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Characterization of molecular structures and properties of polyurethanes using molecular dynamics simulations

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Abstract Thermotropic polyurethanes with mesogenic groups in side chains were prepared from two diisocyanates and four diols with stoichiometric ratios of reactive isocyanate (NCO) and hydroxy (OH) groups. Their thermal behavior was determined by differential scanning calorimetry. The effect of structure modifications of the diisocyanates and diols, in particular changes in the mesogen, were investigated. Introduction of mesogenic segments into the polymers suppresses the ordering. Stiff end substituents (phenyl and alkoxy groups) of the mesogens stabilize the mesophases to such an extent that the negative influence of long polymer chains is compensated and the liquid-crystalline properties are recovered. All-atom molecular dynamics simulations in the *Cerius*² modeling environment were carried out to characterize the structures of the polymers. Analysis of the dynamic trajectories at 20, 100, 120 and 170 °C revealed changes in conformation of macromolecules, which correlate with DSC measurements.

Keywords Mesogenic diols · Polyurethanes · DSC measurements · Temperature transitions · Molecular dynamics simulations

Introduction

Liquid crystalline (LC) materials show a long-range orientational order but little, if any, positional order. This order originates from the anisotropic nature of their intermolecular interactions. Such materials have properties between those of liquids and crystalline solids. Of spe-

cial practical importance are liquid-crystalline polymers (LCP); [1, 2] these systems have been studied widely because of their versatile physical and chemical properties, such as thermal stability, electro-activity, non-linear optical activity, etc. The liquid crystallinity in LCPs is associated with ordering of polymer chains, which are stiffer than those in amorphous polymers. The stiffness and strength of polymer chains, which are of key importance, are usually achieved by increasing the content of stiff (mesogenic) groups in the molecules. In thermotropic LCPs, the LC phase exists only in a particular temperature range. To set up the LC phase into a reasonable broad temperature range is one of the primary objectives in the design of LCPs.

Many polyurethane systems with amorphous, semi-crystalline, or liquid-crystalline structures have been studied in the literature. [3] The driving forces for molecular order are the shape, flexibility, and miscibility of initial reactants—diols and diisocyanates. Thermotropic LC polyurethanes (LCPUs) are formed when a stiff anisotropic mesogenic group is introduced into a diol or diisocyanate. Interesting systems are formed if mesogenic groups are combined with flexible spacers such as $(\text{CH}_2)_n$, because both the LC and isotropic states are then available in such polyurethanes. [2, 4]

The synthesis and physical properties of main-chain LCPUs prepared from LC diisocyanates and/or LC diols by polyaddition have been reported in the literature. [4, 5, 6] In our previous paper, [7] we showed that the thermal behavior of PUs based on a mesogenic diol, 6,6'-[ethylenebis(1,4-phenyleneoxy)]dihexan-1-ol (PDH), depends strongly on the flexibility of the diisocyanate used. Less attention was devoted to side-chain LC polyurethanes [8, 9] prepared from LC diols with the mesogenic group in the side chain. Direct linkage of the mesogenic group to the backbone, or just to a one- or two-atom spacer, usually only leads to isotropic thermal behavior above the glass transition temperature T_g because thermally induced main- and side-chain motions are coupled. [9] Finkelmann et al. [10] suggested that, in order to obtain LC properties, it is necessary to separate the main-chain

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motion from the mesogenic group by a long flexible spacer. In such a way, various SCLCPs with different combinations of the backbone structure with mesogenic group and spacer in side chains were prepared. [9]

The phase behavior of LCPs is not well understood from the molecular point of view. Computer simulation offers an alternative way to gain insight into complex systems such as LCPs at a molecular level. The large increase in the computer power over the last decade makes it possible to form liquid-crystalline models built on individual atomic sites. Clearly, these models are computationally expensive to simulate, with a large number of interactions needed to be considered, thus restricting the type and size of systems that can be studied. Two significant problems in simulations of such systems are: reaching equilibrium on a finite computational time scale, and sampling a sufficiently large region of the configuration space of the system.

In our previous work [11] we investigated the mechanism of the phase transitions in molecular crystals of a mesogenic main-chain diol, 4,4'-bis[(11-hydroxyundecyl)oxy]biphenyl, using molecular dynamics. Analysis of the dynamic trajectories at temperatures of 25, 100, 120 and 170 °C revealed changes in the conformations of the diol molecules and, consequently, changes in crystal packing and crystal structure and enabled us to understand the mechanisms of the phase transitions that were detected by DSC.

Previously, [12] we have described the synthesis of LC diols of various structures based on diethanolamine derivatives with a mesogenic group in the side chain. In this work we have investigated side-chain LC polyurethanes prepared from the four synthesized diols and two commercial diisocyanates. DSC has been used to investigate their thermal behavior. We have carried out molecular dynamics (MD) simulations of single side-chain LC polyurethanes molecules at various temperatures and analyzed the structure and structure-physical properties relationships using the *Cerius*² modeling environment. The effect of structure changes in the diiso-

cyanates and diols, in particular changes in the end substituents bound to mesogenic group as well as in the flexible spacer, was investigated.

Experimental

Materials and sample preparation

For side-chain LC polyurethanes preparation, four mesogenic diols D1–D4 based on structure DX (Fig. 1a) were used. Structure of the diols: D1 ($n=5$, X=H), D2 ($n=6$, X=H), D3 ($n=5$, X=O-*n*-C₈H₁₇) and D4 ($n=6$, X=phenyl). The synthesis and purification of the diols was described earlier [12] and their structure was checked by NMR measurements. Further, two commercial diisocyanates, 4,4'-methylenediisocyanate (MDI) and 2(4-methyl-1,3-phenylene diisocyanate (TDI) (Fig. 1b), were used. The urethane bond formed between the hydroxy (OH) group of diol and isocyanate (NCO) group of diisocyanate is shown schematically in the Fig. 2. The polymerization of the diols and diisocyanates was performed at a 1:1 molar ratio of reactive –OH and NCO– groups in the bulk above the melting temperatures of the diols in a closed glass vessel under dry nitrogen. The polymerization proceeded for 24 h (full conversion of reactive groups). The polymers were dissolved in THF, precipitated into acetone and vacuum dried to a constant weight. In this way six samples were prepared (Table 1).

The number-average (M_n) and the weight-average (M_w) molecular weights of the polymers were determined by the gel-permeation chromatography (GPC) in THF using polystyrene standards. For samples D1/MDI, D2/MDI, D3/MDI, D4/MDI, D3/TDI and D4/TDI the M_n values were 21,850, 44,030, 30,570, 22,680, 30,280 and 22,320, respectively; the polydispersity (M_w/M_n) changed from 1.6 to 2.5. From the M_n values of polymers and the molecular weights of diols and diisocyanates, the number-average degree of polymerization $P_n=35, 69, 43, 32, 45$ and 35 for D1/MDI, D2/MDI, D3/MDI, D4/MDI, D3/TDI

Fig. 1 Molecular structure of diols DX (a) (D1: $n=5$, X=H. D2: $n=6$, X=H. D3: $n=5$, X=O-*n*-C₈H₁₇. D4: $n=6$, X=phenyl) and diisocyanates MDI and TDI (b)

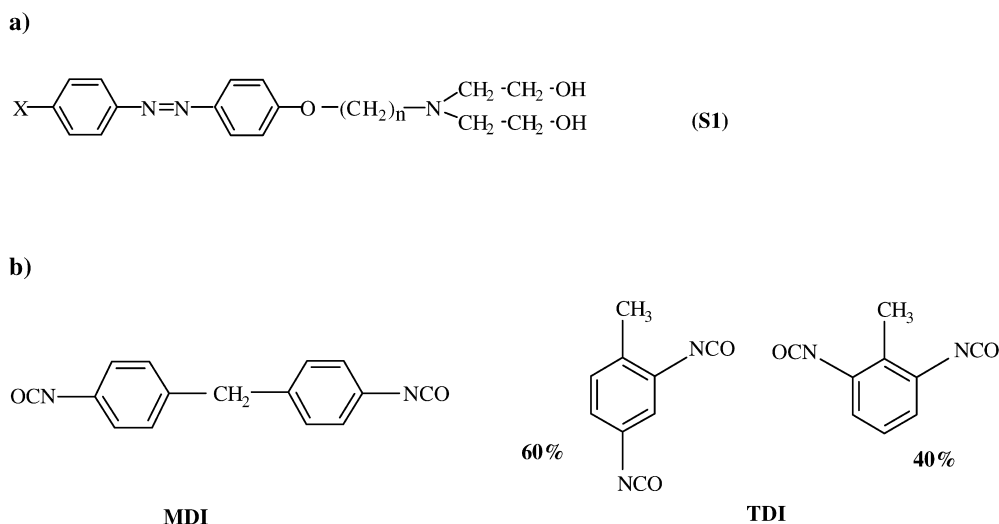


Fig. 2 Urethane bond formed between OH group of diol and NCO group of diisocyanate

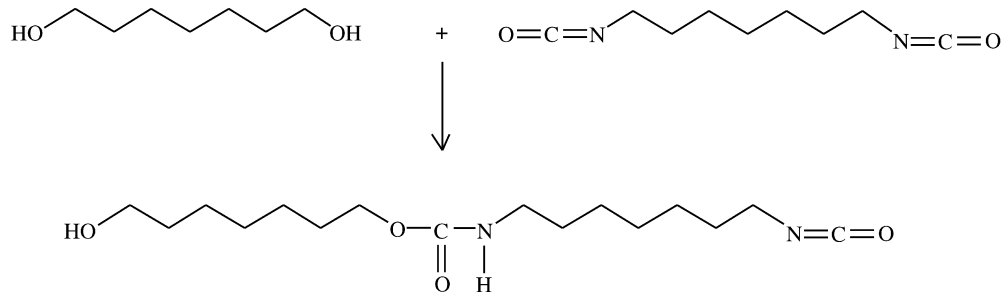


Table 1 DSC transitions determined on cooling from isotropic melt and molecular dynamic simulations. The value in parentheses represents the sum of $\Delta H_1 + \Delta H_2$; $d1$ is the length of whole side chain from backbone nitrogen to the last carbon of the flexible alkoxy group (in case of polymers based on diol D3) or benzene

ring (in case of polymers based on diols D1, D2 or D4); the index 0 indicates the initial value and the index 140 indicates the value after 140 ps of chain relaxation; Φ_0 is the initial cross-section of the polymer molecule

Diol/ Polymer	T_g (°C)	Δc_p (J/g K)	T_{m1} (°C)	ΔH_1 (J/g)	T_{m2} (°C)	ΔH_2 (J/g)	T_{m3} (°C)	ΔH_3 (J/g)	$d1_0$ (Å)	$d1_{140}$ (Å)	Φ_0 (Å)
D1			55.5	-105.8					17.41		
D2			67.7	-118.0	52.5	-29.1	113.6	-54.6	19.04		
D3			-18.5	-11.1	132.6		139.5	-13.3	28.97		
D4			129.7	(-32.9)					23.33		
D1/MDI	59.6	0.42							17.25	15.41	30
D2/MDI	44.0	0.38							18.66	16.27	33
D3/MDI			99.7	-24.0					28.69	21.83	49
D4/MDI			91.3	-9.9					22.72	18.85	41
D3/TDI	53.7	0.32	88.8	-1.9	114.6	-6.5			28.71	21.43	32
D4/TDI			103.2	-10.8	126.6	-4.2			22.94	19.51	33

and D4/TDI samples, respectively, could be determined (the monomer unit consists of pair of diols and one diisocyanate).

Modeling and DSC measurements

Molecular dynamics simulations

All-atom MD simulations were performed using the *Cerius²* program [13] from Accelrys Inc. The model polymer chains consist of 40 or 43 monomer units; these values roughly correspond to the average P_n value found for prepared polymers. The following procedure generated the initial conformation of model polymer chain. First, we optimized the structure of individual monomers and then minimized the energy as a function of the torsion angle between two adjacent monomer units in order to optimize the contacts between them. The values of the optimized torsion angle differed only slightly for the same diisocyanate (i.e., the same backbone) and different diols (different side chains), so we decided to use two values of the torsion angle in accord with the type of diisocyanate (110° and -170° for MDI and TDI, respectively). Second, the most advantageous torsion angle value was used to build the model chain from monomer units; thus we have obtained the helix of a polymer molecule (Fig. 3). Due to different torsion angles, the 5/1 and 17/2 helix structures were found in TDI- and MDI-based polymer molecules. The total number of monomer units was chosen to adjust

to the same end-to-end distance for the MDI and TDI backbones (40 and 43 monomer units for MDI and TDI molecule, respectively); the end-to-end distance was 206 Å. Before using the MD simulations, we optimized the structure of the whole chain.

After minimization, we carried out the molecular dynamics simulations of the isolated single polymer chain in vacuum at a temperature of 20 °C; for polymers with TDI, simulations were also performed at 100, 120 and 170 °C. The atomic force field used was the *cff91* potential [14] parameterized for hydrocarbons. The cut-off distance for the real-space part of van der Waals interactions was 11 Å. Equations of motion for all atoms were solved numerically using the leapfrog version of the Verlet algorithm. [15] The simulations were carried out in the constant-number-of-atoms, volume and temperature (NVT) ensemble. In order to keep the temperature of the system constant, we used the Berendsen temperature bath method. [16] The integration time step was 1 fs and the thermostat relaxation time was 0.1 ps. The length of the entire simulation was 140 ps.

Characterization of macromolecular structures

Radius of gyration

The stiffness and rigidity of a single polymer chain was described by the change of the chain shape after molecular dynamics; the ratio of the radii of gyration $r_g/r_{g0} = [r_g/$

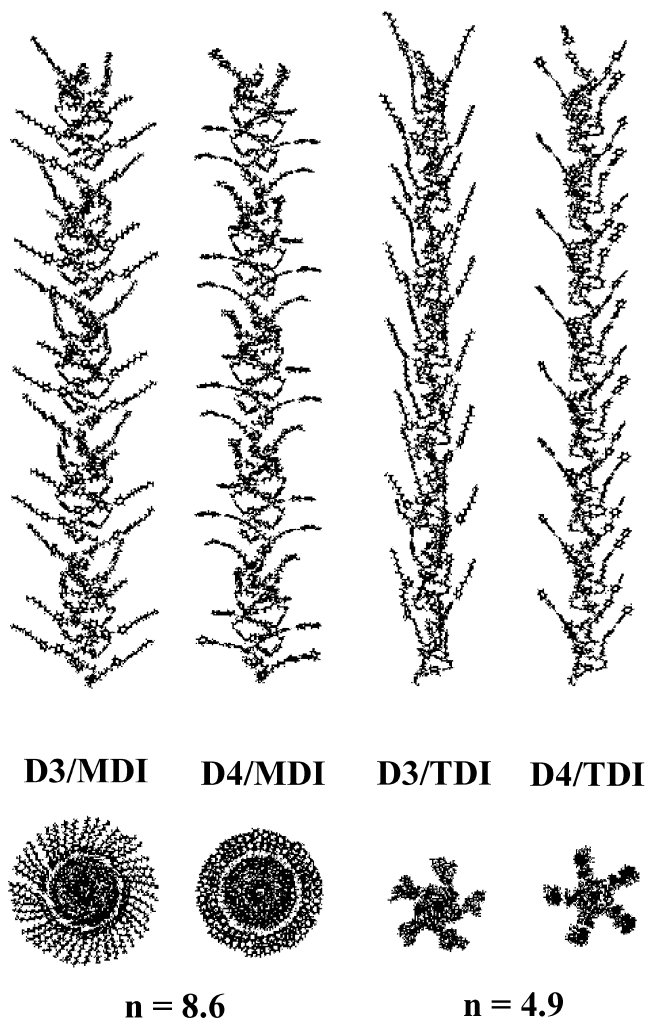


Fig. 3 Initial model structures of MDI- and TDI-based molecules

r_g^0] (superscript 0 indicates the value at time $t=0$) was used as a parameter that describes the shape change quantitatively. The radius of gyration tensor, S , of a polymer chain is defined as:

$$S_{ij} = \overline{(x_{iA} - x_{i0})(x_{jA} - x_{j0})}, \quad i, j = 1, 2, 3$$

where:

(x_{10}, x_{20}, x_{30}) = position of the center of gravity

$r_A(x_{1A}, x_{2A}, x_{3A})$ = position of atom A

and the average is over all atoms. Diagonalization of the S matrix gives its principal values S_1^2 , S_2^2 and S_3^2 . The radius of gyration r_g is the square root of the first invariant of S :

$$r_g = \sqrt{(S_1^2 + S_2^2 + S_3^2)}$$

and describes the way in which the cross-section area is distributed around its centroidal axis.

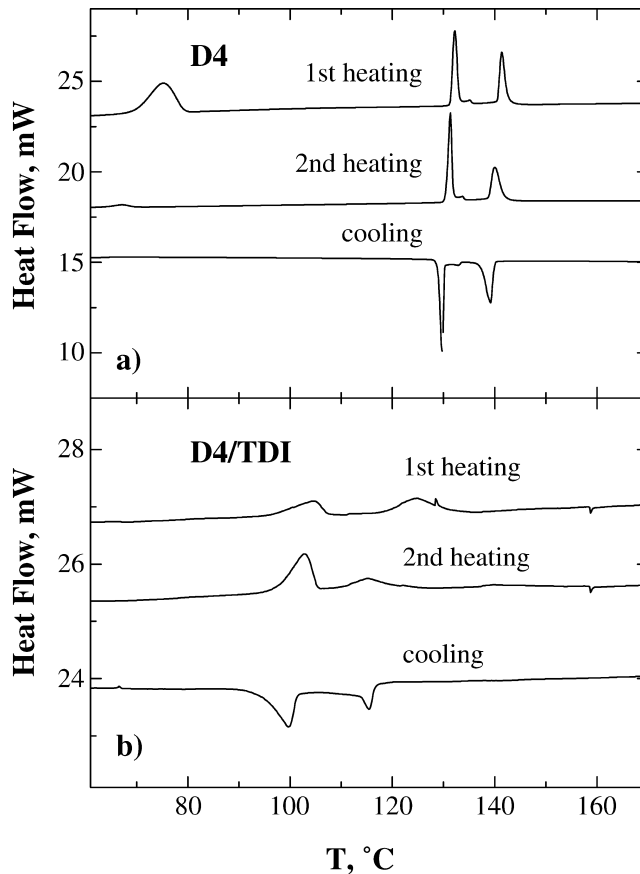


Fig. 4 DSC traces of diol D4 (a) and D4/TDI polymer (b)

Side-chain length

The rigid length $d1$ of side chains was calculated as the distance from the backbone nitrogen to the last carbon of the flexible alkoxy group (in case of polymers based on diol D3) or benzene ring (in case of polymers based on diols D1, D2 or D4). The index 0 in Table 1 indicates the initial value and the index 140 indicates the value after 140 ps of chain relaxation.

We determined the length $d2$ of the mesogenic group of diols D3 and D4 as the length between the first and the last carbons of the benzene rings (in D3 two rings and in D4 three rings).

DSC measurements

Thermal properties were measured using a Perkin-Elmer differential scanning calorimeter DSC-2. To avoid any preparation or thermal prehistory, samples were first heated until the isotropic state was reached and experimental data were collected on cooling at a rate of 10 °C/min. In Fig. 4, an example of measured DSC scans for diol D4 ($n=6$, X=phenyl) and D4/TDI polymer is shown.

Results and discussion

Thermal behavior of the diols

The transition temperatures obtained by DSC on cooling from isotropic melts for the diols and polymers are summarized in Table 1. As can be seen from Fig. 4a, on cooling from an isotropic melt of diol D4, three (two pronounced and one small) transitions, located at 129.7, 132.6 and 139.5 °C with enthalpy values -32.9 and -13.3 J/g (the former value is the sum for both the low-temperature processes as no reasonable splitting was possible), respectively, could be detected on the DSC scan. While the transition at the highest temperature is associated with the smectic phase formation, that at the lowest temperature with the highest enthalpy is associated with crystallization. On heating, all three transitions are reproducible with transition temperatures slightly shifted to higher values (at 131.4, 133.7 and 140.2 °C with enthalpies 33.7 and 14.2 J/g, respectively). The D4/TDI polymer exhibits two transitions (Fig. 4b) with transition temperatures and enthalpies substantially lower than those found for the diol (Table 1). Cooling the isotropic melt of the D4/TDI polymer leads to the formation of a smectic mesophase at ~ 127 °C accompanied by an exothermic peak ($\Delta H_2 = -4.2$ J/g) and subsequent crystallization at ~ 103 °C ($\Delta H_1 = -10.8$ J/g); in such a way polymerization (increasing the chain length) decreases the ordering of mesogens in the side chains.

For diols D1 and D2 with X=H, no mesophases were detected; on cooling and subsequent heating only crystalline phase formation and its melting occur (Table 1). Diol D2 with an even number of CH₂ groups in the spacer ($n=6$) exhibits a ~ 10 °C higher crystallization temperature on cooling than diol D1 with $n=5$. Similar results are usually observed in the literature. [9] Diol D3 with a long alkoxy substituent ($n=5$, X=O- n -C₈H₁₇) exhibits three pronounced transitions. On cooling from the melt, the first transition, at $T_{m3}=113.6$ °C, with the highest value of $\Delta H_3=-54.6$ J/g, is probably associated with ordering (crystallization) of the main chains. After that the next structural transformation is found at $T_{m2}=52.5$ °C ($\Delta H_2=-29.1$ J/g). The third transition at T_{m1} occurs at -18.5 °C with the lowest $\Delta H_1=-11.1$ J/g; we believe that the T_{m2} transition is due to the ordering of mesogenic groups of the side chains and the T_{m1} transition is due to the arrangement of their alkoxy substituents.

Modeling and thermal relaxation of polyurethane chains

An example of changes in the chain conformations with simulation time at 20 °C is shown in Fig. 5a for the D4/TDI polymer molecule with side chains. Figure 5b shows the configurations of the backbone of the molecule at the same simulation times. As expected, with increasing time, more coiled backbone structures are formed. While one can see a pronounced decrease in the backbone length

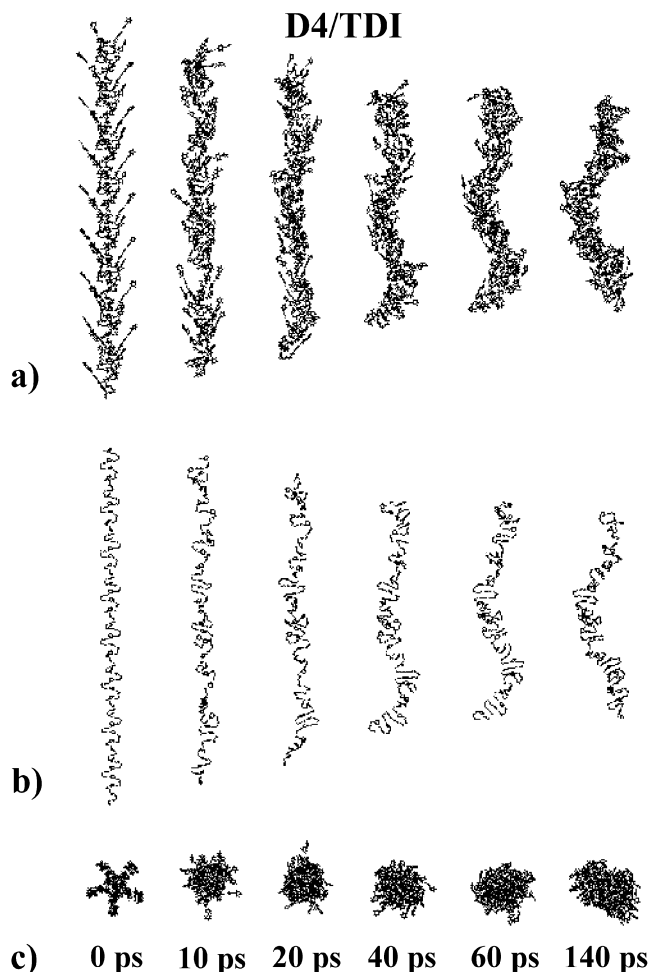


Fig. 5 Example of structure relaxation of D4/TDI molecule at indicated simulation times (temperature 20 °C): complete structure (a); backbone structure (b); top view of molecule (c)

with simulation time, the changes in cross-section, Φ , are much lower (Fig. 5c).

Figure 6 shows an example of the relaxation of the side chain length with simulation time for D3/TDI and D4/TDI molecules at various temperatures; d_1 is the length of whole side chain—from the backbone nitrogen to the last carbon—of the flexible alkoxy group (Fig. 6a) or benzene ring (Fig. 6b). As expected, the initial length of D3 is greater (~ 29 Å) than that of the D4 diol (~ 23 Å, Table 1) and the d_1 values decrease with simulation time and increasing temperature. The relative decrease in d_1 with time is twice as large for the flexible side chain with the alkoxy group ($\sim 30\%$) in comparison with the stiff side chain with a phenyl substituent ($\sim 16\%$). The largest differences in the dependences of d_1 on time with simulation temperature can be seen between 20 and 100 °C for the D3/TDI molecule (Fig. 6a) and between 120 and 170 °C for the D4/TDI molecule (Fig. 6b). It is interesting to note that at ~ 100 °C the side-chain motion of D3 is already free while in the case of the D4 diol the motion is released above 130 °C (Table 1). In such a way single-chain-simulation data correspond to DSC measurements.

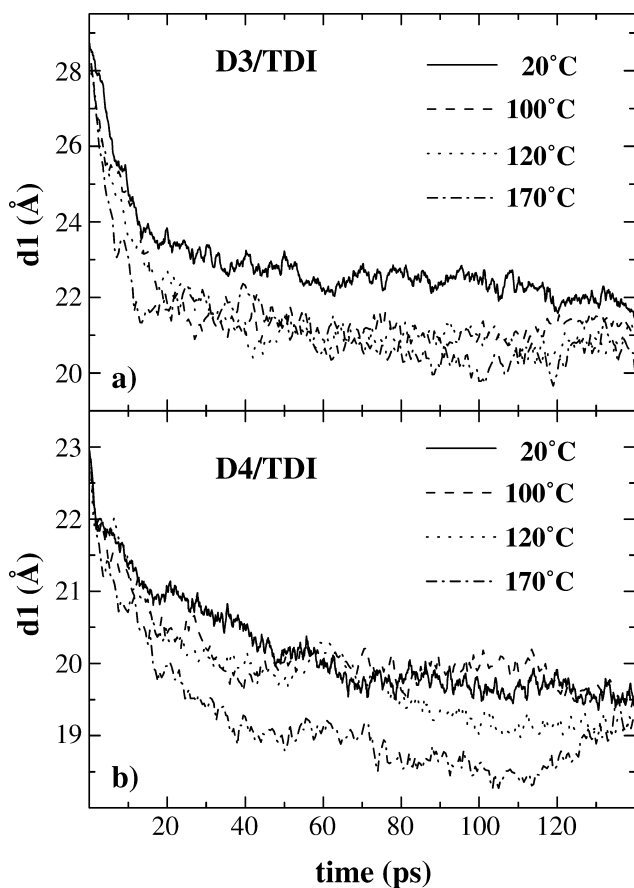


Fig. 6 Example of side chain lengths d_1 relaxation of D3/TDI and D4/TDI molecules on simulation time at temperatures 20, 100, 120 and 170 °C; d_1 is the length of whole side chain from backbone nitrogen to the last carbon—of the flexible alkoxy group—D3/TDI molecule (a) or benzene ring—D4/TDI molecule (b)

For D3/TDI and D4/TDI, we further determined the length of the mesogenic group, d_2 , in side chains as the length between the first and the last carbon of benzene rings (in D3/TDI – two and in D4/TDI three rings). As expected, the d_2 value of D3/TDI was lower (~ 9 Å) than that of D4/TDI (~ 13 Å). The simulation also showed that the d_2 values of both molecules are constant, regardless of simulation time and temperature.

For a few polymers, not only the melting temperatures T_{mi} but also the glass transition temperatures T_g could be detected by DSC on cooling from the isotropic melt (Table 1). As one can see, there are large differences in thermal behavior of PUs depending on the structure of both diisocyanate and diol. This is why individual changes in the structure of PUs will be discussed separately.

Effect of the number of CH_2 groups in side-chain of diol

The effect of the structure of the flexible spacer in the diol can be demonstrated on the D1/MDI and D2/MDI polymers. As follows from Table 1, the thermal behavior of amorphous polymers, with only one glass transition was

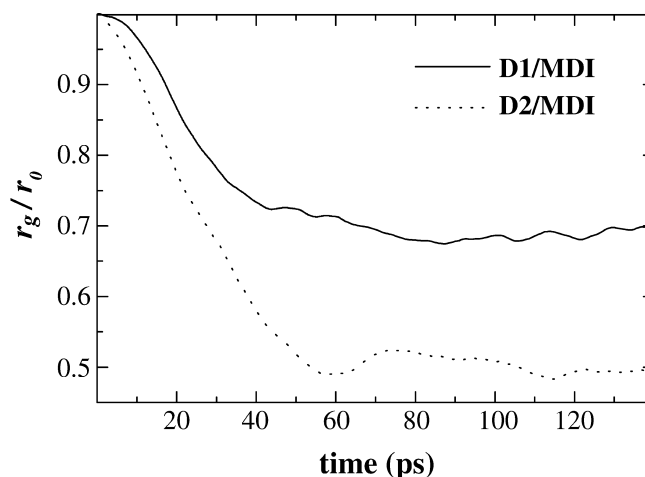


Fig. 7 Time dependence of the ratio r_g/r_0 for molecules D1/MDI and D2/MDI; the simulation temperature 20 °C

found for both polymers; for the D2/MDI with the longer flexible spacer ($n=6$), the T_g temperature is ~ 15 °C lower than that found for the D1/MDI polymer. The change in the specific heat Δc_p found for glass transitions has an average value of $\Delta c_p=0.40$ J/g K, typical of amorphous polymers. [17] The Δc_p value found for the more flexible D2/MDI polymer is slightly lower than that found for the stiffer one.

In Fig. 7, the results of molecular-dynamics simulations at 20 °C are shown for the D1/MDI and D2/MDI molecules as the changes in the ratio of the radii of gyration r_g/r_0 with time. One can clearly see that the dynamics trajectories, which characterize the changes in conformations of polymer chains, are different. The time change of the r_g/r_0 value as well as the r_g/r_0 values at 140 ps of simulation (0.7 and 0.5) are much greater for the more flexible D2/MDI chain with a lower glass transition temperature in comparison to the stiffer D1/MDI molecule (Table 1); in such a way the results from simulation of chain relaxation correlate with the DSC measurements.

Effect of end groups bound to diol mesogen

The effect of the structure of the end groups bound to the mesogen on thermal behavior and simulations can be discussed in the pairs of polymers: D1/MDI, D3/MDI ($n=5$) and D2/MDI, D4/MDI ($n=6$). While for the D1/MDI polymer only an amorphous structure was found, the D3/MDI polymer with long flexible alkoxy substituent exhibits a semicrystalline structure (Table 1). For the D3/MDI polymer, only an isotropic state/crystal transition was detected at $T_{m1} \approx 100$ °C ($\Delta H_1 \approx -24$ J/g) on cooling. We believe that the reason why the glass transition was not detected in the DSC scan for the D3/MDI polymer is that its T_g temperature is close to T_{m1} (in comparison with the D1/MDI polymer one can expect for the D3/MDI $T_g > 60$ °C, so that crystallization is associated with the glass transition).

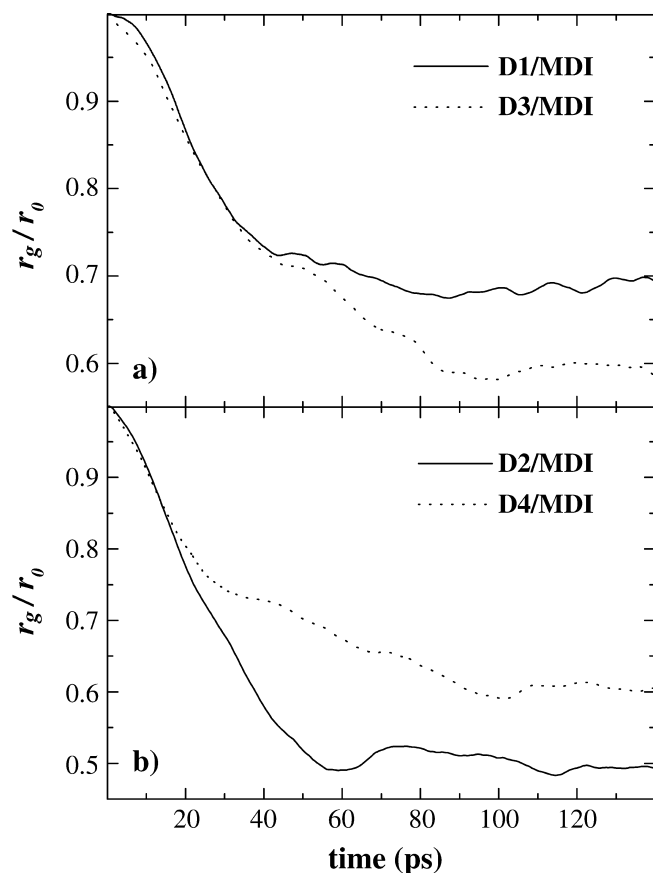
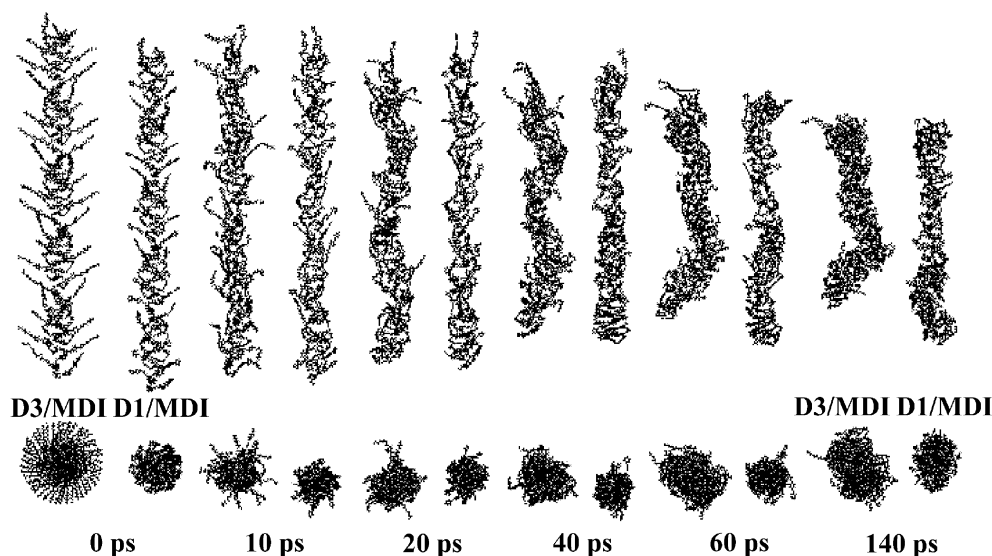


Fig. 8 Time dependence of the ratio r_g/r_0 for MDI-based chains: D1/MDI and D3/MDI (a) and D2/MDI and D4/MDI (b); the simulation temperature 20 °C

The results of molecular dynamics simulations shown in Fig. 8a for the D1/MDI and D3/MDI chains are not in accord with our DSC measurements. The time change of r_g/r_0 is greater and the r_g/r_0 value obtained after 140 ps simulations is lower for the D3/MDI chain (~ 0.6) in

Fig. 9 An example of comparison of time dependence of conformations of D1/MDI and D3/MDI molecules at 20 °C



comparison with the amorphous D1/MDI molecule (~ 0.7). In such a way, the molecule of the semicrystalline D3/MDI polymer exhibits larger conformational changes than that of the amorphous D1/MDI polymer. If we assume that the long alkoxy group ($X=O-n-C_8H_{17}$) at the end of the mesogen leads to greater interactions between side chains, these interactions may allow more bent conformations of the backbone. These results are in accord with the data shown in Fig. 9; the overall length of D3/MDI molecule after 140 ps simulation is shorter than that of the D1/MDI molecule.

A similar comparison can be made for the D2/MDI and D4/MDI chains. The molecule based on the stiffer D4 diol with a phenyl substituent exhibits a more complex thermal (semicrystalline) behavior in comparison with the amorphous D2/MDI polymer (Table 1). In such a way the benzene ring increases the stiffness of the mesogenic group of the side chain. On cooling the D4/MDI polymer from the isotropic melt, only formation of a crystalline structure at $T_{m1} \approx 91$ °C ($\Delta H_1 \approx -10$ J/g) was found. As in the previous case of the D3/MDI polymer, the glass transition could not be detected in the DSC scan.

The simulation data, shown in Fig. 8b, corroborate the DSC measurements. The values of the ratio r_g/r_0 after 140 ps of molecular dynamics of the D2/MDI and D4/MDI chain are 0.5 and 0.6, respectively. Therefore, the change in r_g/r_0 is slightly greater (i.e., larger conformational changes take place) for the amorphous D2/MDI polymer in comparison with the semicrystalline D4/MDI.

Combination of effect of flexible spacer with end group in side-chain

Comparison of the dynamics trajectories of the D3/MDI and D4/MDI polymer chains shown in Fig. 10a suggests that the conformational-chain relaxation of the D3/MDI (D3, $n=5$, $X=O-n-C_8H_{17}$) molecule is similar to that of the D4/MDI (D4, $n=6$, $X=phenyl$). The value of the ratio

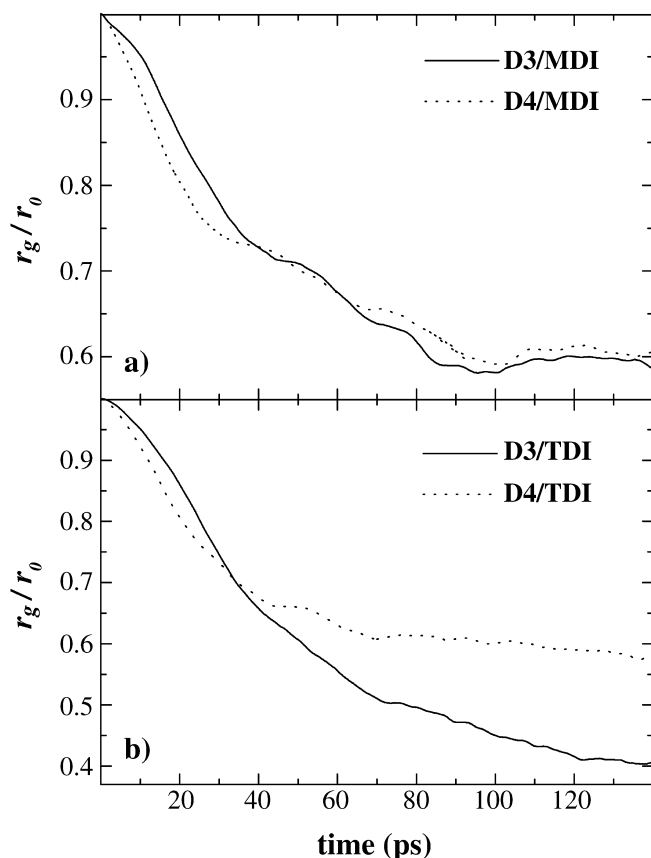


Fig. 10 Time dependence of the ratio r_g/r_0 for diols D3 and D4 in case of MDI- (a) and TDI-based molecules (b); the simulation temperature 20 °C

of the radii of gyration, r_g/r_0 , after 140 ps of molecular dynamics in both cases is about 0.6. This observation is also in accord with the DSC data shown in Table 1. For the D3/MDI polymer, the crystallization temperature T_{m1} is ~ 8 °C higher than that found for the D4/MDI polymer (the difference is too small to cause the changes in conformational relaxation of both polymer chains). This means that the flexible effect of a longer spacer of D4 ($n=6$) in the D4/MDI polymer is compensated by the stiff phenyl end group in comparison with a shorter spacer of D3 ($n=5$) in the D3/MDI molecule with a flexible alkoxy group in diol D3.

The results of molecular dynamics simulations of the D3/TDI and D4/TDI chains shown in Fig. 10b are different. In this case the value of the ratio of radii of gyration r_g/r_0 after 140 ps of molecular dynamics of the D3/TDI chain is 0.4, while the corresponding value in the case of D4/TDI is about 0.6. The trajectories also show that D3/TDI is more flexible than D4/TDI. These results are in accord with the DSC measurements shown in Table 1. Both T_{m1} and T_{m2} transition temperatures are higher for the D4/TDI polymer than for D3/TDI.

Effect of diisocyanate structure

The most complex liquid-crystalline thermal behavior was found for the D3/TDI and D4/TDI polymers (Table 1). On cooling of the D3/TDI sample, the formation of a mesophase takes place at $T_{m2}=114.6$ °C; the relatively high enthalpy value ($\Delta H_2=-6.5$ J/g) suggests that probably a smectic phase is formed. Surprisingly, an additional small transition at 88.8 °C with the enthalpy value $\Delta H_1=-1.9$ J/g was also found. We believe that this transition is associated with a structural change in the aliphatic ends of the side chains (formation of a smectic phase as in the neat diol, Table 1). Finally, the glass transition temperatures T_g was detected at 53.7 °C with a Δc_p value slightly lower than usually found for amorphous systems. [17]

The D4/TDI polymer exhibits similar LC thermal behavior. Cooling its isotropic melt leads to the formation of smectic mesophase at ~ 127 °C accompanied by an exothermic peak ($\Delta H_2=-4.2$ J/g) and subsequent crystallization at 103.2 °C ($\Delta H_1=-10.8$ J/g, Table 1). In such a way the TDI in combination with the D4 diol leads to the crystalline phase and mesophase formation. As no T_g was observed, we assume that crystallization in the cooling scan is associated with the glass transition and a semi-crystalline glass is formed below 90 °C (as in the case of the D4/MDI polymer). We believe that the LC thermal behavior of the D3/TDI and D4/TDI polymers is associated mainly with the short length of TDI, which increases the concentration of mesogens in a unit volume of the TDI-based PUs in comparison with the MDI-based ones.

Figure 11 shows the effect of the diisocyanate structure on the relaxation of D3- and D4-based chains. While for the stiffer D4 diol the time dependence of the r_g/r_0 ratio is practically the same for both the D4/TDI and D4/MDI chains, for molecules based on the more flexible D3 diol, large differences in the time dependence of r_g/r_0 , especially at long times, are observed. These results are in accord with DSC measurements (Table 1). While the transition temperatures and corresponding enthalpies of the two D4-based polymers are roughly the same, the D3/TDI polymer exhibits transitions with lower enthalpy (a glass transition could also be determined) in comparison with D3/MDI.

For D3/TDI and D4/MDI, the effect of the chain length was investigated; the molecular dynamic simulations were applied on chains with 40 and 20 monomer units. As can be seen from Fig. 12, the time changes of r_g/r_0 ratios are more pronounced and the equilibrium (after 140 ps simulation) r_g/r_0 ratios are lower for shorter chains.

Effect of temperature

For two molecules based on TDI, the simulations were performed at various temperatures 20, 100, 120 and 170 °C (Fig. 13). While all polymers at 20 °C are in the amorphous state (D1/MDI and D2/MDI) or ordered (D3/MDI, D4/MDI, D3/TDI and D4/TDI) glassy state, at

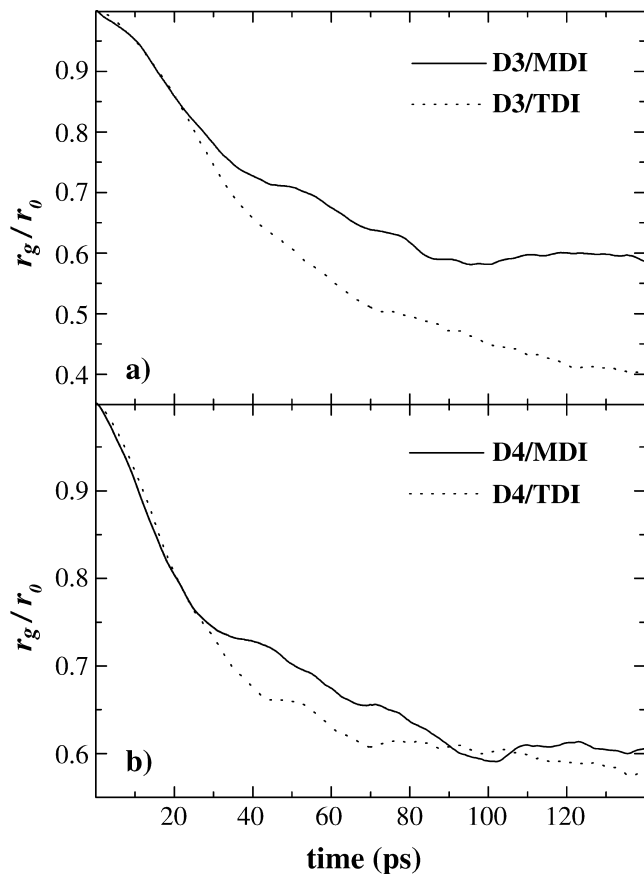


Fig. 11 Comparison of the ratio r_g/r_0 for MDI- and TDI-based molecules; the simulation temperature 20 °C

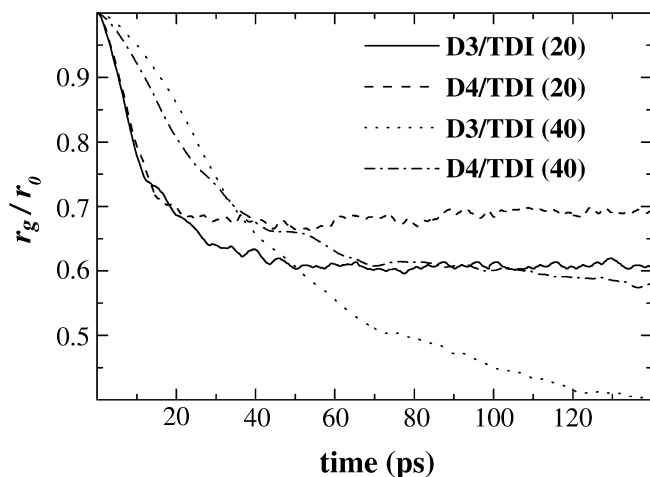


Fig. 12 Time dependence of the ratio r_g/r_0 for TDI-based molecules with different number of monomer units 20 and 40; the simulation temperature 20 °C

170 °C all are in the isotropic melt state. Below 115 °C, the D3/TDI polymer and below 125 °C, the D4/TDI polymer are in the ordered LC state (Table 1). As expected, the most pronounced time dependences and the lowest equilibrium values of the r_g/r_0 ratio were found

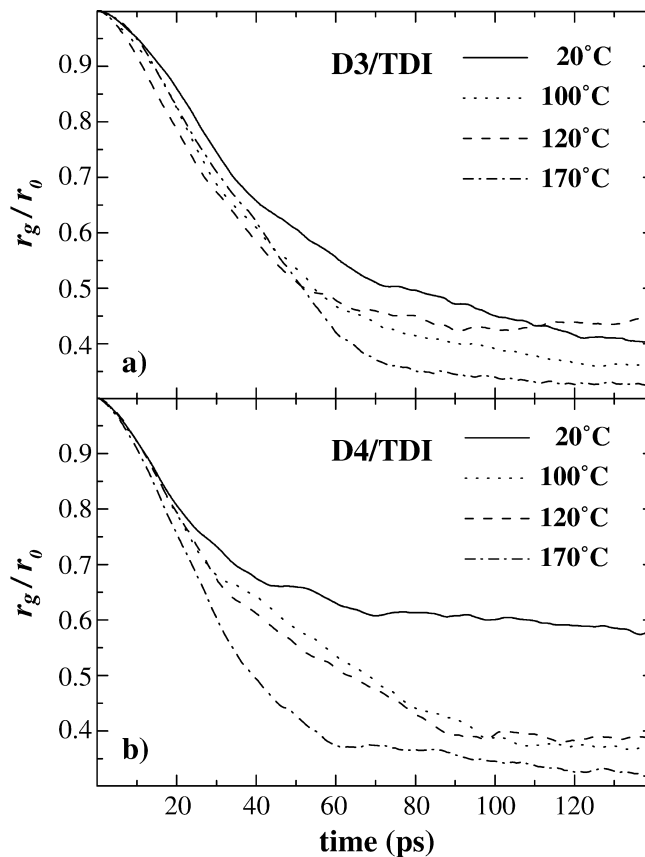


Fig. 13 Comparison of time dependence of the ratio r_g/r_0 on simulation temperature for D3/TDI and D4/TDI polymers

for the highest simulation temperature (Fig. 13). From Fig. 13, it further follows that larger conformational changes of the molecule are associated with the ordered glass/LC transition than with the LC/isotropic one, especially for stiffer D4/TDI polymer. Qualitative agreement between DSC data and the simulation results suggests that intramolecular interactions are, in the first approximation, responsible for molecular conformational changes. Conversely, intermolecular interactions seem to play an important role when a long flexible group is attached to the side chain. We assume that this can also be the reason why comparison of dynamic trajectories of D1/MDI and D3/MDI chains (see Fig. 8a) does not agree with DSC measurements.

Conclusions

From DSC measurements and molecular simulations of polyurethanes (PUs) based on diols with mesogenic groups in side chains and two diisocyanates of different lengths, the following conclusions can be made:

- The neat diols with X=H exhibit only a crystal/isotropic state transition. More complex side-chain end groups (phenyl or O-*n*-C₈H₁₇) lead to formation of mesophases and to LC thermal behavior.

- (b) Incorporation of mesogenic diols into polymers suppresses the occurrence of mesophases in comparison with neat diols; only the polymers prepared from a short stiff diisocyanate (TDI) and phenyl- or *O-n*-C₈H₁₇-substituted diols show the LC thermal behavior. The polymers prepared from diols with no side-chain end group exhibit only amorphous structure regardless of the used diisocyanate.
- (c) The evolution of the ratio of the radii of gyration r_g/r_0 of polymer chains with time was investigated by molecular dynamics simulations at various temperatures. It was found that dynamics trajectories, which characterize the changes in conformation of single polymer molecules, are different for various polymers and temperatures. The results from simulation of relaxation on single chains correlate with DSC measurements if one assumes that a stiffer structure is associated with higher equilibrium values of the r_g/r_0 parameter.

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