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DSC, dielectric and dynamic mechanical behavior of two- and three-component ordered polyurethanes

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Abstract

Liquid crystalline (LC) polyurethanes were made from two diisocyanates (flexible HMDI and stiff TDI) (DIs), mesogenic diol (D) and a polybutadiene-diol (B) with stoichiometric ratios of reactive hydroxy (OH) and isocyanate (NCO) groups $((NCO)_{DI}/((OH)_D+(OH)_B)=1/1)$. Two- (B/DIs, D/DIs) and three-component ((D+B)/DIs, D/B=1/1 by weight) polymers were prepared and their dielectric, dynamic mechanical and DSC behavior was investigated. For neat B, the glass transition temperature T_{gB} (~ -46 °C) was detected. Two-component B/HMDI and B/TDI polymers have exhibited a homogeneous structure with the glass transition temperatures $T_{gU}\sim -9$ and 2 °C. On the other hand, for D/DI polymers on cooling from the melt and subsequent heating the glass transitions at $T_{gU}\sim 41$ °C (D/HMDI) and 58 °C (D/TDI) together with nematic and smectic mesophases were found. In three-component systems, additional glass transitions at $T_{gB}\sim -41$ °C (B/D/HMDI) and -31 °C (B/D/TDI) were observed. This means that the polymers exhibit a distinct two-phase structure with soft polybutadiene (B) and hard polyurethane (D/DI) phases. In hard polyurethane phase, the glass transitions at T_{gU} and LC mesophases similar to those found in two-component D/DI polyurethanes were detected. Dielectric and dynamic mechanical results correlate well with DSC measurements.

Keywords: Liquid-crystalline polyurethanes; Dielectric and mechanical spectroscopy

1. Introduction

Linear polyurethanes (PUs) of various chemical compositions and morphologies with amorphous, semicrystalline or liquid-crystalline (LC) structures have been studied [1]. The driving forces for molecular order in PUs are the shape, length, flexibility and miscibility of initial reactants — diols and diisocyanates. Segmented PUs are formed from thermodynamically incompatible hard and soft domains; while the soft domains usually consist of long diols, the hard segments are formed by short diols and stiff diisocyanates. In order to obtain anisotropic mesophases in the hard domains, mesogenic units are introduced into chain extenders as it is known that introduction of a stiff group into a diol or diisocyanate together with a short flexible spacer generally leads to thermotropic LCPUs [2–4]. Usually, mesogenic diols have been used as chain extenders in linear block thermotropic LCPUs elastomers [3,5] together with long flexible diols (e.g. poly(oxybutane-1,4diols). In these systems, LC properties of LCPUs were dependent on both the length of mesogenic unit in a short diol as well as on the length of a long diol.

Dielectric and dynamic mechanical spectroscopy were often used for investigation of LC polymers [6–9]. It was found that dependences of mechanical and dielectric functions on frequency and temperature are sensitive to the ordered state due to more or less aligned macromolecules. The transitions detected by dielectric and mechanical spectroscopy were also observed by DSC, X-ray scattering and polarizing microscopy.

In this work, we have studied the effect of structural transitions in two- and three-component LCPUs, based on two commercial diisocyanates, a synthesized mesogenic diol and polybutadiene diol, on the DSC and dielectric and dynamic mechanical behavior. As was shown previously [4]

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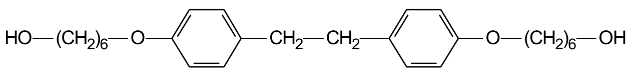
by DSC, X-ray scattering and polarizing microscopy, the two-component LCPUs exhibit mesophase formation on cooling from the melt and subsequent heating.

2. Experimental

2.1. Materials and preparation of samples

Synthesis of mesogenic diol, 6,6′[ethylenebis(4,1-phenyleneoxy)]hexanol (D) of the structure



was described previously [4] ($M_n = 416$). Two-component LCPUs were prepared from D and two diisocyanates (DI)—4,4′-methylenedicyclohexyl diisocyanate (HMDI) and 4(2)-methyl-1,3-phenylene diisocyanate (TDI) at stoichiometric mole ratios of hydroxy (OH) and isocyanate (NCO) groups ($[\mathrm{OH}]_D/[\mathrm{NCO}]_{DI} = 1/1$). Three-component LCPUs with polybutadiene diol (B, $M_n = 3300$), with the weight ratio B/D = 1/1 and stoichiometric ratio of the reactive groups, ($([\mathrm{OH}]_D + [\mathrm{OH}]_B)/[\mathrm{NCO}]_{DI} = 1/1$), were also synthesized. Mesogenic diol and all polyurethanes were prepared in powder form.

2.2. Methods of measurement

Thermal properties were measured using a Perkin–Elmer DSC-2 calorimeter. In order to avoid any thermal prehistory, samples were first heated to an isotropic melt, and data were collected on cooling and subsequent heating scans at the rate 10 K/min.

Dynamic mechanical measurements were performed on a Bohlin CVOR instrument in the parallel-plate mode. The complex shear modulus G^* ($G^* = G' + iG''$, where G' and G'' are storage and loss modulus, respectively) and the loss tangent, $\mathrm{tg}\delta = G''/G'$, were determined at a constant frequency $f = 1$ Hz. The cooling and subsequent heating scans were measured from isotropic (liquid) state ($T \sim 160$ °C) down to the glassy state ($T \sim -80$ °C); the rates of cooling and heating were 2 K/min.

The dielectric measurements covered the frequency range from $f = 5$ to 10^7 Hz using a Hewlett–Packard impedance analyzer (HP 4192A). Measurements of the complex permitivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ (ε' is the storage and ε'' is the loss component) were carried out at constant temperatures on cooling from 180 °C (isotropic liquid state) to −80 °C and subsequent heating. The powder was placed on a rust free circular electrode 11 mm in diameter and heated above the melting point. After the polymer was liquid, the upper electrode of the same diameter one was applied to the sample. The fixed distance between electrodes was kept with two quartz fibers 0.05 mm in diameter placed between the electrodes.

The frequency dependences of complex permitivity ε^* can be, particularly in its imaginary part ε'', divided into relaxation (ε_d^*) and conductivity (ε_c^*) contributions

$$\varepsilon_d^* = \varepsilon_d^* + \varepsilon_c^* \tag{1}$$

The relaxation contribution ε_d^* could be described by non-symmetrical Havriliak–Negami empirical formula [10]

$$\varepsilon_d^* = \varepsilon_\infty + \Delta\varepsilon/[1 + i(f/f_r)^\alpha]^{-\beta} \tag{2}$$

with five, generally temperature-dependent parameters: high-frequency (unrelaxed) value of the real part of permitivity ε_∞, the relaxation strength $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$ (ε_0 being the relaxed low-frequency value of permitivity), frequency f_r corresponding to the most probably relaxation time τ_r ($2\pi f_r \tau_r = 1$) and two shape parameters α and β. The parameter f_r is related to the peak frequency f_m at which the loss component ε'' attains its maximum value according to the equation

$$\left(\frac{f_m}{f_r}\right)^\alpha = \frac{\sin\left(\frac{\alpha\pi}{2(\beta+1)}\right)}{\sin\left(\frac{\alpha\beta\pi}{2(\beta+1)}\right)} \tag{3}$$

In the case of symmetrical Cole–Cole distribution ($\beta = 1$), the frequencies f_r and f_m are identical [11]. A computer program based on the Marquardt procedure [12] was developed for determination of all parameters from ε' and ε'' frequency dependences separately.

The temperature dependence of frequency f_m could be described either by the Arrhenius formula

$$f_m = A\exp(\Delta U/kT) \tag{4}$$

where ΔU is an activation energy and A is pre-exponential factor, or by the WLF equation [13] in the form

$$\log\left(\frac{f_m}{f_s}\right) = \frac{8.86(T - T_s)}{101.6 + T - T_s} \tag{5}$$

where f_s is a value of frequency maximum of dielectric losses at reference temperature T_s($T_s \sim T_g + 50$ °C, where T_g is the glass transition temperature).

The conductivity part of complex dielectric permitivity ε_c^* is manifested most notably on dielectric losses at low frequencies and can be described by equation (6)

$$\varepsilon_c^* = \left(i\frac{f}{f_0}\right)^\eta \tag{6}$$

f_0 is an adjustable parameter and the exponent η would have the value −1 in the ideal case of pure time-independent DC conductivity.

3. Results and discussion

3.1. Thermal and dielectric behavior of diols

DSC thermograms of mesogenic diol D and two- and three-component polyurethanes from D are shown in Fig. 1;

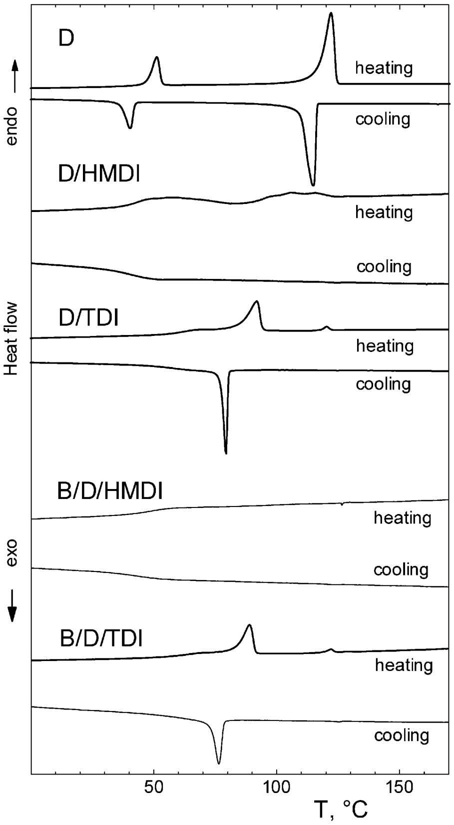


Fig. 1. DSC traces of diol D and two- and three-component polymers formed from D (heating/cooling rate 10 K/min).

corresponding melting (T_{mi}) and glass (T_{gi}) transition temperatures determined from thermograms are summarized in Table 1. For the mesogenic diol, two melting transitions are detected; as expected, the transition temperatures on heating are about 10 °C higher than those on cooling. Wide-angle X-ray and polarizing microscopy measurements proved [4] that the transition at T_{m1} corresponds to a transition from one crystal structure to different one and the transition at T_{m2}, located at higher temperature, is associated with crystal-isotropic state melting. Simple amorphous behavior with the only glass transition at $T_{gB} \sim -46$ °C was found for polybutadiene diol (B); the changes in the specific heat $\Delta c_{pB} \sim 0.40$ J/gK have the values typical of amorphous polymers [13].

Frequency dependences of the real (ε') and imaginary (ε'') components of complex permitivity determined for mesogenic diol D at various constant temperatures in heating scan are shown in Fig. 2; the temperature dependences of corresponding dielectric parameters are shown in Fig. 3. Three temperature regions with boundary values T_{m1} and T_{m2} (correspond well with those determined by DSC measurements on heating) can be distinguished. At the highest temperatures ($T > 123$ °C, isotropic state of diol), in the frequency region from 2 kHz to 10 MHz, the ε' value is practically independent of frequency ($\varepsilon' \sim 5$) and the frequency dependence of ε'' in the whole frequency region (up to 2 MHz) is given by a neat conductivity contribution ($\sigma_{10\ \mathrm{Hz}} = 7.10^{-6}$ S/m and $\eta \sim -1$, Fig. 2). In the temperature region from 55 to 123 °C (between T_{m1} and T_{m2}; reorganized crystalline diol structure), the DC conductivity remains high but a small relaxation contribution to frequency dependencies of ε' and ε'' appears. At temperatures lower than 50 °C (below T_{m1}; initial crystalline diol structure), the DC conductivity decreases rapidly and the relaxation contribution is clearly seen ($\eta \sim -0.5$; Fig. 2). While in the temperature region between T_{m2} and T_{m1} the temperature dependence of f_m is described by the Arrhenius equation (4) with activation energy $\Delta U \sim 0.5$ eV, below T_{m1} slightly higher $\Delta U \sim 0.8$ eV was found (Fig. 3). It can be seen that with decreasing temperature at T_{m1} the frequency of maximum f_m jumps to higher values by about 2 decades. In a narrow temperature interval near T_{m1} both dielectric relaxations are observed (see data at 54 °C in Figs. 2 and 3).

Table 1
DSC data for diol (D), polybutadiene-diol (B) and two- or three-component polyurethanes

Sample	Run	T_{gB} (°C)	Δc_{pB} (J/gK)	T_{gU} (°C)	Δc_{pU} (J/gK)	T_{m1} (°C)	ΔH_1 (J/g)	T_{m2} (°C)	ΔH_2 (J/g)
D	C					40.3	−23.3	114.6	−97.1
	H					51.3	28.7	122.2	98.5
B	C	−47.3	0.39						
	H	−44.2	0.42						
B/HMDI	C			−9.1	0.40				
	H			−8.3	0.38				
B/TDI	C			1.4	0.36				
	H			2.7	0.39				
D/HMDI	C			41.6	0.36				
	H			40.3	0.29	105.8	11.6	115.7	9.5
D/TDI	C			56.9	0.23	79.6	−18.0		
	H			59.5	0.31	92.2	19.1	120.4	1.3
B/D/HMDI	C	−42.2	0.26	42.9	0.20				
	H	−39.5	0.27	44.9	0.29				
B/D/TDI	C	−31.9	0.27	60.2	0.16	76.1	−11.9		
	H	−30.1	0.25	59.1	0.17	89.2	9.6	121.8	1.1

T_{gB} and T_{gU} and Δc_{pB} and Δc_{pU} are corresponding glass transition temperatures and changes in the specific heats of polybutadiene and polyurethane phases, respectively; T_{mi} are melting temperatures and ΔH_i are melting enthalpies.

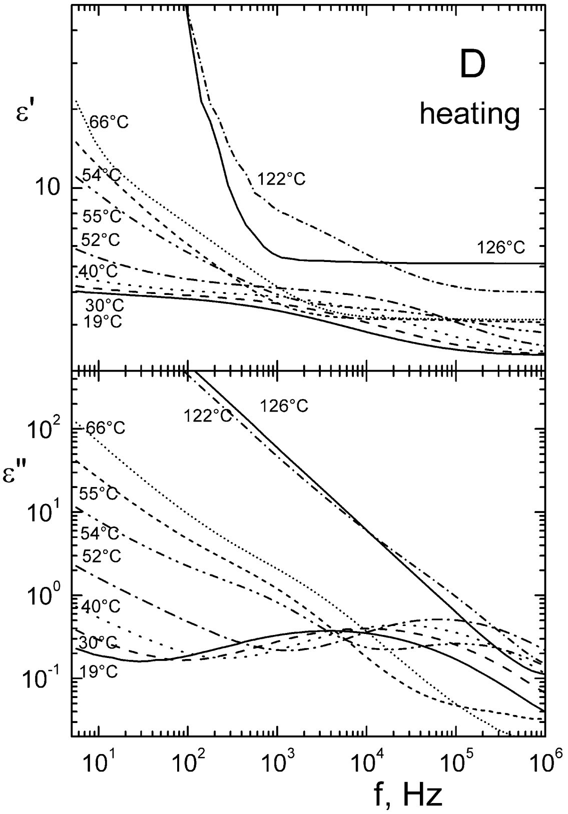


Fig. 2. Frequency dependences of the storage ε' and the loss ε'' component of permitivity for diol D measured at indicated temperatures.

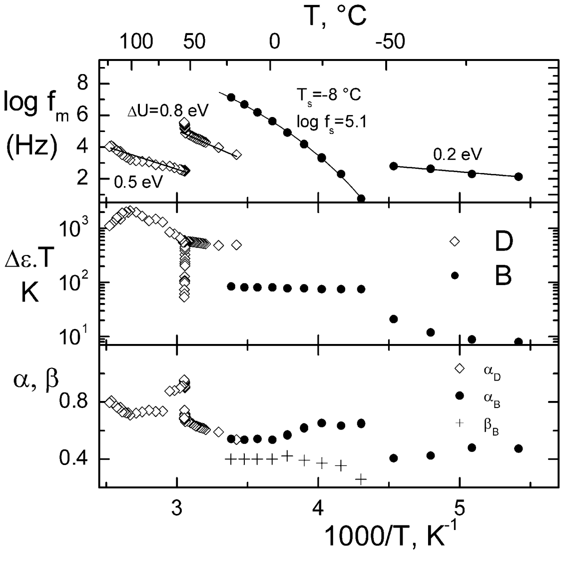


Fig. 3. Temperature dependences of the peak frequency f_m, reduced relaxation strength $\Delta\varepsilon T$ and shape parameter α for polybutadiene diol B and diol D.

The final rate of crystallization is responsible for this phenomenon. The reduced dielectric strength $\Delta\varepsilon T$ is independent in the low-temperature region ($\Delta\varepsilon T\sim 500$ K). At temperatures higher than 55 °C this quantity varies from 500 to 1500 K. The shape of dielectric absorption was roughly symmetrical (Cole–Cole distribution with $\beta=1$ in Eq. (2)) in the whole temperature region. The shape parameter α is quite high (~ 0.8) in the temperature region between T_{m1} and T_{m2}. This means that the distribution of relaxation times is narrow and the size of relaxing units and their environment is uniform. At lower temperatures (below T_{m1}), the relaxation becomes broader and the shape parameter α changes to the value ~ 0.6.

Polybutadiene diol (B) exhibited dielectric behavior typical of amorphous structure with one glass transition region. The temperature dependence of the peak frequency f_m in the main transition region fulfils the WLF Eq. (5) (Fig. 3); the T_s temperature was found to be -8 °C and $\log f_s=5.1$ (Hz). Below -50 °C, the secondary relaxation was detected; the f_m–T dependence of this transition follows the Arrhenius equation with $\Delta U\sim 0.2$ eV. The absorption curves for both transitions are non-symmetrical with average value of parameters α and β equal to 0.6 and 0.35. The reduced relaxation strength amounts to $\Delta\varepsilon T\sim 90$ K glass transition) and 10 K (secondary transition); no conductivity contribution was detected on loss permitivity for diol B in our experimental frequency region.

3.2. Thermal, mechanical and dielectric behavior of two-component polymers

The simplest thermal behavior with only one glass transition temperature T_{gU} was detected on DSC traces for two-component B/DIs polyurethanes (Table 1); this means that amorphous structure was formed in both polymers. As expected, the polymer with a stiffer diisocyanate (TDI) exhibits a higher T_{gU} value (~ 2 °C) in comparison with the polymer prepared from the flexible one (HMDI, ~ -9 °C); for both polyurethanes, the changes in the specific heat at transitions are roughly independent of composition ($\Delta c_{pB\text{-}}\sim 0.38$ J/gK, Table 1) and attend the values typical of amorphous polymers [13].

As it follows from DSC measurements, the two-component polyurethanes based on B exhibit homogeneous structure. This is in accord with Fig. 4 where the temperature dependences of peak frequencies f_m, the reduced relaxation strength $\Delta\varepsilon T$ and the shape parameters α and β (Eq. (2)) found from dielectric measurements are shown. The f_m–T dependences of both polymers obey the WLF equation (5). In agreement with DSC data the T_s temperature of B/TDI is roughly 6 °C higher than that of B/HMDI ($T_s=14$ vs. 8 °C). Within experimental error, reduced strength of the transition $\Delta\varepsilon T$ as well as shape parameters α and β are temperature- and composition-independent for both polymers ($\Delta\varepsilon T\sim 200$ K and $\alpha\sim 0.6$ and $\beta\sim 0.4$ for both polymers).

For two-component D/DIs polyurethanes (prepared with mesogenic D), formation of mesophases and the glass transition at temperatures T_{gU} were detected on DSC traces (Fig. 1, Table 1). Amorphous behavior with $T_{gU}\sim 41$ °C was found for the D/HMDI polymer on cooling; the change in specific heat $\Delta c_{pU} = 0.36$ J/gK correlates with preceding values of amorphous polymers. On subsequent heating D/HMDI the glass transition occurs at practically the same temperature with slightly lower Δc_{pU}. Above T_{gU}, ordered structure formation takes place, and this structure melts in a broad temperature interval (Fig. 1). The D/TDI polymer shows more complex thermal behavior. On cooling from the melt the formation of a mesophase at $T_{m1} \sim 80$ °C takes place and this structure is frozen-in below the glass transition ($T_{gU} \sim 57$ °C). On subsequent heating, the T_{gU} is slightly higher (~ 60 °C) and two mesophase transitions (T_{m1} and T_{m2}) were determined. Optical microscopy and the wide-angle X-ray scattering measurements have revealed [3] that, after melting of the nematic phase ($T_{m1} \sim 92$ °C), a new, better-ordered smectic structure shows up melting at $T_{m2} \sim 120$ °C. As expected, higher T_{gU} was found for the D/TDI from stiff diisocyanate in comparison with that for D/HMDI.

Fig. 5 shows temperature dependences of the storage modulus G' and the loss tangent tgδ measured at $f = 1$ Hz for two-component D/DIs polymers. The D/HMDI based on flexible diisocyanate exhibits, on cooling the melt, a thermorheologically simple mechanical behavior with glass transition. On subsequent heating, the sample shows a slightly different mechanical behavior with glass transition and two small maxima on the loss tangent tgδ, for $T > 90$ °C. This behavior is probably due to the formation and melting of a small amount of an ordered structure and corresponds to the transitions at T_{m1} (106 °C) and T_{m2} (116 °C) found in DSC measurements (Table 1). The D/TDI polymer based on the stiffer diisocyanate exhibits, on cooling the melt, a pronounced increase in G' at $T < 90$ °C; this is due to the formation of a nematic mesophase at ~ 80 °C (Table 1) which is subsequently frozen-in in the glassy state. On subsequent heating, a sharp drop in G' at ~ 80 °C (Fig. 5) is associated with the glass transition and melting of the mesophase; a subsequent sharp increase in G' for $T > 95$ °C is associated with the formation of a more ordered smectic structure which finally melts above 125 °C.

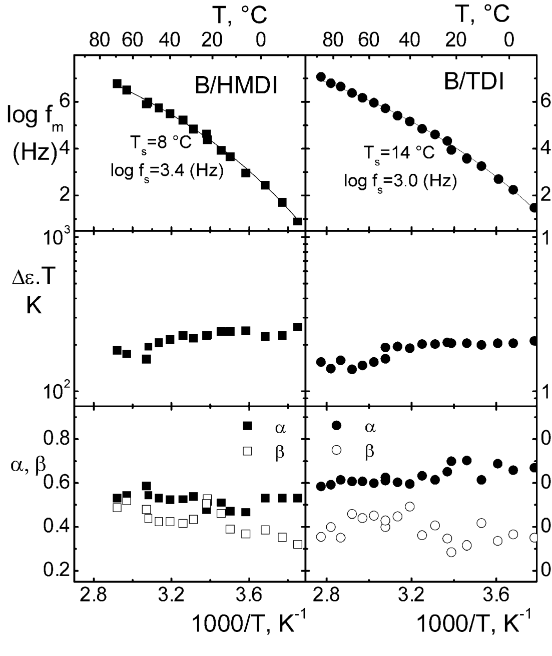


Fig. 4. Temperature dependences of the peak frequency f_m, reduced relaxation strength $\Delta\varepsilon T$ and shape parameters α and β for two-component polymers based on polybutadiene diol B.

An example of temperature dependences of the storage ε' and the loss ε'' components of permitivity, measured at $f = 10$ Hz for two-component polymers, are shown in Fig. 6. On cooling the melt, a sharp decrease in both dielectric components in the flow region (at highest temperatures) and relaxation region, associated with the glass transition, were detected for D/HMDI. On subsequent heating, the glass dispersion is practically unaffected but a pronounced shift of an increase in ε' component to higher temperatures was found. As the formation of a small amount of an ordered structure was detected in this temperature region, we believe that melting of the ordered structure contributes to DC conductivity in high-temperature region and increases the ε' values. As in the case of mechanical measurements, a more complex behavior was found for the D/TDI polymer. On cooling, a decrease in ε' and ε'' in the flow region and a dispersion process (shifted to higher temperatures compared with D/HMDI polymer in accord with Table 1) can be seen again as in the previous case. On heating an increase in ε' and ε'' due to the glass transition is detected; the following pronounced decrease in ε' is associated with the formation of smectic structure followed by an increase in ε' and ε'' in the flow region associated with melting of mesophase.

The temperature dependences of the peak frequencies f_m, reduced relaxation strengths $\Delta\varepsilon T$ and shape parameters α found from dielectric measurements for two-component polyurethanes are shown in Fig. 7. The f_m–T dependence for D/HMDI polymer on cooling obeys the WLF equation (5) with $\log f_s = 4.9$ (Hz), $T_s = 100$ °C in the temperature region from 135 to 65 °C; for $T < 65$ °C one can observe only secondary relaxation with the peak frequency f_m described

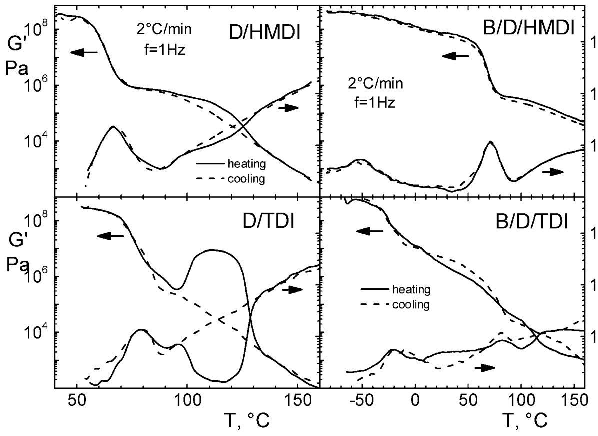


Fig. 5. Temperature dependence of the storage modulus G' and loss tangent tgδ (at frequency $f = 1$ Hz) for two- and three-component polymers.

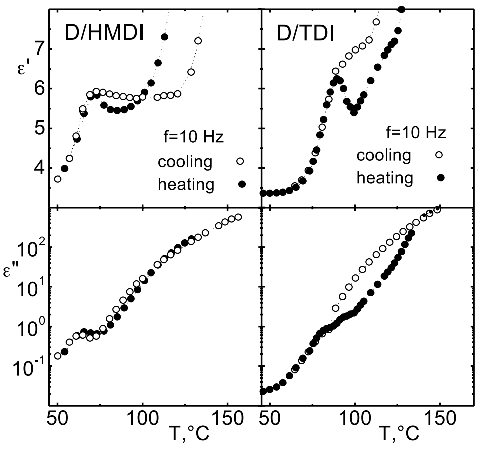


Fig. 6. Temperature dependence of the storage ε' and loss component ε'' of permitivity (at $f = 10$ Hz) for two-component polymers based on diol D.

by the Arrhenius equation with $\Delta U = 0.2$ eV. On subsequent heating, the f_m–T dependence is roughly same at the highest temperatures ($T > 110$ °C); at lower temperatures the deviations from WLF equation are observed and the f_m–T dependence follows rather the Arrhenius equation with activation energy $\Delta U = 2.8$ eV (70–105 °C) and 5.3 eV ($T < 70$ °C).

The f_m–T dependence found for the D/TDI on cooling can also be described by the WLF equation at the highest temperatures (Fig. 7). Applying Eq. (5) to the data obtained at 150–85 °C, we get $\log f_s = 3.8$ (Hz) and $T_s = 85$ °C. For $T < 95$ °C (mesophase and glass formation temperature region), a small jump in the f_m–T dependence can be observed and the WLF equation is no longer satisfied; in this region the peak frequency f_m is almost independent of temperature ($\Delta U = 0.1$ eV). On heating, roughly the same dependence of f_m on T as on cooling was observed at the lowest temperatures. For $T > 80$ °C a jump on the f_m–T dependence (to lower frequencies) takes place and the Arrhenius equation can be used for the description of f_m on T with activation energy $\Delta U = 6.7$ eV. Another change in activation energy is found for $T > 95$ °C ($\Delta U = 2.4$ eV). As expected for the highest temperatures ($T > 125$ °C; isotropic state of the polymer), f_m is independent of the heating/cooling regime. The relaxation processes between 80 and 125 °C are associated with the changes in structure–formation and melting of mesophases. The formation of the ordered structure during the heating scan, connected with a jump on the f_m–T dependence, influences also the value of shape parameter α and the reduced dielectric strength $\Delta\varepsilon T$ (Fig. 7). Different temperature dependences of α and $\Delta\varepsilon T$ in cooling and heating scans indicate the formation of the ordered structure at 95–130 °C for both D/HMDI and D/TDI polymers.

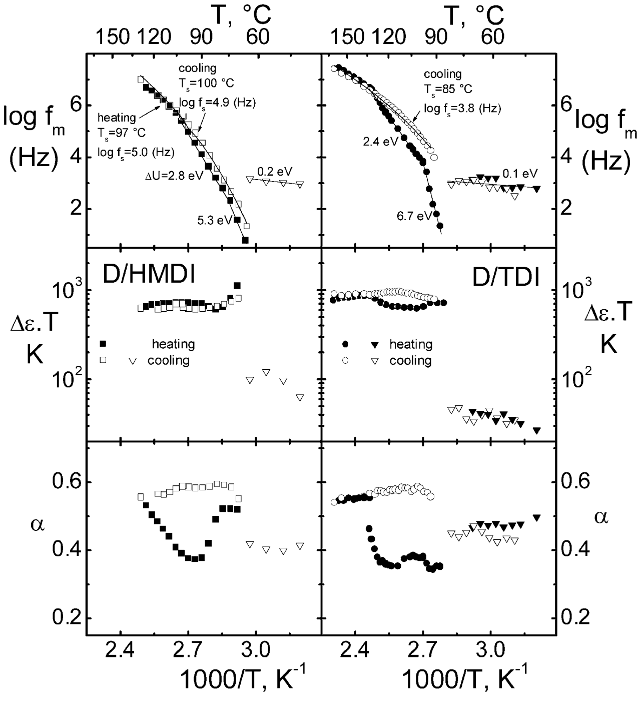


Fig. 7. Temperature dependences of the peak frequency f_m, reduced relaxation strength $\Delta\varepsilon T$ and shape parameters α and β for two-component polymers based on diol D.

3.3. Thermal, mechanical and dielectric behavior of three-component polymers

In three-component polymers with polybutadiene (B), two glass transitions were observed on DSC thermograms (Table 1); the lower one (T_{gB}), corresponds to the soft polybutadiene (B) phase and the other (T_{gU}), at higher temperatures, corresponds to the stiffer polyurethane (U) phase (formed by the D and DIs). Thermal behavior with only two glass transitions ($T_{gB} \sim -41$ °C and $T_{gU} \sim 44$ °C) was observed in cooling and heating scan for B/D/HMDI sample; in this respect the three-component polymer differs from the two-component D/HMDI sample where on heating mesophase formation was observed. As both transition temperatures correlate well with neat B and D/HMDI ones (Table 1), we can conclude that a two-phase structure with soft polybutadiene (B) and hard D/HMDI (U) phase was formed and that both the phases are practically immiscible. For the B/D/TDI polymer, thermal behavior is different. While the T_{gU} (~ 60 °C) value of the polymer correlates well with that found for D/TDI ($T_{gU} \sim 58$ °C), the T_{gB} value of a three-component sample ($T_{gB} \sim -31$ °C) is about 15 °C higher than that of neat B. This means that some B/TDI and/or D/TDI chains were dissolved in the soft B phase. For the B/D/TDI polymer, also two mesophases on heating and one on cooling were observed (Table 1). It is interesting to note that transition temperatures and heat enthalpies correspond well to those found for the two-component D/TDI polymer; this means that similar mesophases were formed in the two-component polymer and in the hard polyurethane phase of three-component sample.

Fig. 5 shows a dependence of the storage modulus G' and the loss tangent tgδ on temperature in cooling and heating scan for B/D/HMDI and B/D/TDI three-component polymers. For both samples, two glass transitions were observed (see maxima in tgδ); the temperatures of the transitions correspond well to the glass transitions determined by DSC and suggest a two-phase structure of samples. While for B/D/HMDI, temperature dependences of mechanical functions on heating and cooling are practically the same (amorphous behavior), for B/D/TDI larger differences in temperature dependences on cooling and heating are observed. In accord with DSC data, the glass transition of the B phase of B/D/TDI is shifted to higher temperatures in comparison with the B/D/HMDI. Above 100 °C, temperature dependences of mechanical functions of B/D/TDI are complex and correspond to melting and formation of mesophases.

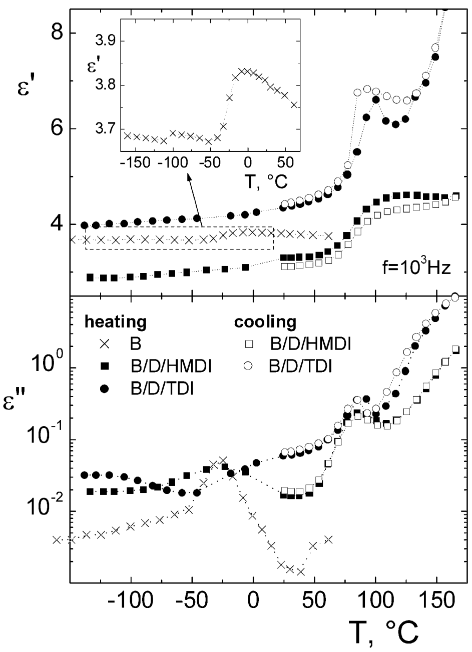


Fig. 8. Temperature dependence of the storage ε' and the loss component ε'' of permitivity (at $f = 1000$ Hz) for three-component polymers and diol B.

Two glass transitions for three-component polymers could be detected also in dielectric behavior (see temperature dependences of ε'' in Fig. 8). Quantitative analysis of the results obtained on three-component polymers is more complicated than for two-component ones. This is due to two-phase structure of these samples. While the relaxation behavior in high-temperature region (corresponding to hard PU phase) is quite similar to that of two-component polymers, it is more complex at lower temperatures. At low temperatures, two relaxation regions with nearly the same relaxation strengths are mixed together. While the first corresponds to the main transition of soft polybutadiene phase, the other corresponds to ordered phase of diol D. For this reason, we assumed that the relaxation corresponding to crystallization is symmetrical as it was found for neat D and for two-component LCPUs and the other, corresponding to polybutadiene (B) phase, is unsymmetrical (Havriliak–Negami equation, Eq. (6)). For separation of experimental results, we assumed that the asymmetry does not change with temperature and we have taken a constant value of parameter $\beta = 0.4$; this value was obtained for B/HMDI and B/TDI polymers. The results of such separation are shown in Fig. 9. The f_m–T dependence of hard PU phase of B/D/HMDI sample follows the WLF Eq. (5) on cooling and heating scan. The T_s temperature obtained from these dependences is 101 °C on cooling and 97 °C on heating. For the B/D/TDI polymer, a more complicated dielectric behavior was found. On cooling, the f_m–T dependence corresponds to the WLF equation up to 110 °C with $T_s \sim 74$ °C. On subsequent heating this dependence follows the Arrhenius equation (4) with activation energy $\Delta U = 6.9$ eV up to 100 °C. At higher temperatures, the WLF equation behavior is restored again with T_s temperature 85 °C. At temperatures lower than 80 °C two dispersion regions were detected in both polymers, the first corresponding to soft B phase and the other corresponding to hard polyurethane phase. We can see that the temperature dependence of f_m, below 75 °C (transition in B phase), especially for B/D/TDI, is in a good agreement with that of neat B/TDI sample; the T_s temperatures determined from separated f_m values are (4 ± 5) °C for B/D/TDI and (0 ± 5) °C for B/D/HMDI sample. Temperature dependences of f_m in a secondary low-temperature region (crystallization of D) have the activation energy 0.4 and 0.5 eV for B/D/HMDI and B/D/TDI, respectively. These values are in a reasonable agreement with that obtained for neat D.

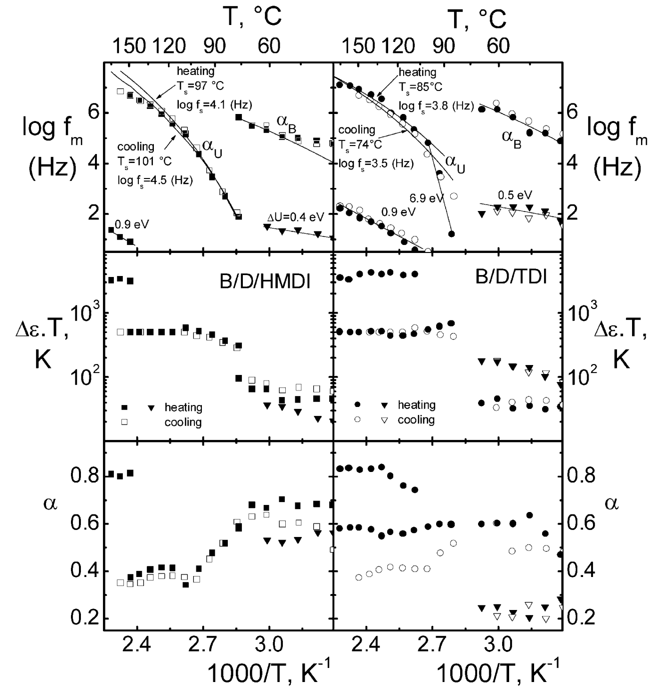


Fig. 9. Temperature dependences of the peak frequency f_m, reduced relaxation strength $\Delta\varepsilon T$ and shape parameters α and β for three-component polymers.

At highest temperatures and low frequencies pronounced absorption hidden under conductivity was observed ($\Delta\varepsilon T \sim 3\times10^4$ K for B/D/TDI and $\Delta\varepsilon T \sim 4\times10^3$ K for B/D/HMDI). The shape of absorption is quite narrow and symmetric with parameter $\alpha \sim 0.8$. With regard to a narrow temperature interval in which we have observed this process we assumed that the temperature dependence of f_m can be described by the Arrhenius equation with $\Delta U \sim 0.9$ eV for both three-component polymers. We suppose that the formation of this region is due to the polarization effects on the surface between hard (U) and soft (B) domains (Maxwell–Wagner–Sillars polarization).

We can conclude that a more complex thermal behavior is found for three-component LCPUs prepared from TDI than for those prepared from HMDI. As it follows from Table 1, mesophase transitions T_{m1} and T_{m2} are detected also in three-component polymers; temperatures of the transitions correlate well with those of two-component polymers. This means that both phases are practically immiscible.

4. Conclusions

DSC, dielectric and dynamic mechanical measurements of polyurethanes based on mesogenic diol (D), polybutadiene diol (B) and two commercial diisocyanates have shown that structure of two- and three-component polymers strongly depends on flexibility of diisocyanate. While polymers formed from a more flexible diisocyanate (HMDI) exhibit amorphous structure those based on a stiffer TDI diisocyanate exhibit LC behavior. Two-component D/TDI polymer forms on cooling the ordered (nematic) phase, which is frozen in the LC glassy state. On heating, melting of mesophase takes place and, subsequently, a better ordered (smectic) phase is formed, which melts at high temperatures. Three-component polymers exhibit a distinct two-phase structure with a soft polybutadiene and hard polyurethane phase; the mesophase transitions observed in the two-component D/TDI polymer are preserved also in three-component B/D/TDI one.

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