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Motional heterogeneity of segmented polyurethane–polymethacrylate mixtures: an influence of functional groups concentration

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Abstract

The motional heterogeneity in the polymer mixtures of segmented polyether polyurethane (PU) with carboxylic groups and methacrylic copolymer (PM) with tertiary amine groups was studied by the electron spin resonance (ESR)—spin probe and spin label methods. Pure polymer components containing varying amounts of functional groups and their 1:1 mass ratio mixtures have been analysed. The results of motional heterogeneity and polymer interaction were complemented with the glass transition temperatures, structural and morphological characteristics. Spin probed PU/PM mixtures indicate that the probe motion and the phase separation deduced from the temperature-dependent ESR spectra are sensitive to a free volume determined by the polymer–polymer interactions. The interaction between the two components in PU/PM mixture with the highest functional groups concentration disorganizes hard segment domains with spherulitic character at the microscopic level as compared with the ordered hard phase in the corresponding pure PU sample. The influence of PU hard and soft segments on the motional dynamics of PM chains is analysed from the ESR spectra of spin labelled PM chains in the mixtures with unlabelled PU components. The fractional amount of the PM fast motion depends on the temperature and concentration of functional groups.

Keywords: Polyurethane/polymethacrylate mixtures; Functional groups; Heterogeneity

1. Introduction

Polyurethane block copolymers and their mixtures with vinyl polymers are of considerable interest for many years. The domain morphology of segmented polyurethanes and their structure is the origin of some interesting and unique properties of polyurethane based materials [1]. The mixing of segmented polyurethanes with methacrylate based copolymers either as blends or in a form of interpenetrating networks results in property variations [2,3]. The miscibility between the two polymer components is enhanced by noncovalent interactions, namely hydrogen bonding of functional groups incorporated in the polymer backbone [4,5].

The present paper deals with the miscibility of polyether polyurethane (PU) with carboxylic groups and methacrylic copolymer (PM) with tertiary amine functional groups depending on the concentration of functional groups. The electron spin resonance (ESR) of stable nitroxyl radicals is applied to study molecular dynamics and degree of phase separation in the PU and PM mixtures at the molecular level. The major objective of this work is to assert how the molecular dynamics and phase separation are affected by functional groups in a wide temperature range. Nitroxyl free radical is either mixed with the polymer as a reporter molecule (a 'probe') or is covalently linked to the backbone (a 'label'). The probe or label was already quite successfully applied to study interpenetrating networks or polymer blends based on polyurethane [6–8]. The complex ESR spectra of polymer mixtures that evolve in a certain temperature range appear to be the most valuable contribution of the method to differentiate more than one phase. Slow motion of the complex spectra refers to immobilized nitroxyl radical and fast motion to isotropic motion [9,10]. From temperature-dependent spectra several important parameters can be derived, such as temperature at which the complex spectra appear or the phase separation begins and the temperature range of motional heterogeneity. The other parameters obtained from the spectra are the outer maxima separation, $2A_{zz}$, and rotational correlation time, τ_R. Also important characteristic is the ratio of fast and slow component of the spectra. Since the dynamic properties of polymer mixtures depend on the density of molecular

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Table 1
Concentration of functional groups and molecular mass of PU and PM components

Polymer	Concentration of *tert* amine groups (mmol g^{-1})	M_n (g mol^{-1})	Polymer	Concentration of carboxylic groups (mmol g^{-1})	M_n (g mol^{-1})
1PM	0.00	11400	1PU	0.00	11700
2PM	0.15	10000	2PU	0.15	10900
3PM	0.25	10100	3PU	0.25	10100

packing influenced by the structure and interactions the amount of free volume and its distribution can be derived. In order to explore to what extent and which segments of PU chain interact with PM chain, PM chains were spin labelled and mixed with PU. Spin probed PU/PM mixtures and their dynamical behaviour have been compared with the corresponding spin probed pure components. Parallel observations were carried out by DSC, wide-angle X-ray diffraction (WAXD) and optical microscopy.

2. Experimental

2.1. Materials

Polyether polyurethane (PU) with carboxylic functional groups in the hard segments of polymer chain were synthesized from isophoronediisocyanate, polytetramethylene oxide, 1,4-butanediol and 2,2-bis-(hydroxymethyl) propionic acid according to the procedure described previously [11,12]. Methacrylic (PM) components with tertiary amine functional groups were prepared from methyl methacrylate, *N*,*N*-dimethylaminoethyl methacrylate and hydroxylethyl methacrylate. The concentration of functional groups in both polymers varied from 0 to 0.25 mmol g^{-1} (Table 1). The small amount of OH groups in PM copolymer was constant [12]. For convenience the functional group concentrations in each polymer are designated with number 1–3 as shown in Table 1.

Preparation of spin labelled and spin probed polymers. Nitroxyl free radical 2,2,6,6-tetramethyl-4-aminopiperidine-1-oxyl was covalently attached to the PM by the amide–ester interchange reaction [13]. PM was labelled by way of a 2 mass% solution in benzyl alcohol containing sodium benzoxide (10% by mass) and nitroxyl radical (0.1% by mass). The amide–ester interchange was allowed to proceed for 24 h at 303 K. After removal of solvent isopropyl alcohol was added, and labelled PM was repeatedly dispersed and filtered in order to remove remaining unattached nitroxyl radical. The samples were annealed under vacuum at 363 K for 3 days. Labelled PM were mixed with PU containing the same concentration of functional groups in 1:1 mass ratio in toluene at 303 K. After the solvent had slowly evaporated off, mixtures were annealed in a vacuum at 313 K for 3 days.

Table 2
Spectral parameters (the accuracy of T_{5mT} determination is ±3 K) for PU, PM and PU/PM mixtures doped with spin probe

Samples	T_{5mT}(f) (K)	T_{5mT}(s) (K)	$\tau_R \times 10^{10}$ (s)
1PU	303	363	6.1
2PU	313	378	7.3
3PU	323	378	8.2
1PM		401	
2PM		404	
3PM		393	
1PU/1PM	293	374	5.7
2PU/2PM	303	386	6.8
3PU/3PM	308	395	7.6

The pure polymers of PM and PU and their corresponding mixtures were doped with 2,2,6,6-tetramethyl-4-aminopiperidine-1-oxyl in toluene. The solvent was slowly evaporated at 308 K and the samples were further annealed under vacuum a few degrees above glass transition temperature for 3 days.

The following nomenclature of spin labelled or spin probed samples will be used. For example $2PM_L$ indicates spin labelled 2PM with 0.15 mmol g^{-1} functional group, $2PU/2PM_L$ indicates a mixture with labelled PM (Table 4), while 2PU/2PM is a mixture containing spin probe (Table 2).

2.2. Methods

2.2.1. Electron spin resonance

The ESR spectra were recorded on a Varian E-109 *x*-band spectrometer operating at 100 kHz modulation. The attenuation power (2 mW) and modulation amplitude (0.1 mT) were adjusted well below saturation and distortion of the spectra. A variable temperature unit controlled the temperature. The complex ESR spectra above the glass transition were analysed as a superposition of two motionally different spectral components. The fraction of each component in the ESR bimodal spectra was calculated by using a slow PM labelled spectrum as a standard. The fraction of each component is determined with a deviation of less than 3%. The ESR spectra were measured at least 3 days after the annealing was completed. Rotational correlation times, τ_R, are calculated according to Kivelson [14].

2.2.2. Optical microscopy

A Leica light microscope with digital camera was used for observations of thin specimen films.

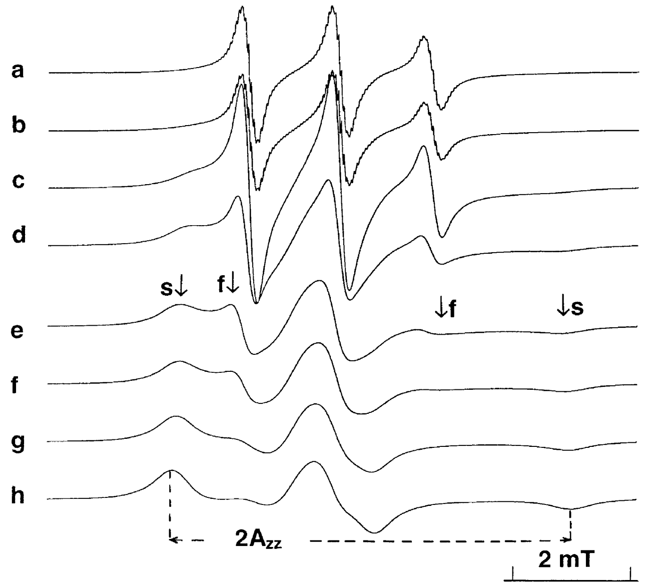

Fig. 1. ESR spectra of spin probed 1PU without carboxylic groups at (a) 378 K, (b) 363 K, (c) 353 K, (d) 333 K, (e) 313 K, (f) 303 K, (g) 283 K and (h) 253 K. At 313 K the low field slow and fast components are indicated by s and f, respectively.

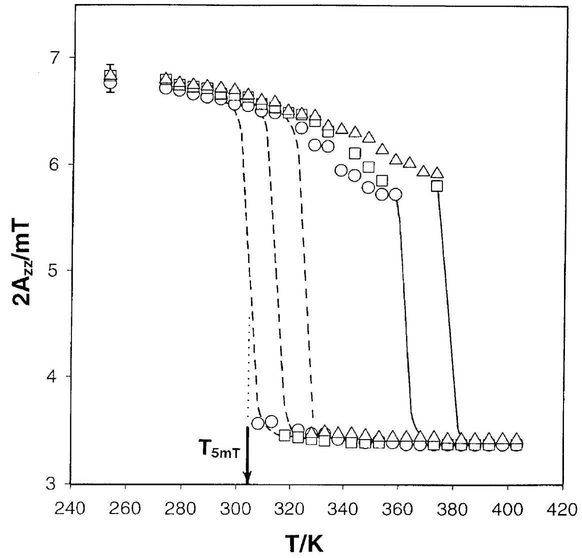

Fig. 2. The temperature dependence of the outer maxima separation, $2A_{zz}$, of 1PU(○), 2PU (□) and 3PU (△). The dashed line denotes the change of the fast component, the solid line represents the slow component.

2.2.3. *Wide-angle X-ray diffraction*

The wide-angle X-ray diffractograms of the rotated samples were taken by a Philips diffractometer with monochromatized Cu K_α radiation in the diffraction range $2\theta =$ 4–50°. Degree of crystallinity, $w_{c,x}$, is evaluated according to Kilian and Jenckel [15].

3. Results and discussion

3.1. *Dynamic heterogeneity of spin probed PU/PM mixture*

In order to explore the extent of miscibility in a two component polymer mixture of polyurethane and polymethacrylate copolymer the ESR spectra of spin probed pure components and their corresponding mixtures were measured in a wide temperature range. Some typical ESR spectra of spin probed polyurethane without functional groups, 1PU, are shown in Fig. 1. The occurrence of two spectral components differing in spin probe mobility above the characteristic temperature is observed in all three PU samples. This characteristic temperature, however, depends on the concentration of functional group content in the PU backbone. Two spectral components, fast and slow, are the consequence of two-phase morphology of segmented polyurethanes [16,17]. Since the PU samples after 3 days of annealing appear to be amorphous (according to WAXD measurements) the fast component corresponds to spin probes incorporated in the soft domains, while the slow component represents spin probes in the hard domains. The lowest temperature at which a narrow component, corresponding to fast motion, appears is marked as $T_{5\mathrm{mT}}$(f) (Table 2). $T_{5\mathrm{mT}}$ is the temperature at which the outer maxima separation, $2A_{zz}$, becomes 5 mT owing to the onset of rapid motion of the polymer segments (Fig. 2). The motional averaging of the slow component corresponds to phase transition of the PU hard segments, $T_{5\mathrm{mT}}$(s). Between $T_{5\mathrm{mT}}$(f) and $T_{5\mathrm{mT}}$(s) temperatures ESR spectra appear to be a superposition of the two spectra. The fraction of a fast or slow spin probe population sensing motionally different environments changes with temperature depending on the functional group concentration. With an increase of temperature the intensity of the fast component is increasing. This is expected due to the gradual increase of local free volume, and consequently, the number of spin probes attaining fast motion. The influence of functional group content can be seen from the $T_{5\mathrm{mT}}$(f) and $T_{5\mathrm{mT}}$(s) temperatures, respectively. The temperature shift of both $T_{5\mathrm{mT}}$(f) and $T_{5\mathrm{mT}}$(s) to higher temperatures is related to an increase of functional group content (Fig. 2). This temperature shift is most likely a consequence of the external and possible internal interactions [18] that may restrict segmental mobility of both soft and hard segments. These interactions could also reduce available free volume for the spin probe molecule and thus change the rates of motion of a probe. As a consequence restricted spin probe motion would require higher temperature to reach dynamical averaging. According to polarizing micrographs of freshly annealed polyurethanes, 1PU sample reveals homogeneity at macroscopical level while 2PU and 3PU specimens with functional groups show phase-separated morphology. The net-like interconnection and clustering of hard segments would also contribute to the motional restriction of polymer segments. Specific interactions between the probe molecules due to the polarity of spin probe molecule having $-NH_2$ group and polyurethane chains, should be considered [19]. Motional

Table 3
Glass transition temperatures of PU, PM and PU/PM mixtures determined by DSC

Sample	T_g of PU soft segment (K)	T_g of PM component (K)	T_g of soft phase in PU/PM mixture (K)	T_g of hard phase in PU/PM mixture (K)
1PU	198 ± 2			
2PU	197 ± 2			
3PU	197 ± 2			
1PM		367 ± 2		
2PM		67 ± 2		
3PM		368 ± 2		
1PU/1PM			250 ± 5	335 ± 2
2PU/2PM			262 ± 5	334 ± 2
3PU/3PM			268 ± 5	334 ± 2

restriction of a probe molecule due to the functional groups concentration is indicated also by the rotational correlation times, τ_R, above 378 K (Table 2). Since the τ_R is longer as the concentration of –COOH group is increasing polymer–polymer interactions and the corresponding available free volume could be considered to be predominant factor in modifying the spin probe motion.

Spin probed pure PM components and the corresponding T_{5mT} temperatures are given in Table 2. In the case of PM copolymer an introduction of tertiary amino groups into the backbone chain increases the spin probe mobility. According to the T_{5mT} shifts to lower temperatures greater probe mobility could be a consequence of less dense chain packing or larger available free volume. The spin probe is sensing local free volume in its close vicinity and a probe motion will depend on the temperature. Contrary to ESR T_{5mT} results, T_g determined by DSC measurements (Table 3) is not affected by the functional group concentration in PM chain. Since the spin probe is sensitive to segmental motion on a length scale shorter than those responsible for the glass transition temperature, differences in local dynamic can be clearly observed.

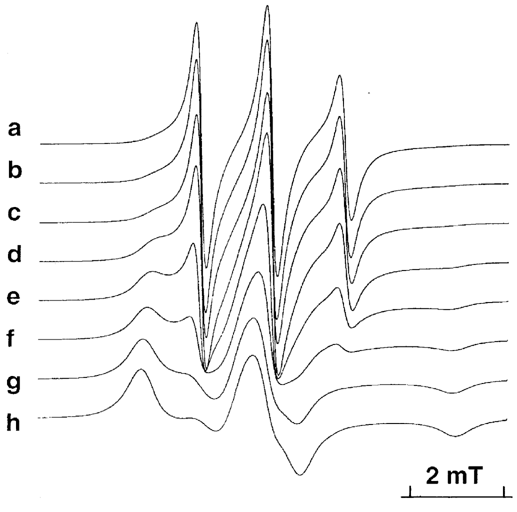

Fig. 3. ESR spectra of spin probed 1PU/1PM mixture without functional groups at (a) 378 K, (b) 363 K, (c) 353 K, (d) 333 K, (e) 313 K, (f) 293 K, (g) 273 K and (h) 245 K.

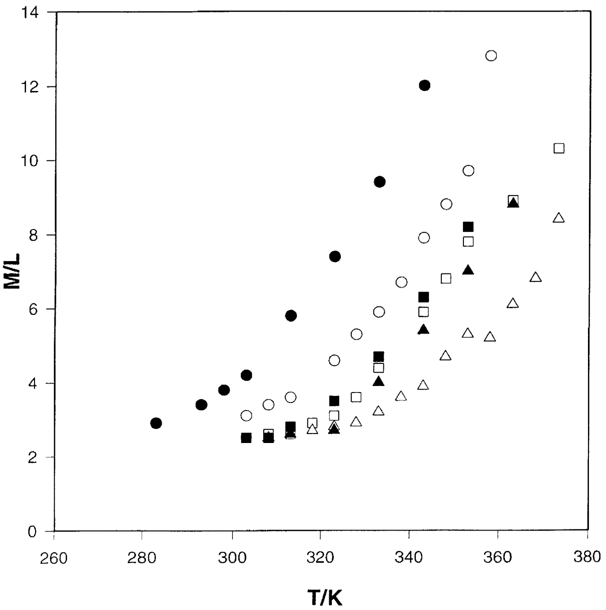

Fig. 4. The temperature dependence of the amplitude ratio *M*/*L* of the bimodal ESR spectra of spin probed pure PU components: 1PU (○), 2PU (□), 3PU (△) and PU/PM mixtures: 1PU/1PM (●), 2PU/2PM (■) and 3PU/3PM (▲).

ESR spectra of spin probed polymer mixture 1PU/1PM are shown in Fig. 3. The phase separation observed in all three mixtures is expected since the pure PU component exists in two dynamically different phases. However, fast motional component of the spectra becomes prominent at lower temperatures as compared with the pure PU soft segments. The same behaviour is observed for the slow component in the mixture. T_{5mT}(s) of the mixtures appears to be between the T_{5mT} of PU hard component and T_{5mT} of the PM component. The difference in the T_{5mT} temperatures or the temperature at which dynamical phase separation is observed, between the pure components and their mixtures suggests an interaction between the two polymer components [6]. The temperature-dependent ESR line shapes and the corresponding T_{5mT} temperatures of PU/PM mixtures indicate a plasticizing effect of PU soft segments on the PM chains and the question arises how to deduce the extent of mixing. In the case of doped probe molecule in the mixtures a probe being free may be located in various regions of the polymer matrix; namely soft phase, hard phase and interphase. Since in this case it is difficult to simulate the multicomponent spectra and calculate the contribution of the each phase the amplitude ratio of the central line (*M*) and the low field slow motion (*L*) component of the bimodal spectra has been used [20]. The temperature dependence of *M*/*L* represents a generation of free volume with temperature. Fig. 4 shows a fast motion increase in the pure PU components and PU/PM mixtures. It can be seen that the mobile fraction is higher in polymer

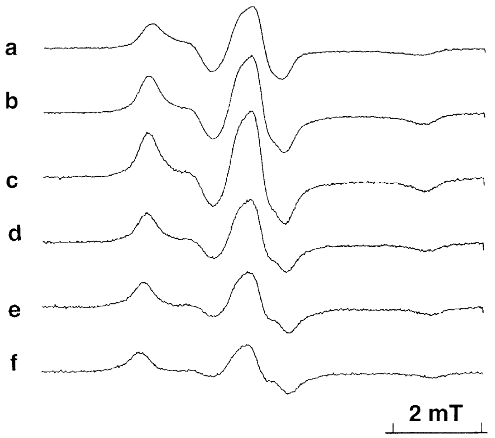

Fig. 5. ESR spectra of spin labelled 3PM at (a) 393 K, (b) 373 K, (c) 363 K, (d) 343 K, (e) 303 K and (f) 258 K (concentration of $-NR_2$ groups is 0.25 mmol g^{-1}).

mixtures as compared with the corresponding pure PU components in the region of dynamical heterogeneity or phase-separated system. Cameron et al. [21,22] have shown that chain ends in PMMA/PEHMA blends of immiscible polymers with end labelled PMMA chains are located in the interphase where they experience the combined effects of accumulated free volume and the presence of the second polymer. These observations of the interphase of two immiscible polymers are in accordance with a theoretical prediction of Helfand et al. [23,24]. On the bases of increased fast motion in PU/PM mixtures and the results for PMMA/PEHMA blends, which confirm an increase of free volume in the interphase, it could be concluded that the PU/PM interphase is diffuse and relatively thick. Since the free probe in spin probe experiment is expected to seek regions in the polymer mixture with the greatest free volume [25], a rather diffuse interface may be one of the reasons for an increase of free volume in PU/PM mixtures. On the other hand partly plasticized PM chains would also contribute to an increase of the fast component corresponding to the soft segment rich phase. Furthermore, in the phase-separated system, where the polymer chains attain different mobility, restricted PM chains would create vacancies during the separation [26], and more mobile PU soft segments trapped in these vacancies may have higher mobility. A lower $T_{5\mathrm{mT}}$(f) of PU soft segments in the mixture could also be a consequence of higher mobility of some chains trapped in the vacancies created by the more rigid PM chains. The loss of order in PU/PM mixtures with higher functional groups concentration after 3 days of annealing, as seen from contrasted optical micrographs, is in agreement with the increased fast motional component or available free volume.

3.2. Dynamic heterogeneity of PU and spin labelled PM mixtures

In order to evaluate the influence of PU phases on the molecular dynamics of PM component the PM chains were covalently labelled prior to mixing. The ESR spectra of labelled PM having the highest functional group content, $3PM_L$, are shown in Fig. 5. In the range from 258 to 393 K the spectra are motionally restricted differing only in a small narrowing of the outer peak splitting. The $2A_{zz}$ for all three PM samples in the measured temperature range are within the error of linewidth determination, indicating that the dynamics of PM chains is not markedly influenced by functional group concentration. $T_{5\mathrm{mT}}$ for labelled PM is not reached in the measured temperature range. If the labelled PM component is mixed with the PU component the ESR spectra of PM begin to differ at given temperatures. Two spectral components, fast and slow, appear, indicating that the PM segments partition in two environments with different mobilities. Similar effects are found in the blends of labelled PVC and segmented PU [6]. The occurrence of two spectral components above the characteristic temperature, $T_{5\mathrm{mT}}$(f), is observed for all mixtures (Fig. 6). However, the characteristic temperature is shifted to higher temperatures with an increase of functional group concentration (Fig. 6). The existence of two components in the ESR spectra of labelled PM in the mixture, irrespective of the functional group content, clearly shows that a part of the PM segments are plasticized by the PU soft segments. However, the intensity of the fast component in bimodal ESR spectra at a given temperature depends on the functional group content. Table 4 displays the percentage of the PM fast component in the mixture deduced from the simulation of the spectra. The fast component decreases with an increase of the functional group concentration. Though our results confirm that PU soft segments exert a plasticizing effect on the part of PM chains the question arises whether the

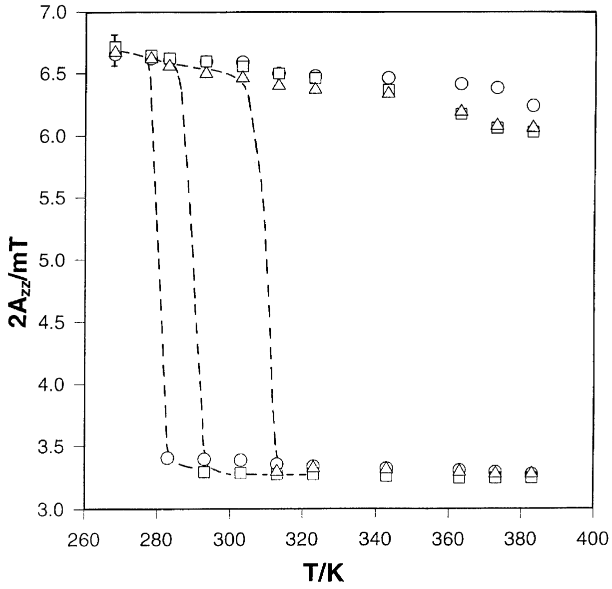

Fig. 6. The temperature dependence of the outer maxima separation, $2A_{zz}$, of spin labelled PM component in the mixtures: $1PU/1PM_L$ (○), 2PU/2PM (□) and $3PU/3PM_L$ (△).

Table 4
Fractions of the ESR fast component of polymer mixtures (%)

Sample	343 (K)	363 (K)	373 (K)	383 (K)
1PU/1PM$_L$	19	21	24	47
2PU/2PM$_L$	15	18	19	23
3PU/3PM$_L$	9	15	17	21

remaining PM slow component represents a separated pure PM phase or/and in which extent PU hard segments interact with the PM segments.

Considering specific interaction between the carboxyl groups bound to the PU hard segments and tertiary amino groups on the PM chains an increased functional group content will contribute to the stronger interaction between the two components. These kind of interaction between the two components contributes to the restriction of both PM and PU segmental motion. As a consequence the appearance of the ESR fast components shifts to higher temperature in 2PU/2PM$_L$ and 3PU/3PM$_L$, respectively. T_gs of the soft component in the mixtures are also shifted to higher temperatures, as expected (Table 3). Previous results of Anžlovar et al. [2] have shown that PU hard segments and PM copolymer were miscible to some extent and that the mass fraction of PU hard segments in the PM rich phase increases by augmenting the concentration of functional group. Furthermore, Santra et al. have observed in some similar systems that the T_g of the soft segment shifts towards a higher temperature, and T_g of the hard segment towards a lower temperature [3]. Our DSC results (Table 3) are in accord with these findings. The T_gs of soft segments in PU/PM mixtures appear at higher temperatures as compared with the pure PU component. The second T_g is lower than the corresponding pure PM component. However, both glass transitions are rather broad indicating less extensive interpenetration of the two components [27]. Yet the two intermediate T_gs confirm that some interpenetration or mixing had occurred.

According to ESR results the mixtures are motionally heterogeneous up to 383 K. The size and shape of a nitroxyl molecule, labelling or doping determine the absolute values of the ESR transition temperatures. Though the difference between T_g and T_{5mT}(f) has been discussed in many papers and a correlation was found [9,10] these correlations are not of primary interest. Our goal is to follow motional heterogeneity and molecular dynamics of the two components. It can be seen in Fig. 6 that the $2A_{zz}$ values of the outer maxima separation of all three mixtures are similar within the error of measurements up to 340 K. Above this temperature at which the PU hard segments begin to move and PM labelled segments are still rigid, $2A_{zz}$ values begin to differ. PM chains in 2PU/2PM$_L$ and 3PU/3PM$_L$ mixtures are less restricted than the PM chains in 1PU/1PM$_L$. PU hard segments with higher concentration of functional groups are in closer contact with PM chains and it could be expected that a greater number of PM segments is incorporated in the PU hard phase that is already mobile. The characteristic temperature at which the slow PM component becomes a narrow one is shifted to higher temperature. It was not possible experimentally to reach this temperature due to the degradation of nitroxyl radical.

3.3. Structural and morphological observations

To examine spatial microhomogeneity or heterogeneity and to extend the framework of ESR investigation, pure polymer components and their mixtures were investigated by optical microscopy and WAXD. Both methods allow to consider three-dimensional structure of the matrix and to connect the microphase images with the dynamical heterogeneity confined to the motion of several segments.

Polarizing micrographs of polyurethanes and PU/PM blends after 3 days of an annealing do not reveal a spherulitic or any crystal morphology. Contrasted optical micrographs show the matrix homogeneity of 1PU sample at microscopical level and phase-separated morphology of 2PU and 3PU samples with functional groups (Fig. 7). It is well known that the differences in composition of polyurethane blocks lead to the segmental incompatibility which causes microphase separation of hard from soft blocks forming thus hard domains in a soft matrix; strong interactions, like hydrogen bonding, stabilize hard segments, enhance phase separation and can lead to internal ordering within hard segment domains [16,17,28,29]. The higher extent of interactions between hard segments due to higher concentration of functional groups in present case (3PU in comparison to 2PU and 1PU), capable to decrease segmental compatibility, lead to higher phase separation and to longer hard segment macrodomains [28,30]. The micrograph of 3PU sample shown in Fig. 8 reveals also some degree of the disarrangement and clustering of hard segment macrodomains with relative wide size distribution. At lower magnification the hard PU domains, interconnected in net-like arrangement with great-elongated meshes, are observed. Optical micrographs of freshly prepared PU/PM mixtures under parallel and crossed polars show specimens homogeneity at microscopic level without any visible form. Contrasted optical micrographs of PU/PM mixtures irrespective of the functional groups concentration reveal homogeneity at microscopic level even after 2 months at higher magnification (Fig. 8). It has been recently observed that the addition of an active component to polyurethane, like crosslinking agent diethanol amine, may reduce the observed level of hard domain size and interconnectivity [31]. In this work the additional effect of phase separation caused by introducing of functional groups in polyurethane macromolecule, is annulled and hard segment macrodomains with spherulitic character are disorganized by the interaction of PM chains and PU hard segments.

The interaction on the segmental level has been already discussed. The X-ray diffractograms, as well as ESR measurements and polarizing micrographs, of PU samples

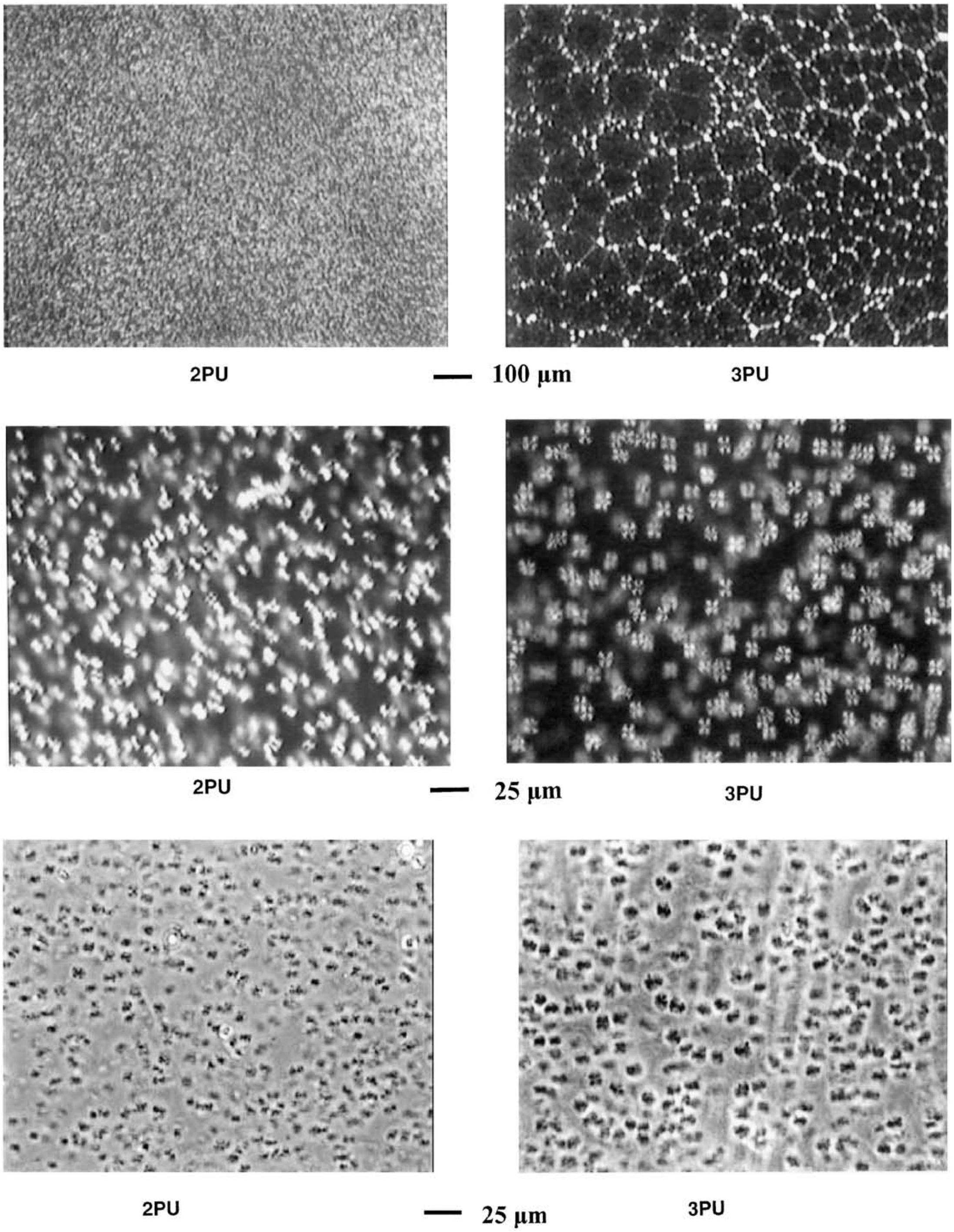

Fig. 7. Polarizing micrographs with different magnification and contrasted optical micrographs (bottom) of annealed 2PU and 3PU after 2 months.

and their corresponding PU/PM mixtures after 3 days of annealing confirm their amorphous character (Fig. 9). Even hard domains in 2PU and 3PU are amorphous. Diffractograms of PU samples are similar with an interplanar spacing value $d_A = 0.455$ nm at the top of most intensive diffuse maximum. For a comparison a diffractogram of the 3PU/3PM mixture is given in the same figure. The addition of PM to PU component broads the main diffuse amorphous maximum and shifts its top to the smaller diffraction angle ($d_A = 0.474$ nm).

Polarizing micrographs of 2PU and 3PU specimens kept under cover glasses 2 months at room temperature exhibit spherulitic morphology (Fig. 7). Short order amorphous hard domains in 2PU and 3PU samples reorganize into microcrystalline state within spherulites because the annealing time of sufficiently long hard domains was sufficiently

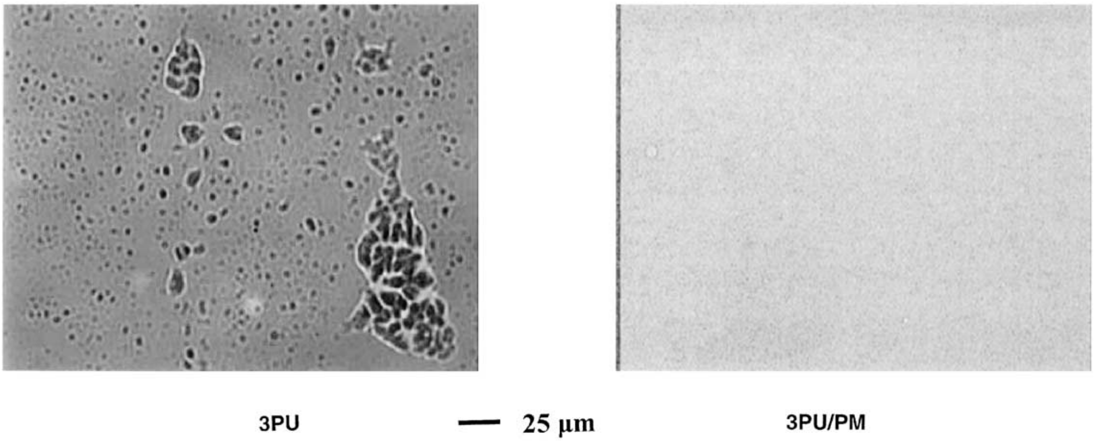

Fig. 8. Optical micrographs of 3PU sample and 3PU/3PM mixture annealed 3 days.

long [29,32,33]. The micrograph of 2PU sample reveals ellipsoidal spherulites (~5 μm thick (wide) and 10–15 μm long) with unclear boundaries. On the micrograph of 3PU sample greater and more regular spherulites with clear boundaries (~15 μm in diameter) can be seen together with their planar net-like arrangement; the spherulites are connected like pearls in necklaces. Because the examined PU films were very thin, the spherulites may be plate-like disks.

Contrasted optical micrographs of these samples exhibit more regular arrangement of spherulitic hard domains and more uniform in size in comparison to polyurethanes measured immediately, confirming also greater hard domains in 3PU than in 2PU sample (Fig. 7). The increase of functional groups content in PU samples (1PU $<$ 2 PU $<$ 3PU) causes the increase of phase separation and aggregation of (lamellar) hard microdomains into thickened hard segment macrodomains [29,31]. After 2 months of annealing the superstructural ordering seems to be completed. Their diffractograms exhibit two crystal reflections ($d_1 = 0.426$ and 0.352 nm) superimposed on amorphous maximum confirming thus semicrystalline nature of the segmented polyurethanes. The degree of crystallinity depends on the functional groups content ($w_{c,x} = 1\%$ for 1PU, $w_{c,x} = 6\%$ for 2PU, and $w_{c,x} = 14\%$ for 3PU). The hydrogen bond interaction contributes to the higher ordering of polymer segments in hard microdomains and their aggregation increasing thus the degree of crystallinity [29].

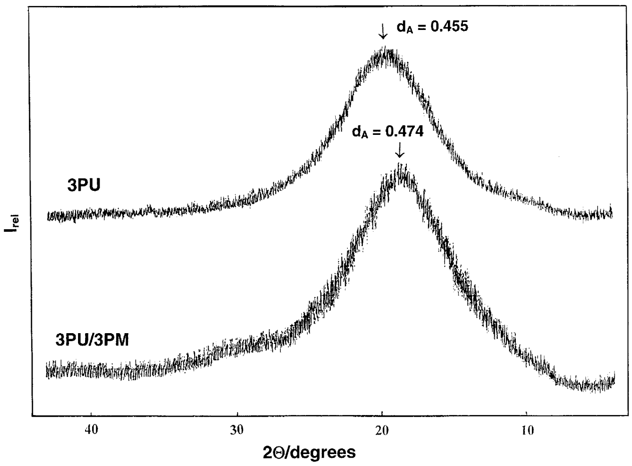

Fig. 9. Diffractograms of 3PU sample and 3PU/3PM mixture annealed 3 days.

The ESR spectra of the PU samples and their corresponding mixtures after the prolonged crystallization could not be measured due to the decay of ESR signal. Since the optical micrographs of PU/PM mixtures after 2 months show a loss of order of hard microdomains resembling the micrographs of freshly prepared mixtures, the interaction of PM chains with PU hard segments disturbs regular arrangements of polymer mixtures. However, the ESR measurements confirm motional heterogeneity of PU/PM mixtures due to the presence of motionally restricted PU hard segments and PM chains in a given temperature interval.

4. Conclusions

Polymer mixtures of segmented polyether polyurethane (PU) with carboxylic groups and methacrylic copolymer (PM) with tertiary amine functional groups in 1:1 mass ratio were examined. The major point of this study is the observation of motional heterogeneity and the extent of mixing in the PU/PM mixtures depending on the functional groups concentration. The ESR spectra of spin probed and spin labelled pure polymer components and their mixtures are sensitive to the intermolecular interactions imposed by functional group concentration and provide information about motional dynamics on a segmental level in a wide temperature region.

Two ESR components were detected in pure PU components and their corresponding mixtures, respectively. The lowest temperature where an isotropic component in PU samples is observed is shifted to higher temperature with an increase of functional groups content. This local heterogeneity is not revealed in the glass transition temperature, T_g, measurements performed by the DSC method. Obviously the heterogeneity observed by spin probe/label method responds to a domain size on a length scale smaller than ~50 nm. X-ray diffractograms have also confirmed that the PU samples are amorphous. The difference in the T_{5mT} values (or the temperatures at which two-phase spectra are observed) between the pure polymer components and their mixtures suggests an interaction of the two polymers.

Much faster generation of free volume or an increase of ESR fast component with temperature above T_{5mT}(f) in PU/PM mixtures as compared with the pure PU components indicates that the PM chains are partly plasticized by the PU polymer and contribute to the soft segment rich phase in motionally separated system. However, the generation of free volume is slower in the mixtures with higher functional groups content or increased polymer–polymer interactions. Specific interactions between the polymer components, namely that in the ordered hard phase, are confirmed by the loss of hard domains morphology in 3PU/3PM mixture as seen from the contrasted optical micrographs and loss of long-range order proved by WAXD and the change of T_g.

The effect of PU phases on molecular motion of the PM chains was deduced from spin labelled PM component in the mixtures. Two spectral components, fast and slow, confirm that the PM chains partition between the two PU phases. However, the appearance of the motional heterogeneity is shifted to higher temperatures with an increase of functional groups concentration. The percentage of the mobile PM component is lowered by the specific interactions between the carboxyl groups bound to the PU hard segments and tertiary amine groups on the PM chains. Though the T_g of hard segments of all three mixtures is 334 K, the ESR measurements of labelled PM reveal, on a segmental level, the existence of immobile PM segments in the measured temperature interval up to 383 K.

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