the ratio, $f$, of the molecular volume of the probe to the polymer segment can be calculated. As an alternative to the Eq. (1), Bullock et al. [21] derived the following expression, which is based on fewer assumptions, and in which there is no upper limit for $f$:

$$T_{50\ G} - T_g = C_{2g}\left[\frac{2.303C_{1g}f}{13.8}-1\right] \qquad (2)$$

where $C_{1g}$ and $C_{2g}$ stand for the WLF parameters. If no particular values of those parameters are available, the average values of 17.4 and 51.6 for $C_{1g}$ and $C_{2g}$, respectively, are used. This method employs the estimated values of $\tau_{50\,\mathrm{G}}$ and $\tau_\infty$ with the assumption that they are applicable to all probes in all polymers. To avoid such approximation another expression is suggested by the same authors as giving more reliable value of $f$ [21], which requires, however, the determination of the $\tau$ values in the temperature range of interest:

$$\ln\tau = \ln\tau_\infty + f\left[\frac{2.303C_{1\mathrm{g}}C_{2\mathrm{g}}}{T - T_\mathrm{g} + C_{2\mathrm{g}}}\right] \tag{3}$$

The results of the calculation of the parameter $f$ for the series of the PUs studied using each of the procedures presented above are given in Table 3.

From the comparison of the data from Tables 2 and 3, it can be seen that the values of $f$ increase with decreasing the $T_\mathrm{g}$ values. The same trend is observed independently of the method of the $f$ estimation, however, the values computed from the Eq. (2) are approximately twice the values obtained using Eq. (1). The $f$ values calculated from the Eq. (3) lie between the former two sets of the $f$ values. It can also be seen that these values are slightly more sensitive to the structural variations of PUs. Since the same spin probe was used to study the series of PUs, the comparison of the relative volumes of the relaxing segments within the whole series has been made by plotting the $T_\mathrm{g}$ vs. $1/f$ values. The results shown in Fig. 6 indicate that there is an approximately linear relationship between both variables.

This observation fits the trend described by Bullock et al. [21] that a higher $T_\mathrm{g}$ is associated with a bulkier segment involved in the glass-to-rubber transition. This is physically reasonable and means that the rotation of a probe requires cooperative motion of a greater number of the –(O–$(CH_2)_4$)– units in PU with shorter soft segments than it is necessary for the same probe in PU with longer ones. However, the scatter of the points observed in Fig. 6, which can be attributed to the inaccuracies in the determination of the $T_\mathrm{g}$ values discussed previously, and those introduced by using the average values of $C_{1\mathrm{g}}$ and $C_{2\mathrm{g}}$, suggests that the conclusions resulting from the comparison of the effective volume of the relaxing segments in various PUs can only be justified for polymers showing distinctly different and well defined $T_\mathrm{g}$s. As expected, the greatest scatter of the points has been observed for the $f$ values evaluated using Eq. (1), representing the approximate version of the relation between ($T_{50\,\mathrm{G}} - T_\mathrm{g}$) and $f$.

Table 3
Values of the parameter f for TEMPO doped PUs

| Polymer | $f_\mathrm{A}$[a] | $f_\mathrm{B}$[b] | $f_\mathrm{C}$[c] |
|---|---|---|---|
| PU(0)-2000 | 0.24 | 0.58 | 0.38 |
| PU(PP,1)-2000 | 0.29 | 0.65 | 0.53 |
| PU(PP,3)-2000 | 0.33 | 0.69 | 0.38 |
| PU(0)-1000 | 0.22 | 0.55 | 0.33 |
| PU (PP,1)-1000 | 0.22 | 0.56 | 0.33 |
| PU(BHBP,3)-1000 | 0.25 | 0.60 | 0.38 |
| PU(PP,3)-1000 | 0.28 | 0.63 | 0.28 |
| PU(0)-650 | 0.18 | 0.49 | 0.25 |
| PU(BHBP,1)-650 | 0.17 | 0.47 | 0.23 |
| PU(PP,1)-650 | 0.19 | 0.50 | 0.20 |

[a] From Eq. (1).
[b] From Eq. (2).
[c] From Eq. (3).

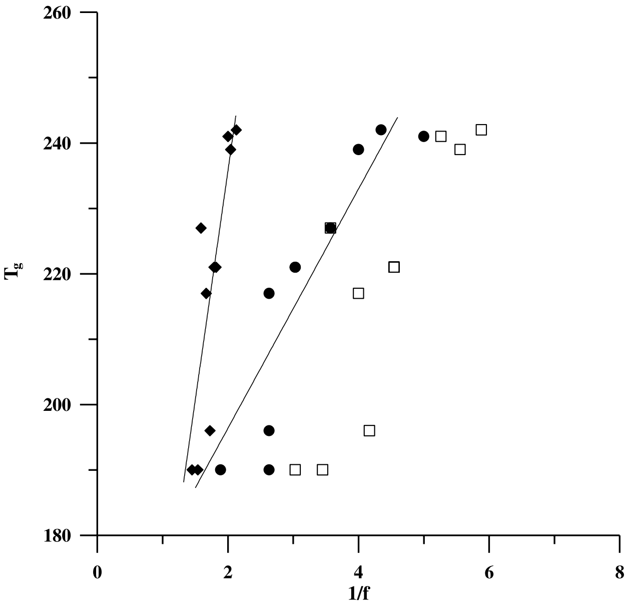

Fig. 6. Relationships between $T_\mathrm{g}$ and 1/$f$; □ $f_\mathrm{A}$, ◆ $f_\mathrm{B}$, ● $f_\mathrm{C}$.

### 3.4. Segmental mobility from rotational correlation times

The rotational correlation time $\tau$ is another parameter characterising the rotational diffusion of a nitroxide probe dispersed in a polymer matrix. The various methods can be used for calculating the correlation time, which depend on the type of the ESR spectra. From the motionally narrowed ESR spectra, it is possible to determine $\tau_\mathrm{C}$ using Eq. (4) derived from the Kivelson theory [19]:

$$\tau_\mathrm{C} = 0.65\times10^{-9}\Delta H_0\left[\left(\frac{I_0}{I_{+1}}\right)^{1/2} + \left(\frac{I_0}{I_{-1}}\right)^{1/2} - 2\right] \tag{4}$$

where $I_{+1}$, $I_0$ and $I_{-1}$ are the peak-to-peak heights of the low-, central-, and high-field lines of the first derivative ESR spectrum, respectively, and $\Delta H_0$ is the peak-to-peak line width of the central line. In the slow motion region, $\tau_\mathrm{R}$ may be estimated using method developed by Freed et al. [22]. In this approach $\tau_\mathrm{R}$ is obtained from the outer peak splitting $2A'_z$ according to the Eq. (5):

$$\tau_\mathrm{R} = a(1-S)^b \quad S = \frac{2A'_Z(T)}{2A'_Z(100\ \mathrm{K})} \tag{5}$$

where the ratio $S$ is a temperature depended parameter with the rigid limit value of $2A'_z$ measured at 100 K. The coefficients $a$ and $b$ depend on the applied motional model and the intrinsic line width of the spectrum. The values of $\tau_\mathrm{R}$ discussed here were determined for $a = 5.4\times10^{-10}$ and

$b=-1.36$ with the assumption of a Brownian rotational diffusion model and the intrinsic line width of 3 G [22].

The $\tau$ calculations performed for both fast and slow motional regions have been limited to the temperature range set by the assumptions used in calculating $\tau$ from the observed ESR line shapes using both equations. For the slow motional region, $\tau_R$ was estimated from the spectra recorded over a range of temperature from 100 K up to a temperature where $S$ is undefinable, since the outer lines begin to converge to the motionally narrowed spectrum. In the fast motional region, the correlation time $\tau_C$ was determined over a range of temperature from $T_i$, a temperature at which the ESR spectrum transforms into its 'isotropic' form characterised by the three relatively sharp hyperfine lines, up to 450 K. The upper temperature limit results from the distinct loss of signal intensity at higher temperatures due the decay of the TEMPO radicals. For both motional regimes, reproducible data were obtained upon cooling the samples, except for poly(urethane-urea)s with the lower soft segment weight fraction. The differences in the $\tau_C$ values estimated for these polymers from the heating and the cooling part of a cycle will be commented on in the next section.

The values of a temperature at which the motionally narrowed spectrum was detectable, $T_i$, are presented in Table 2. It is evident from the data of Table 2 that these temperatures are strongly structure related, despite some inaccuracy in the $T_i$ values determination. As shown in Fig. 3, the $T_i$ values determined for the PU(PP,1)-M series with a fixed hard segment vary nearly linearly with the soft segment molar mass. The similar behaviour to those observed for the $T_g$ or the $T_{50\ G}$ and $T_n$ variations leads to the conclusion that temperature at which TEMPO molecules begin tumble freely is closely related to the intrinsic mobility of the soft segments. From Fig. 4, it is also demonstrated that $T_i$ changes linearly with the hard segment length showing much higher values for longer hard segments. This effect provides evidence that the hard segment domains, as well as the hard segments alone being mixed into the soft domains, exert some restrains on the movement of the polymer chain segments, and thus on the mobility of the TEMPO spin probes. Although no clear correlation has been found between $T_i$ and $T_g$, there is a general tendency for $T_i$ to increase with an increase of $T_g$. The strong sensitivity of the spin probe motion on PU's molecular structure expressed by the $T_i$ values supports additionally our interpretation [12] that the ESR spectra of PUs recorded at lower temperatures reflect the anisotropic motion of a probe embedded in a homogeneous polymer matrix.

The $\tau$ values calculated from the ESR spectra using Eqs. (4) and (5) and plotted in the form of the Arrhenius relation were found to give straight lines within the adopted temperature limits for most of the PUs investigated and in both motional regimes. The exceptions are PU-2000 and polymers from the PU-1000 series with a high soft segment content, for which the deviation from linearity has been observed in the high temperature region. The temperature dependences of $\tau$ for the two representative PUs have been demonstrated in Fig. 7.

From the plots in Fig. 7, it can be seen that the values of $\tau_C$ for PU(0)-2000 increase unexpectedly with temperature increasing when the temperature limit of 330 K is passed, and that from this point the Arrhenius relation is no longer obeyed. It has also appeared that such a sharp change in the $\tau_C$ values occurs at about 330 K for all PUs from the PU-2000 series, and at about 350 K for PU(0)-1000 and PU(PP,1)-1000 (Fig. 8). One possible explanation for this behaviour is motional broadening of the spectra caused by translational diffusion, which is also involved in the motion of the probe [23,24], and whose effect may become large at certain conditions. Therefore, it seems reasonable to find that the segmental motions of PUs with long soft segments are less constrained than in case of PUs with shorter ones. Moreover, when the amount of the hard segments is low, the restrains imposed by those segments do not prevent some sections of a chain from their relatively free motion. Raising the temperature enhances the micro-Brownian motion of such units and weakens the molecular interaction between neighbouring macromolecules, allowing the probe molecules to diffuse through polymer matrix more easily.

The ability of TEMPO molecules to diffuse through the soft domains of PUs with a higher segmental mobility may be related to the transport behaviour of those polymers. Since the same effect of making the polymer move more freely can be expected in case of increasing the temperature or adding the solvent to the system, these polymers can be regarded as expanding more easily and to a greater extent

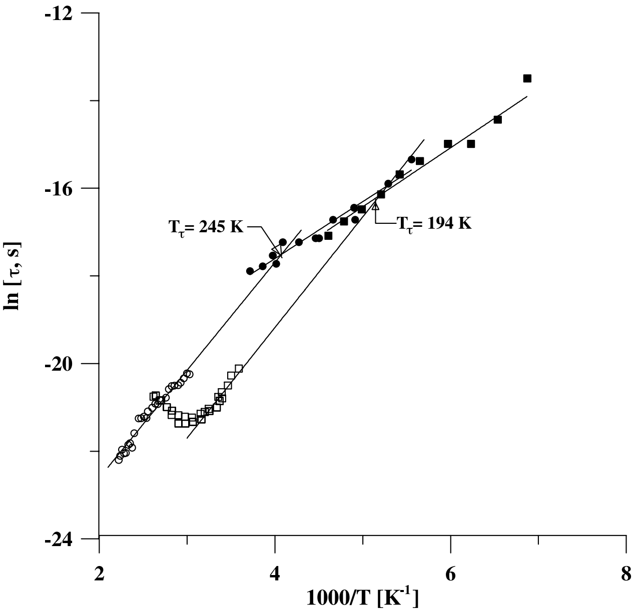

Fig. 7. Arrhenius plots of $\tau$ for PU(0)-2000: (□)-$\tau_C$, (■)-$\tau_R$, and PU(PP,1)-650: (○)-$\tau_C$, (●)-$\tau_R$.

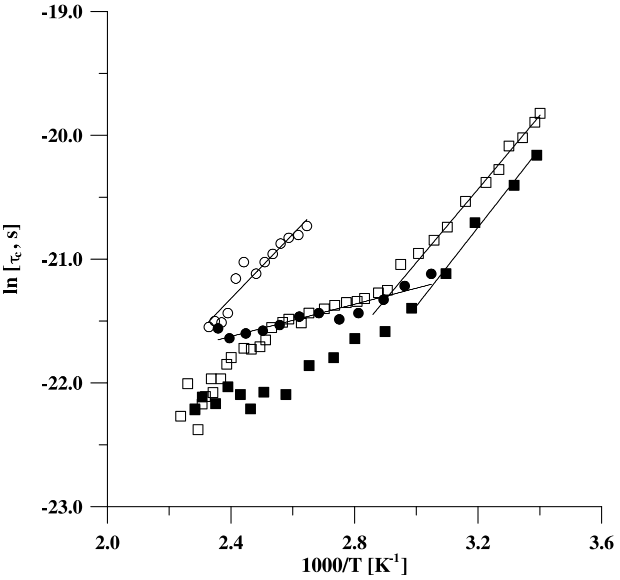

Fig. 8. Arrhenius plots of $\tau_C$ determined from heating and cooling runs for PU(PP,3)-1000: (○) heating; (●) cooling; and PU(PP,1)-1000: (□) heating; (■) cooling.

than other PUs. This in turn implies that their solubility and diffusivity, especially toward solvents of a high swelling power, can be much higher than expected for the members of the homologous series of PUs. The results of the recent studies have appeared to be consistent with those predictions [25].

The $\tau$ values from the linear regions of the ln $\tau$ vs. $1/T$ correlations were used to determine the activation energy, $E_a$, for the PUs studied.

In the high temperature regime, the $E_a$ values seem to be similar for all systems showing the values from the range of 20–29 kJ/mol. The lack of any dependence on PU structure indicates that the same molecular process activates the molecular motion of the spin probe. The comparison of the correlation times calculated at a given reference temperature for various TEMPO doped PUs shows, however, a very clear dependence on the molecular structure of the polyurethanes. The structure-spin probe mobility correlations have been discussed in details in the previous paper [13].

In the low temperature regime, $E_a$ is significantly smaller (in the range of 5–9 kJ/mol) and hardly dependent on the system. Similar value of the activation energy, around 8 kJ/mol, has been found for TEMPO and other nitroxide probes in some amorphous polymers [26]. These results seem to suggest that the spin probe is located at defect sites of similar size and its motion is rather insensitive to the specific location. The very close values of the correlation time $\tau_R$ ($\tau_{R\ av.} = 1.4\times10^{-7}$ s) calculated at a reference temperature $T = 183$ K, lower than $T_g$ of each of PUs, may support this description. According to this, the differentiation in the $\tau_R$ values observed for temperatures around $T_g$ indicates that the spin probe motion is no longer a function of temperature only, but also depends on the increased free volume of a polymer. The values of preexponential factors deduced for both temperature regimes, which fall within the range of $1.6\times10^{-9}$ s to $5.2\times10^{-11}$ s for low temperature regime, and of $1.1\times10^{-12}$ s to $9.8\times10^{-14}$ s for high temperature regime, demonstrate the validity of the Arrhenius expression for the thermal behaviour of a spin probe in PU.

An interesting feature of Fig. 7 is that the temperature dependencies of the $\tau_C$ and $\tau_R$ data fit the respective Arrhenius relations, showing a distinct crossover point if extrapolated over a broader temperature range. This point, designated as $T_\tau$, represents the temperature at which a significant change in type of dynamics occurs. According to Schlick et al. [27], $T_\tau$ can be correlated with $T_g$ and used as a new parameter better indicating the glass transition than $T_{50\ G}$ because of its lesser sensitivity to the probe size. The comparison of the data listed in Table 2 conforms that the $T_\tau$ values are generally close to the $T_g$ ones from the DSC method, excepting PUs of a low soft segment content. The values for those polymers, however, fit very well the linear dependencies of $T_\tau$ on the segment length, lending support to the view that all the ESR parameters are strong structure sensitive (Figs. 3 and 4).

### 3.5. *Effect of thermal history*

As mentioned before, the experimental data used for fitting of the Arrhenius relations were based on the results of the both heating and cooling runs for most PUs, except for poly(urethane-urea)s.

Fig. 8 shows the Arrhenius plots representing the heating and cooling runs for two PUs of various content of the PP-based hard segments. Although the plots follow the Arrhenius relation within the assumed temperature limits for both runs, they show either the change in the slope or the shift in the respective values. This effect is strongly structure dependent, and for PU(PP,3)-1000 the slope of the ln $\tau_C$ vs. $1/T$ correlation was found to be nine times greater for the heating process than it is for the cooling one. The slope is practically the same for PU(PP,1)-1000, however, the values of $\tau_C$ are shifted towards lower temperature in the cooling run. The reproduced data from both runs, within experimental error, have only been obtained for PP-based PUs with the longest soft segment of $M = 2000$.

Table 4 reveals the differences in the values of the correlation time $\tau_C$ at $T = 298$ K calculated from the heating and cooling runs for PUs, for which the corresponding changes in both runs have been observed. The comparison of both data sets indicates that the $\tau_C$ values from the cooling run are lower than those obtained from the heating process. It has appeared that the higher the hard segment content the greater is the difference between the values from both runs the higher is the hard segment content, showing for PU(PP,3)-1000 as much as a nine fold increase of the

Table 4
Values of $\tau_C$ at $T=298$ K and values of $E_a$ for PP-based PUs calculated from the heating and cooling runs

| Polymer | Heating | | Cooling | |
|---|---|---|---|---|
| | $\tau_C \times 10^{9a}$ [s] | $E_a$ [kJ/mol] | $\tau_C \times 10^{9}$ [s] | $E_a$ [kJ/mol] |
| PU(PP,1)-1000 | 1.79 | 24.6 | 1.61 | 26.4 |
| PU(PP,3)-1000 | 6.84 | 21.9 | 0.76 | 5.4 |
| PU(PP,1)-650 | 4.73 | 21.0 | 1.65 | 14.0 |

[a] Ref. [13].

tumbling rate in the cooling process. Similarly, the increased mobility of the TEMPO molecules in the cooling run has been observed for PUs with the decreased soft segment length. Moreover, the values of activation energy for TEMPO rotation given in Table 4 has been found to vary significantly with the system in the cooling process. They are the lower the higher is the hard segment content or the shorter is the soft segment length, while for the heating run, the respective $E_a$ values are generally higher and not particularly affected by the PU structure.

In order to explain the thermal behaviour of the PP-based PUs, the ESR studies has been completed by the DSC analysis on the same series of materials. The representative DSC thermograms of some PUs used in the ESR experiments are shown in Fig. 9.

The low temperature DSC behaviour is characterised generally by a single and for shorter soft segments rather broad transition referring to the glass-to-rubber transition of the soft segments. The values of temperature corresponding to this transition for all of the samples investigated have been summarised in Table 2 and discussed earlier. These values are relatively unaffected by the heating process as appeared from the comparison of the initial and the second DSC heating runs. It should be mentioned here that the reproducible values of $T_g$ were obtained in a separate series of DSC experiments performed using procedures described in Ref. [13]. In addition to the glass transition, the PU that have longer soft and hard segments, such as PU(PP,1)-2000, exhibits two peaks at about 248 and 280 K corresponding to soft segment crystallisation and melting, respectively.

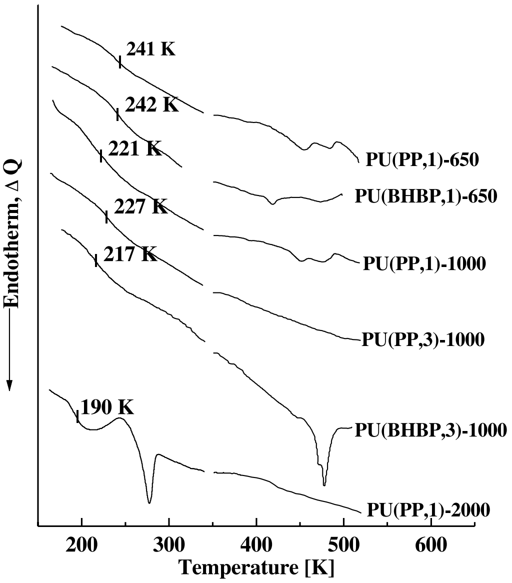

Fig. 9. DSC thermograms of PUs in the first heating run.

The high temperature DSC behaviour shown in Fig. 9 is more complex and strongly depends on the PU structure. Among the PP-based PUs, only polymers with short hard segments exhibit broad multiple melting endotherms. These endotherms appear at temperature above 450 K and are not reproducible in the second run. The BHBP-based PUs show multiple endotherms at lower (PU(BHBP,1)-650) or slightly higher (PU(BHBP,3)-1000) temperatures, which are not repeated in the second run either, except for the later one showing liquid crystalline properties [28]. For all the materials studied, WAXD results gave no indication of crystallinity. Thus, the endotherms observed are probably the results of ordering which occurs on a small scale within the hard segment domains and due to the compositional heterogeneity of those segments has a multiple transition character. The PUs examined do not exhibit the observable hard segment glass transitions. Other segmented polyurethanes have also manifested similar behaviour, and this has usually been ascribed to the small change in heat capacity of the amorphous hard blocks at their $T_g$ combined with a broad temperature range of this transition [29].

Summing up the results obtained, it is to be noticed that the polyurethane properties measured using DSC method, other than $T_g$ of the soft segments, seem not to be relevant to the properties displayed by the ESR results. In most materials, the only transition recorded in high temperature DSC thermograms occurs at a temperature higher than the upper temperature limit of the ESR experiments. Furthermore, the PUs studied generally do not show any significant softening or melting effects within the ESR temperature limits, excepting PU(BHBP,1)-650 which undergoes melting transition at about 418 K. Unlike the PP-based PUs listed in Table 4, however, this PU gives basically reproducible ESR data from the heating and cooling processes.

Thermal behaviour of the PP-based PUs displayed in the ESR spectra requires, therefore, another interpretation than that concerning morphological effect observed in DSC. Since the free volume of the polymer is a major factor controlling the rotation rate of the TEMPO molecules, it seems that this somewhat unique behaviour may be attributed to the increased free volume of the soft domains resulting from the structural changes of some PUs due to their thermal treatment. To give a satisfactory explanation to the effects displayed in Fig. 8 and Table 4, the further investigations of the temperature induced structural changes have been performed recently. The results of these studies and the consequences of the observed behaviour in terms of structure-transport properties relations will be discussed in the separate paper.

## 4. Conclusions

The ESR measurements performed for the selectively doped polyurethane-based membranes have demonstrated the applicability of this method for studying the selected microenvironments of polymers with complex morphology, in this case the regions responsible for the transport of small molecules. It has also been found that the method applied is sensitive to the segmental motions, which are not distinguishable in the DSC thermograms.

The ESR results have shown that the transition temperature determined using extrema separation method, $T_{50\ \mathrm{G}}$, depends on the length of both soft and hard segments, though the effect of the hard segments has not been displayed when the DSC method was applied. Taking into account the linear nature of the $T_{50\ \mathrm{G}}$ vs. $T_{\mathrm{g}}$ relation obtained for several PUs studied, and being in agreement with literature data, these results prove the utility of the ESR method for this type of polymers. This observation contrasts the opinion that ESR measurements generally offer no advantage over conventional method for $T_{\mathrm{g}}$ determination.

In addition to the extrema separation method, a new method has been elaborated, which enables the determination of the transition temperature from the inflection point of the central line width vs. temperature curves. This method gives the $T_n$ values very similar to the $T_{50\ \mathrm{G}}$ ones, and seems to be especially useful for polymers for which the complex ESR spectra are obtained.

An attempt has been made to calculate the size of the relaxing polymer segment using the literature approaches of the relationship between probe and polymer motion. The results of these calculations accord with the relation presented in literature that polymers with higher $T_{\mathrm{g}}$ have bulkier segments. However, the scatter of the experimental points, which seems to result from the inconsistency in the $T_{\mathrm{g}}$ and $T_{50\ \mathrm{G}}$ values for the disputed PUs, makes these results less meaningful.

Two other ESR parameters, $T_i$ and $T_\tau$, determined from the ESR spectra recorded as a function of temperature have also been found to reflect the structural variations introduced into PUs. The $T_i$ parameter, representing the temperature, at which the motionally narrowed spectrum is detectable, seems to be the most structure related, however, the less accurate. The accurate data concerning the transition temperature, $T_\tau$, has been obtained from the crossover point of the respective Arrhenius relations. The $T_\tau$ values have been found to be very close to the $T_{\mathrm{g}}$ ones from the DSC method for those PUs, for which $T_{\mathrm{g}}$ could be precisely established. Thus, it suggests that this parameter allows determination of the reliable $T_{\mathrm{g}}$ values, being presumably independent of the size of the spin probe used.

Two unusual observations have been made in this work that behaviour of some PUs with a high soft segment content deviates from the Arrhenius relation at high temperatures, and that rotation correlation times of TEMPO spin probe in poly(urethane-urea)s with a high hard segment content are much lower during the cooling run than in the preceding heating stage. The first observation, for which the translational diffusion of TEMPO molecules not prevented by the hard domains is the most likely explanation, may appear important when the role of hard domains in the transport of liquids is regarded. The second observation implies that some of the investigated materials undergo significant structural changes with increasing temperature. This view requires further investigations, which are currently in progress.

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