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Permeable domains of segmented polyurethanes studied with paramagnetic spin probe

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Abstract

Studies on the permeable regions of the dense polyurethane-based membranes were performed by electron spin resonance spectroscopy (ESR) using TEMPO spin probe incorporated into the membrane via diffusion from the vapour phase. The ESR spectra were measured as a function of temperature and microwave power for polyurethanes (PU) varying in the molecular structure and morphology. It was found that the TEMPO spin probe exhibited anisotropic rotation whose anisotropy increased as temperature decreased and was more pronounced for PU with shorter soft segments. The simplified method was used to obtain apparent correlation time τ_c enabling the comparison of the polyurethanes studied. This approach was based on the Arrhenius relation of τ_c vs. $1/T$ determined from motionally narrowed ESR spectra and on the assumption that this behaviour prevails over a broader temperature range at temperatures generally greater than T_g of a given polymer.

Keywords: Polyurethanes; Electron spin resonance; Membranes

1. Introduction

The electron spin resonance (ESR) spectroscopy is gaining increasing attention as an important tool for the study of synthetic polymers. Since the pioneering work of Rabold [1] and Stryukov [2] numerous papers on various polymer systems have been presented. Some recent applications of this method refer to different classes of polymers and copolymers [3–5], as well as to more complex polymer systems, like blends and IPN [6–8], or porous polymer resins [9]. The results regarding heterogeneous polymer systems have been summarised in a review article by Veksli [10].

The ESR spectroscopy of current use is based on the response of the ESR spectrum line shape of the stable nitroxide radical to its molecular motion. The paramagnetic molecule can be present either as a ‘guest’, able to move freely within the polymer matrix (spin-probe), or it can be chemically bound to the polymer (spin-label). The motional freedom of the spin-probe reflects the dynamics of the surrounding macromolecules, whereas spin-label mobility provides information about the local dynamics of the chain segment close to the label group. The time scale for the rotational diffusion of a nitroxide radical is characterised by a correlation time, τ_c, which falls within the range of 10^{-6}–10^{-11} s for conventional ESR technique. Generally, two different motional regimes can be distinguished in the ESR spectra of nitroxides. In the fast isotropic motion region, where the motion is faster than 10^{-9} s, the spectrum consists of three, well defined and relatively narrow lines with the extreme separation of ca. 30 G. In the slow or fast but anisotropic motion region, with the motion restricted either in rates or/and in orientations, the spectrum is broad and the extreme splitting between low and high field peaks tends to approach the value of 70 G characteristic for the powder spectrum.

In this work we describe the application of the ESR method to study the permeable regions of the dense, polyurethane-based membranes. Polyurethanes are multiblock copolymers composed of alternating hard and soft segments that are thermodynamically incompatible. As a result, two-phase morphology is observed in those systems.

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It has been postulated that only soft segment domains are permeable to small molecules [11]. The hard segment domains, acting as fillers and physical crosslinks for the rubbery matrix, can only affect the transport process indirectly by changing, for example, the path of the permeating molecules. Therefore, the method adopted in this study was to incorporate the nitroxide radical into the already prepared membrane via diffusion from the vapour phase. It has been expected that the spin-probes will locate themselves in the same regions of the membrane, which are available for the gas or liquid molecules during their diffusion through the membrane. Additionally, the spin-probe TEMPO of the smallest size among other nitroxides should facilitate the comparison of the ESR results with the earlier transport data.

In the present work we report the results obtained for two polyurethanes varying in the molecular structure and the extent of microphase separation along with the analysis carried out to explain the complex ESR spectra of these polymers. In the next papers of this series we will present a comprehensive study of correlations between polyurethane molecular structure, the spin-probe mobility, and the diffusivity of different liquids, as well as the complementary studies regarding the effect of some structural parameters on the polyurethane morphology as deduced from temperature-dependent ESR spectra.

2. Experimental

2.1. Materials

Polyurethanes (PU) were synthesised in DMF solution either by the reaction of poly(oxytetramethylene) diol (PTMO, $M_w = 2000$) with equimolar amounts of 2,4-tolylene diisocyanate (TDI) to obtain PU-1, or by a two-step prepolymer procedure from PTMO ($M_w = 650$), TDI, and 4,4′-diaminodiphenyl methane (PP) to obtain PU-2. The details of the both procedures will be described in the next paper of this series.

The PU membranes were obtained by casting a 15% DMF solution of the polymer onto a glass plate and by evaporating the solvent at 333 K in a dry nitrogen atmosphere for 3 days.

2.2. Preparation of spin-probed polymers

The spin-probe, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), was introduced into the PU membrane by diffusion from a vapour phase at room temperature. The PU sample in a form of a ca. 3 mm wide strip cut from the PU membrane and solid TEMPO were kept in a closed vessel for 30 min. After that, the spin-probed polymer sample was taken from the vessel, put into the ESR tube and kept there at room temperature for 2 weeks to allow the probe to redistribute itself throughout the polymer.

2.3. Measurements

The ESR spectra were recorded with a CW X-band ESR-spectrometer (9.2 GHz, 100 kHz modulation) (Radiopan, Poland) in the temperature range of 110–450 K. The temperature was varied with a special temperature unit. Typical parameters for spectra acquisition were as following: modulation amplitude 0.2 G, microwave power 10 mW, sweep width 200 G, scan time 240 s, time constant 0.3 s.

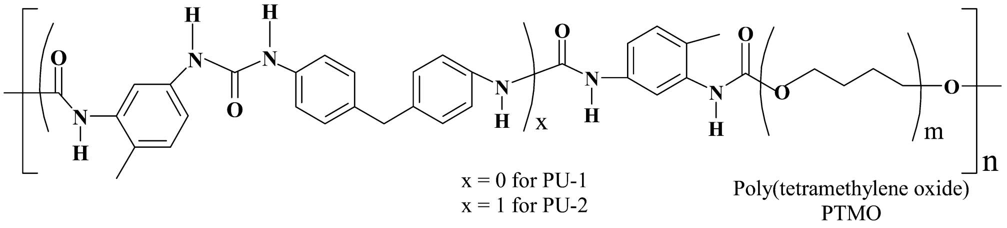
The densities of the polyurethane films were measured by buoyancy in water. The molecular weights of the synthesised PUs were determined using gel permeation chromatography (GPC). The measurements were carried out in DMF solutions at 353 K with a Knauer apparatus, based on polystyrene standards. Differential scanning calorimetry (DSC), used for the glass transition temperature determination, was conducted with a Rheometric Scientific DSC Plus apparatus at a heating rate 10°/min.

3. Result and discussion

The PUs studied in this work belongs to the series of the PTMO-based segmented polyurethanes obtained and investigated by us as membrane materials for organic/organic and organic/water separations [12,13]. Structure of the investigated PUs is shown in Scheme 1, and other details are given in Table 1. PU-1 represents the polymer with the longest soft segments and the shortest hard segments in the whole series. PU-2 on the other hand, is composed of the shortest soft segments and longer hard segments enabling, however, the elastomeric properties of this material to be preserved. The applied variations of the molecular structure produce distinct differences in the morphology of the both polymers. It has been found from the SAXS and AFM data [14] that PU-2 undergoes phase segregation into hard and soft domains. The hard segment domains have been observed via AFM as grains of 50 nm dimensions that are supposed to be composed of the lamellar microdomains with the SAXS interdomain spacing value of 8.8 nm. In contrary, PU-1, due to its much lower hard segment content (8 wt%), exhibits completely homogeneous morphology.

The room temperature ESR spectra of the both PUs doped with the nitroxide spin-probe TEMPO are shown in Fig. 1. A significant dissimilarity between the spectra indicates that the radical chosen is suitable to probe the structural features of interest.

As can be seen from Fig. 1, the spectrum of PU-1 consists of three nearly symmetric lines with the extreme separation of the two outer peaks of 35 G. The pattern of the ESR line shape for PU-2 is more complex and exhibits two additional signals at a low and a high field with the splitting between them of ca. 64 G. There is also a difference in the amplitude and the width of the lines comprising the basic triplet. The central line of the PU-2 triplet is the narrowest and of the



Scheme 1. Structure of segmented polyurethanes.

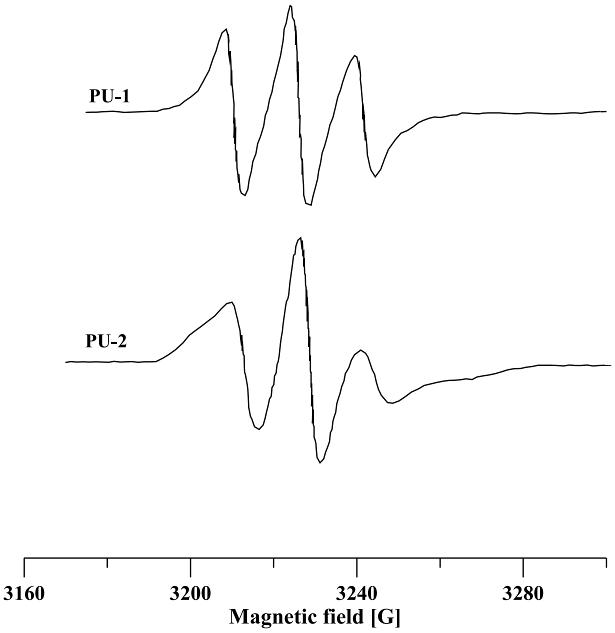


Fig. 1. ESR spectra of spin-probed polyurethanes at 294 K.

highest amplitude, whereas the amplitude of the low field line is higher than that of the high field one.

The pattern of fairly narrow three lines observed for PU-1 resembles that observed for the fast tumbling nitroxides in solution. This triplet is due to the interaction between the unpaired electron on the nitrogen and the magnetic moment of the nitrogen nucleus. The anisotropic effects of these interactions, coming from the axial symmetry of the unpaired electron, are averaged in this case and only one intermediate state is defined for each nuclear spin value. In that motionally-narrowed region the linewidth parameter T_2^{-1}, is given by the relation [15]:

$$T_2^{-1}(M) = A' + B'M + C'M^2 \tag{1}$$

where $M = (0, \pm 1)$ is the nitrogen nuclear spin corresponding to a given line in the spectrum. The parameters A', B' and C' are functions of the spectroscopic splitting (**g**) and the hyperfine splitting (**A**) tensors, and the rotational correlation time τ_c. Thus, the τ_c, of the tumbling nitroxide which represents the length of time over which probe molecules persist in a given orientation, may be calculated from this equation [15]. For fast isotropic motion, the following formula based on Kivelson's theory [16] is used:

$$\tau_c = 0.65 \times 10^{-9} W_0[(h_0/h_1)^{1/2} + (h_0/h_{-1})^{1/2} - 2] \tag{2}$$

where: W_0 is the width of the central line (G), and h_1, h_0 and h_{-1} are amplitudes of the ESR spectrum for low, central and high field lines, respectively.

The spectrum of PU-2 in Fig. 1, showing a low field double maximum and a high field double minimum, may be interpreted as a composite spectrum or as resulting from the motional anisotropy of the spin-probes with the slower tumbling rate. If the rotation motion is slowed, the averaging of the anisotropy of the **g** and **A** tensors becomes incomplete leading to the significant and unequal broadening of the spectrum lines. This effect tends to be the more pronounced the slower rotational reorientation is, and in the extreme the line shape approaches that of the rigid-limit spectrum. Since the superposition of such slow-motion spectrum with the fast-motion one may look, in many instances, to be qualitatively similar to the spectrum of the fast but anisotropic motion, a careful assessment of the experimental data with respect to the system investigated has been made in this work.

The literature on spin-labels and spin-probes in PU is limited and the results strongly depend on the PU structure as well as on the location of the nitroxide radical. For PUs based on PCL glycol and MDI, and spin-labelled at the terminal isocyanate group, the complex ESR spectra were interpreted as the superposition of two motionally different components resulting from the presence of the label in the crystalline and in the amorphous PCL phases [17]. In the

Table 1
Composition and structural characteristics of segmented polyurethanes

Sample	Molar composition PTMO/TDI/PP	Soft segment mol. wt. (g/mol)	Hard segment content, (calc.) (wt%)	Molecular weight (g/mol)	Mass density (g/cm^3)	T_g of the soft segments (K)
PU-1	1/1/0	2000	8	50 000	1.072	196
PU-2	1/2/1	650	46	43 000	1.139	241

ESR spectra of the segmented PUs prepared from PTMO, MDI and BD with the label located at a chain end again, two sites for the label were detected and interpreted as representing the hard and soft domains of PU [18,19]. The occurrence of two spectral components differing in their mobility was also observed for the spin-probed polyether-urethanes with, or without, carboxylate functional groups in the hard segments [8]. It was explained that the fast component corresponded to spin-probes in the soft domains while the slow component represented spin-probes in the hard domains. The partition of the radicals between the both phases seems to be due to the fact that doping procedure was carried out in polymer solution in that case.

For the system studied in this work, the possibility of existence of the TEMPO radicals within the hard domains should be eliminated independently of the domain size and structure. This comes from the fact that, according to the literature data [11], hard segment domains are not accessible for small molecules when transported into the PU films as diffusants. The heterogeneity within the soft domains, with the regions of slow and fast tumbling spin-probes, can also be ruled out since the short PTMO segments of PU-2 have been found unable to crystallise. Moreover, the ESR spectrum of PU-1, composed of the soft segments basically able to form micro-crystalline domains, shows no signs of the presence of a slow component in a broad temperature range. The local inhomogeneity in the distribution of the radicals within the soft domains should not be expected either since the polymer samples have been held at room temperature for an extended time period prior to the ESR measurements. Therefore, it seems necessary to assume that the complex spectrum of PU-2 results from the fact that molecular motion of the spin radicals is not isotropic in this system. Preferential motion about one axis is likely to occur for any elongated free radical, especially when the surrounding medium becomes more viscous. As can be seen from the discussion below, the shape of the spectra shown in Fig. 1 may be explained in terms of anisotropic motion of the spin-probe. Usually, isotropically tumbling nitroxides have **g** and hyperfine components such that in X-band measurements the amplitudes of the central and the low field lines are the same. The both spectra in Fig. 1, however, show that the amplitude of the central line is higher than those of the outer lines, even in case of the motionally narrowed spectrum of PU-1. Thus, instead of assuming the existence of the slow component in the complex ESR spectrum of PU-2, the corresponding subsplitting peaks can be interpreted as arising from the less efficient overlap of the spectral lines coming from radicals of different space position as a result of their slower rate of rotation. This interpretation is in a good accordance with the observation of the temperature dependent ESR spectra of PUs shown in Figs. 2 and 3.

A noticeable feature of these spectra is a distinct temperature dependence of their shape that is very similar for both polymers. The spectra at the lowest temperature limit are typical, broad line, rigid limit spectra with an extreme separation of 66 G. Upon heating, the spectral lines continuously narrow and the outer peaks shift inwards, reaching finally motionally narrowed form of the spectrum. The temperature corresponding to the transformation of the spectrum into its isotropic form appears to be the major parameter differentiating the both sets of the ESR spectra. The observed difference in the value of this parameter can be interpreted as resulting from different mobility of the soft

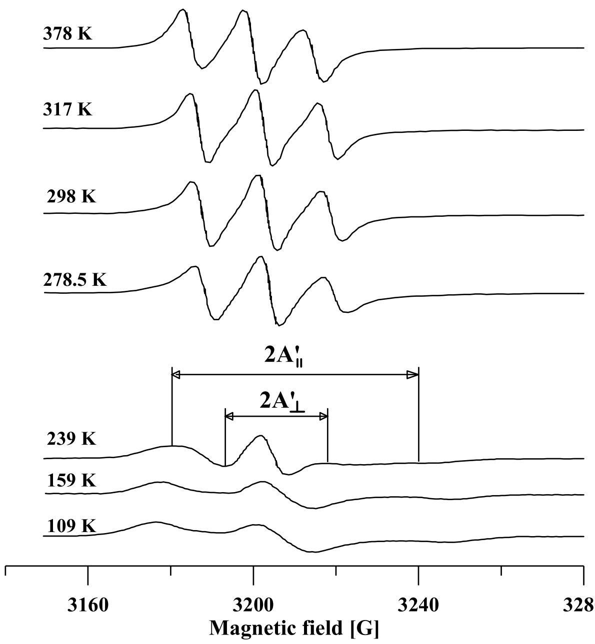


Fig. 2. ESR spectra of spin-probed PU-1 in the temperature range 109–378 K.

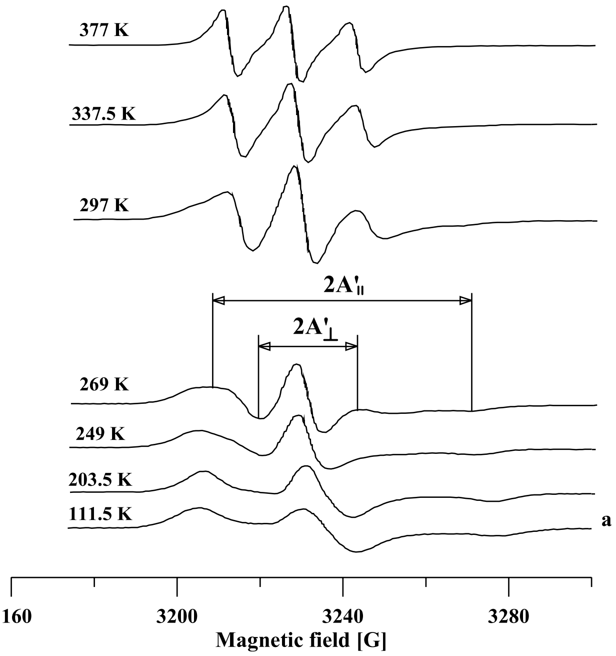


Fig. 3. ESR spectra of spin-probed PU-2 in the temperature range 111.5–377 K.

segments in both PUs. As demonstrated by the T_g values given in Table 1, a decrease in the length of the soft segments leads to their lower mobility manifested by the higher T_g value, that in turn requires higher temperature to enable the spin-probes in the soft domains to begin tumble freely.

The spectral changes demonstrated in Figs. 2 and 3 have been found to be generally reproduced in the heating-cooling cycle, however, a distinct loss of signal intensity due to the decay of the radicals has been observed at temperature above 400 K. The reproducibility of the spectral main features and the resemblance of the spectral variations with temperature for both PUs exhibiting different morphology strongly support the idea of anisotropically tumbling TEMPO radicals in this type of polymers.

The problem of the nitroxide fast isotropic and anisotropic motion was clearly explained by Devaux P. and Davoust J. [20]. For fast anisotropic motion the separation between ESR lines is $2\mathbf{A}'_{\|}$ with $\mathbf{A}'_{\|} < \mathbf{A}_{\|}$, and $2\mathbf{A}'_{\perp}$ with $\mathbf{A}'_{\perp} > \mathbf{A}_{\perp}$, where $\mathbf{A}_{\|}$ and $\mathbf{A}_{\perp}$ are the values of the hyperfine splitting in rigid limit. Such type of motions is strictly observed for both PU-1 (Fig. 2) and PU-2 (Fig. 3). If the nitroxide is allowed to reorient rapidly, $\mathbf{A}'_{\|}$ decreases whilst $\mathbf{A}'_{\perp}$ increases. Therefore, the quantity S expressed by the Eq. (3) is a measure of the extension of the nitroxide fast motion:

$$S = \frac{A'_{\|} - A'_{\perp}}{A_{\|} - A_{\perp}} \tag{3}$$

For PU-2 with $\mathbf{A}'_{\|} = 31.5$ G, $\mathbf{A}'_{\perp} = 11.8$ G, at 269 K, and $\mathbf{A}'_{\|} = 32.9$ G, $\mathbf{A}'_{\perp} = 6$ G in rigid limit, Eq. (3) gives the value $S = 0.73$. This means that 73% of the nitroxide motion is in frozen state at this temperature. The slightly lower value of S has been obtained for PU-1 at 239 K. The hyperfine splitting values for this polymer are: $\mathbf{A}'_{\|} = 30.5$ G, $\mathbf{A}'_{\perp} = 12.4$ G, and in rigid limit: $\mathbf{A}_{\|} = 32.9$ G, $\mathbf{A}_{\perp} = 6$ G, that gives $S = 0.67$. With temperature increasing $\mathbf{A}'_{\|}$ becomes equal to $\mathbf{A}'_{\perp}$ and only three lines are observed indicating that the motion is isotropic.

In Fig. 4 selected spectra are presented which were recorded as a function of microwave power at temperatures where the complex line shape have been observed for each of the PU samples. The results show that an increase in microwave power does not change markedly the spectral main features, neither for PU-1 or PU-2. This behaviour can suggest [21] that one component type of spectra may be assumed for both polymers. However, unequal amplitude ratios of the corresponding lines observed for different microwave power can rise some doubts, despite this fact the different saturation of the hyperfine lines is expected in multilevel system, where the relaxation times, T_1 and T_2, depend on the magnetic number of the nuclei [22]. To help to explain this ambiguity, the saturation method was used at a low temperature limit. The representative ESR spectra measured for various microwave powers are shown in Figs. 5(a) and 6(a). In case of one component spectrum, it was presumed that a full saturation of the signals should take place at the same microwave power. Such an effect has been detected in this study for A and B signals, as shown in Figs. 5(b) and 6(b).

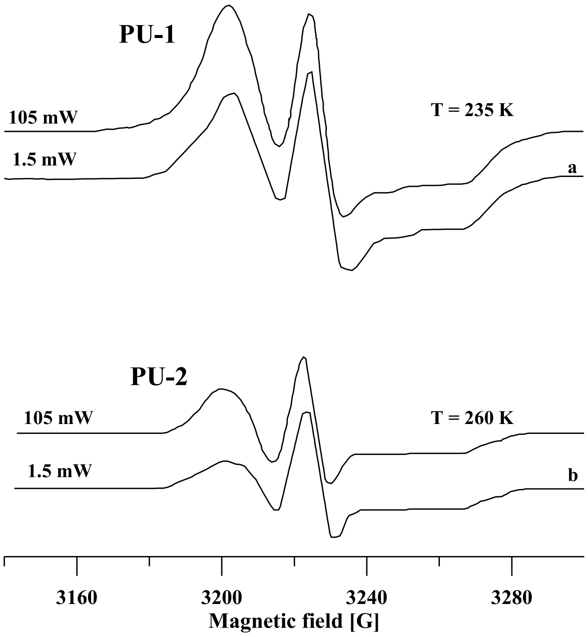


Fig. 4. ESR spectra of spin-probed PU-1 and PU-2 as a function of microwave power. Spectra at 1.5 mW were amplified by a factor of (a) 7.06, (b) 5.14.

Experimental evidences presented above have shown that the nitroxide spin-probes embedded in the permeable regions of the polyurethane-based membranes exhibit anisotropic motion. The anisotropy of this motion is sensitive to the polymer's structure and tends to be more apparent as temperature decreases. For the purpose of comparing the PUs of various molecular structures, a simplified method that allows an estimate of the correlation time has been adopted. In this method, rotational correlation time τ_c has been determined from the spectra obtained in the higher temperature regime using the Eq. (2) derived for fast isotropic motion. The calculated τ_c values for PU-1 and PU-2 plotted against $1/T$ gave straight lines over the most of the temperature range, as shown in Figs. 7 and 8, respectively. The deviation from the linear relation has only been observed for PU-1 at higher temperature (see Fig. 7), where movement of the probe molecules within the domains of much higher segment mobility can involve not only rotation but also translational diffusion. Thus, the correlation time τ_c, calculated from the linear relationships of τ_c vs. $1/T$ for a given reference temperature T_R, has been establish as a parameter characterising the permeable regions of the segmented polyurethanes. Assuming that Arrhenius behaviour prevails over the broader temperature range, down to the temperature corresponding to the T_g value of a particular polymer, the apparent correlation time

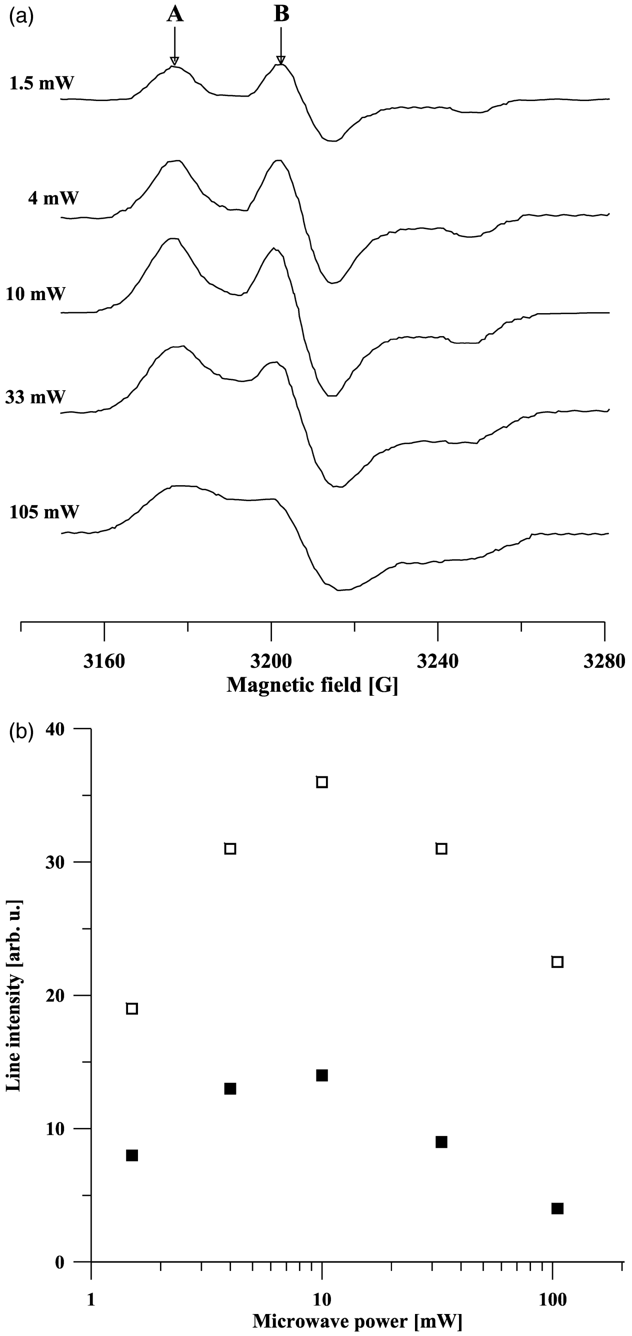


Fig. 5. (a) ESR spectra of spin-probed PU-1 recorded at 107.5 K as a function of microwave power. (b) Line intensity vs. microwave power for the ESR spectra shown in Fig. 5(a) ■—low field line (A), □—central line (B).

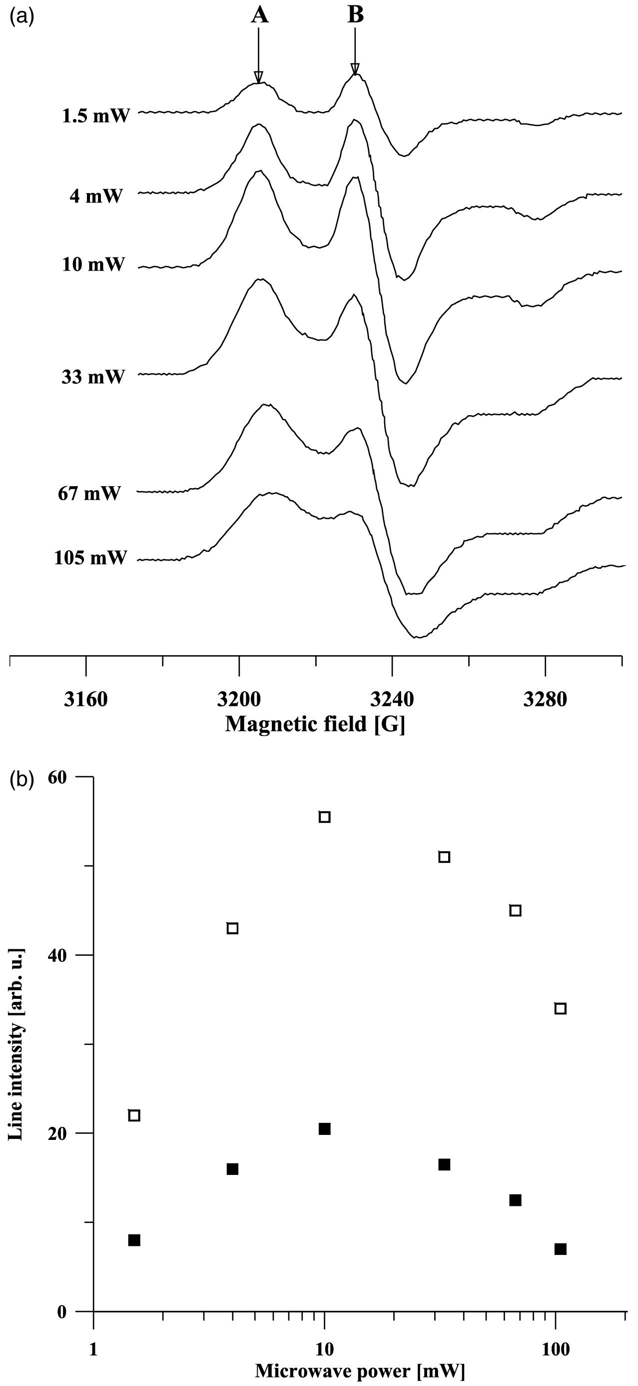


Fig. 6. (a) ESR spectra of spin-probed PU-2 recorded at 111.5 K as a function of microwave power. (b) Line intensity vs. microwave power for the ESR spectra shown in Fig. 6(a) ■—low field line (A), □—central line (B).

can be determined at any arbitrary temperature from this range. In view of this approach, the τ_c values determined at the reference temperature relating to the region of incipient motional narrowing, where slow motional effects have not been dominant yet, should illustrate well the intrinsic differences between the investigated polymers. The values of τ_c at $T_R = 294$ K obtained by this method are equal to 1.03×10^{-9} s and 4.73×10^{-9} s for PU-1 and PU-2, respectively, and indicate that the molecular environment of the spin-probes is significantly different for both polymers. The higher τ_c value for PU-2, reflecting the slower rotating rate of the TEMPO molecules, corresponds with the higher T_g value of the PU-2 soft segments.

From Figs. 7 and 8, activation energies E_a and preexponential factors τ_0 have been obtained. The values of τ_0, 1.95×10^{-13} s and 1.1×10^{-12} s for PU-1 and PU-2,

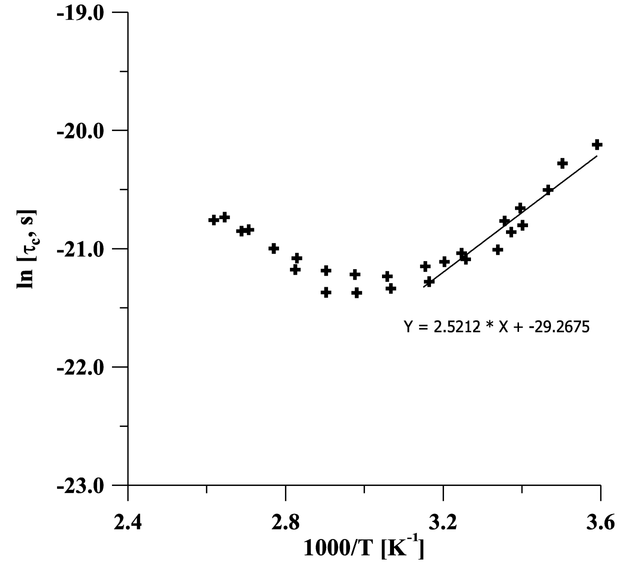


Fig. 7. Variation of the correlation time τ_c with T^{-1} for spin-probed PU-1.

respectively, show that the spin-probe movement is a typical thermally activated process that justifies this type of data treatment. The activation energies E_a determined from the slope of the Arrhenius plots are found to be 20.9 and 20.4 kJ/mol for PU-1 and PU-2, respectively. The similar values obtained for both polymers indicate that the molecular motion of the spin-probe embedded in soft domains of the PUs studied is activated by the same molecular process. The activation energies determined are generally comparable with those obtained for the TEMPO probe in other polymers above their T_g. Therefore, it appears that the method developed can be successfully applied to study the permeable regions of the segmented polyurethanes of various morphology.

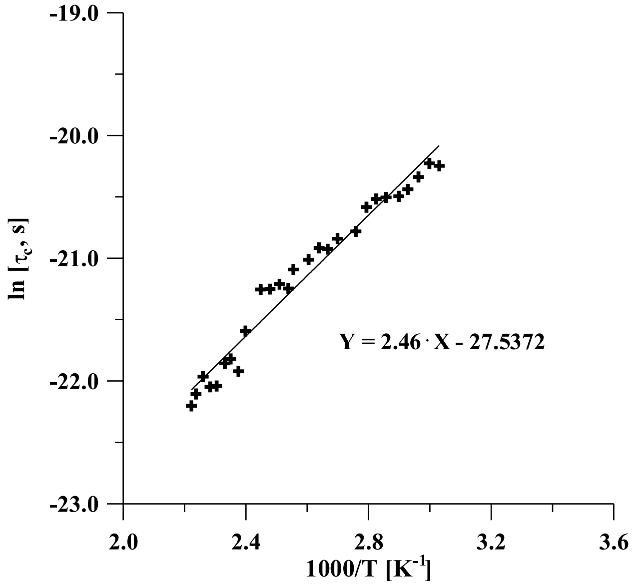


Fig. 8. Variation of the correlation time τ_c with T^{-1} for spin-probed PU-2.

4. Conclusions

The data reported here show that incorporation of the paramagnetic spin-probe into the dense membrane of complex morphology via diffusion is a convenient method for studying the permeable regions of that membrane.

Analysis of the ESR spectra recorded as a function of temperature and microwave power, backed with structural considerations, revealed that TEMPO molecules embedded in the elastomeric soft domains of PUs exhibit anisotropic rotation. The anisotropy of this motion is sensitive to the polymer structure and increases as temperature decreases. It has been demonstrated that PU with longer and more mobile soft segments, as manifested by their lower T_g value, form permeable domains in which TEMPO radicals can tumble isotropically at a lower temperature than that found for PU with shorter soft segments.

A simplified method for quantitative characterisation of the permeable domains by using an apparent correlation time at a reference temperature has been proposed. This method is based on Arrhenius relation of τ_c vs. $1/T$ obtained from ESR spectra representing the fast isotropic motion of the TEMPO probe and on the assumption that Arrhenius behaviour prevails over a broader temperature range, at temperatures generally greater than T_g of a given polymer. The values of the preexponential factors τ_0 calculated from these relations confirm that the spin-probe movement is a typical thermally activated process. The activation energies E_a determined are comparable with those obtained for other polymers.

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