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Modulation of supramolecular structure of linear polyurethane systems by addition of liquid-crystalline polymers in the molecular miscibility range

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The peculiarities of domain structure of segmented polyurethane-urea/liquid-crystalline polyester (PU/LCP) blends were studied in the LCP concentration range of 1–10%, with different lengths of the flexible moiety. Small- and wide-angle X-ray scattering (SAXS and WAXS) and differential scanning calorimetry were used. The position of the SAXS maximum changes discontinuously with increasing LCP concentration. We suggest that the rigid fragments of the LCP tend to be incorporated into the rigid domains of the PU component with the restriction that only each third or fourth fragment is involved. The part of the LCP molecule that fits in the space between rigid PU domains is stretched and determines the interdomain distance.

(Keywords: domain structure; polyurethane; liquid-crystalline polymers)

Introduction

The supramolecular structure of segmented polyurethanes depends greatly on the kinetics of segregation of the flexible and rigid fragments of molecular chains as well as on the density and mobility of a secondary physical network; these are conditioned by the thermodynamic flexibility of the oligomeric blocks[1,2]. Structure–property relations for these polymers have been studied extensively[2–8] during the last three decades, and several models of microdomain structure have been proposed[2–5,7]. Segmented polyurethanes have also been used[9] as the components of polymer blends to modify the super- or supramolecular structure and consequently the properties of polymer systems. An effective way to modify the supramolecular structure is to add an admixture of liquid-crystalline (LC) polymers[10], which keep their structure during the viscoelastic-to-glassy transition. Although we could find no published data on polyurethane/LC polymer blends, results for similar systems[11,12] and our own experience[13,14] indicate that an LC polymer admixture can actively influence the segregation processes in polyurethane/LC polymer blends.

Experimental

We have investigated the structure of binary blends of segmented polyurethane and LC polyesters (LCP) as a function of LCP concentration and the length of their flexible fragments, using small- and wide-angle X-ray scattering (SAXS and WAXS) and differential scanning calorimetry (d.s.c.).

Materials. Polyurethane-urea (PU) was prepared from oligooxypropylene glycol ($M_m = 1500$), 2,4-toluene diisocyanate and diphenylmethanediamine (ratio 1:2:1) following a two-stage method[15]. The structural formula of the elementary link is shown in *Figure 1a.*

The LCP (from a commercial source) was a linear polyester containing terephthaloyl-4-oxybenzoate fragments as mesogenic groups and oligooxypropylene glycol chains, with $M_m = 200$ and 300, as flexible moieties (three or five oxypropyleneglycol links, respectively, *Figure 1b*); these two types of LCP are referred to as PPG-200 and PPG-300, respectively.

Measurements. SAXS measurements were made using a step-scanning diffractometer (DRAM-2.0, constructed at the Institute of Crystallography, Moscow) of combined Kratky-Beeman geometry and a stabilized laboratory X-ray generator (CuKα). WAXS patterns were recorded using a standard diffractometer (DRON-4).

Calorimetric measurements were performed using a differential scanning microcalorimeter (DSC-D, Russia) in the temperature range 243–473 K at a heating rate of 2 K min^{-1}. The accuracy of temperature measurement was ±1 K; the total accuracy of the method was 3%.

Results and discussion

The results of SAXS experiments are presented in *Figure 2.* For pure PU it reveals a pronounced interference maximum, which is usually interpreted as evidence of short-range ordering of rigid domains[2,7,8]. The mean distance between nearest domains is about 10.2 nm. The second component (LCP) has a smectic A structure[16] with a periodicity of 3.1–3.6 nm (see *Table 1*). By extrapolating to zero the linear dependence of periodicity *versus* the flexible moiety length, one can estimate the thickness of the LCP rigid block layer to be 2.3 nm. Consequently the interlayer space (the thickness of the flexible fragment layer) is 0.8–1.3 nm. Comparison

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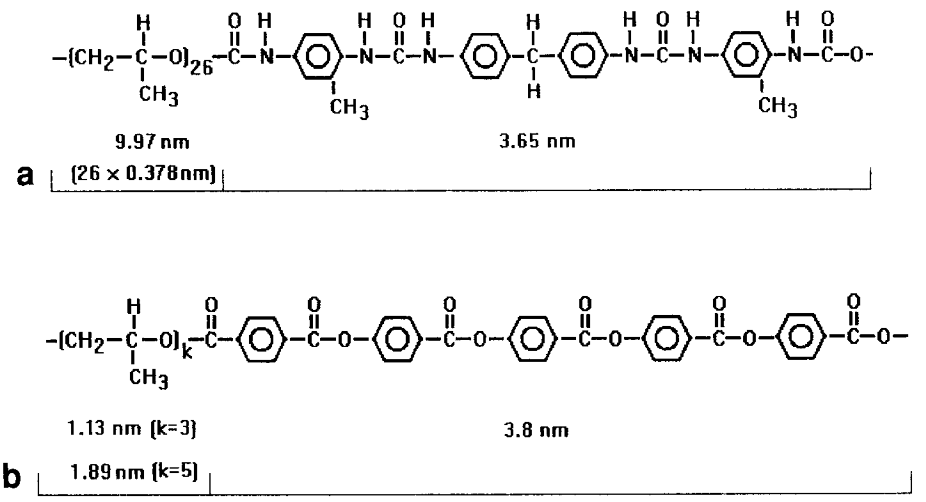

Figure 1 Chemical formulae of the elementary link of (a) PU and (b) LCP. Extended conformation lengths for flexible and rigid (mesogen in the case of LCP) fragments are indicated

Table 1 Some structural and thermodynamic characteristics of pure PU, LCP components and their blends

Sample	Glass transition temperature, T_g (K)	Smectic–isotropic transition temperature, $T_{sm\to i}$ (K)	Interdomain distance, d (nm)	Estimated size of flexible domain, l (nm)
100% PPG-200	100[a]	190[a]	3.1[b]	0.8[b]
100% PPG-250	80[a]	160[a]	3.3[b]	1.0[b]
100% PPG-300	60[a]	137[a]	3.6[b]	1.3[b]
100% PU			10.2	7.9
99% PU/1% PPG-200			10.3	8.0
95% PU/5% PPG-200			6.4	4.1
90% PU/10% PPG-200			9.7	7.4
99% PU/1% PPG-300			7.1	4.8
90% PU/10% PPG-300			10.3	8.0
50% PU/50% PPG-300			6.4 (from peak) 9.7 (from diff. max)	4.1 7.4

[a] From ref. 16
[b] From ref. 14

of the chemical constitution of the rigid blocks of PU and LCP reveals their similarity and close longitudinal size. Thus we can use the value of 2.3 nm as an estimation of PU rigid block length. Then the PU flexible fragment region has a dimension of about 8 nm.

SAXS curves of PU/LCP compositions are also characterized by a broad maximum. However, there is some peculiarity in the angular position of the maximum, which does not change in a continuous manner; it is arranged in the region of 1.15–1.3° or of 0.8–0.9°, but never in between. This fact reflects the peculiarity of the supramolecular structure of the blends under consideration and needs explanation. The mean interdomain distance can be calculated from the position of the maximum (see *Table 1*).

The WAXS patterns of PU, LCP and their blends exhibit a diffuse maximum at the same angular position, which indicates identical short-range ordering and interchain distances in these materials[14,16].

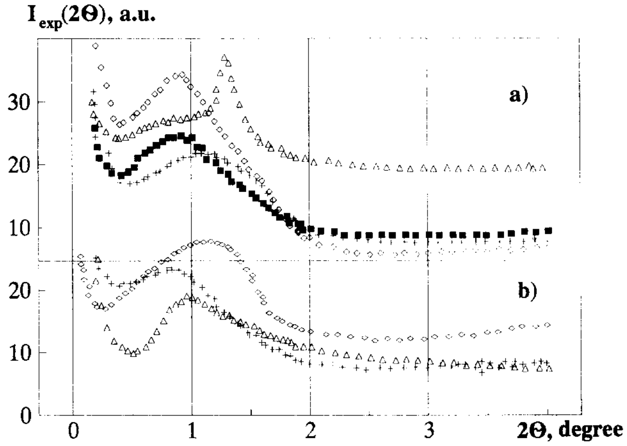

Figure 2 Small-angle X-ray scattering intensity distributions for PU/LCP blends. (a) LCP PPG-200: ■, 0%; +, 1%; ◇, 10%; △, 50%; (b) LCP PPG-300: +, 1%; ◇, 5%; △, 10%

The temperature dependences of heat capacity are shown in *Figure 3*. Glass transition and smectic-to-isotropic transition temperatures (T_g and $T_{sm\to i}$)[16] are reported in *Table 1*. Comparing the data in *Table 1* with our present measurements, we can conclude that the peak on the d.s.c. curves of LCP corresponds to the glass transition and the broad maximum at higher temperature can be accounted for by the smectic-to-isotropic melt transition. We suppose that the glass transition does not significantly affect the orientational ordering in the rigid domains of LCP, which is erased only at $T_{sm\to i}$. Both temperatures decrease with increasing flexible chain length, as expected.

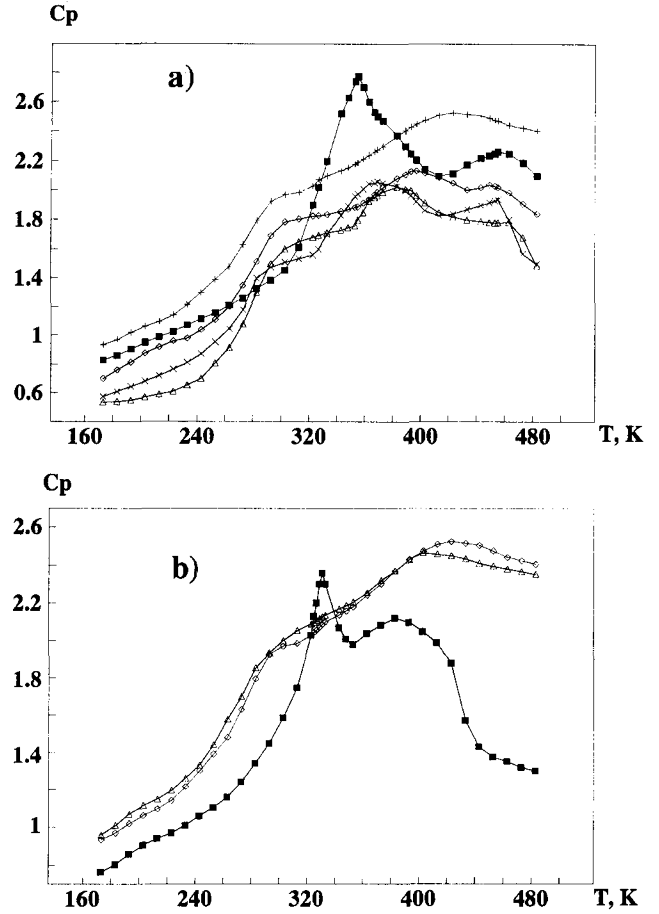

Figure 3 D.s.c. curves for PU/LCP (PPG-200 or PPG-300) blends. (a) ■, 100% PPG-200; +, 100% PU; ◇, 1%; △, 5%; ×, 10% PPG-200; (b) ■, 100% PPG-300; ◇, 100% PU; △, 10% PPG-300

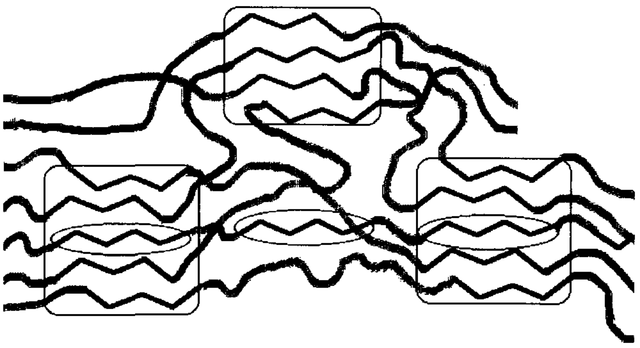

Figure 4 Scheme of the domain structure of PU/LCP blends: rigid domains are represented by rectangles and mesogen blocks by ellipses

The d.s.c. curve of PU is typical of an amorphous polymer. The PU used is a weakly segregated system due to the chemical structure of the rigid blocks (asymmetric toluene diisocyanate). Both urethane and urea groups are able to form hydrogen bonds. A weak domain structure results in broadening of the glass transition of a flexible domain (~290–300 K). Finally, this region is not clearly determined. There is usually a region of intermediate transition[1] which depends on structural rearrangements in the area of restricted compatibility of rigid and flexible fragments. In this case we consider it impossible to resolve this region and the broad high temperature maximum which appears to be due to the destruction of the rigid domains (400–440 K). For PU/LCP blends an additional maximum is observed (~370–390 K) which is not seen for pure PU. It shifts to the glass transition maximum of pure LCP with increasing concentration of LCP admixture. As already pointed out, the last maximum corresponds to the shifting of blocks in rigid domains of LCP without destruction of orientational order. The same process can be expected in PU/LCP blends, and this phenomenon is quite similar to the expected but unobserved intermediate transition in the pure PU, mentioned above. Finally, it is recognized that the LCP admixture affects the domain structure formation in PU/LCP blends. Probably the rigid blocks of the LCP tend to be incorporated into the rigid domains of PU. As we shall see, this results in a stretched domain structure of blends which stimulates the relaxation processes during heating. We have already referred to this phenomenon as the intermediate transition.

The proposal that rigid blocks of LCP are incorporated into the rigid domains of PU is proved by the change in the SAXS patterns. For instance, in PU/LCP (PPG-200) blends the admixture of 1% LCP does not affect the mean interdomain distance d but reduces the height and increases the half-width of the SAXS maximum. This results from the reduced electron density $\Delta\rho$ between rigid and flexible domains due to the incorporation mentioned above. For the 5% admixture the changes are more significant: d is reduced to 6.4 nm, and the maximum becomes more intensive and broad, i.e. $\Delta\rho$ has increased with respect to the 1% blend. Analysing the SAXS curve for the 10% blend, d is seen to increase to 9.7 nm and the maximum height decreases in comparison to the 5% blend.

The proposed arrangement of admixture molecules is able to explain the experimental observations. If the rigid block of the LCP molecule is incorporated into a rigid domain of PU, then another part of the LCP molecule is forced into the flexible-chain domain of PU (see *Figure 4*), and inside the next rigid domain comes the nth rigid block of LCP, where obviously $n=3$, 4 or more. Microphase separation during film formation leads to the fixation of the next rigid block of LCP inside the next rigid domain of PU. The less defective the rigid domains of PU, the earlier the next rigid block of LCP can be fixed. It seems obvious that defects of rigid domains of PU increase with increasing LCP concentration, so the next rigid LCP block can be fixed at later stages of microphase separation, i.e. n becomes higher at higher concentration. For the 5% blend we expect $n=3$ and a closer arrangement of PU rigid domains than in the original pure PU system. This provokes the disturbance in packing of the flexible chains in between the rigid domains as well as the increase of $\Delta\rho$[17]. For the 10% blend we suppose $n=4$, a more distant arrangement of PU rigid domains and a smaller $\Delta\rho$, which corresponds to our observations. Additional evidence of the applicability of the proposed model is the ratio of mean interdomain distances for the 5% and 10% blends (see *Table 1*): $6.4/9.7 \cong (2\times 3.2)/(3\times 3.2) = 2/3$, where 3.2 nm is a somewhat larger value than the periodicity of the smectic structure of LCP (PPG-200); the same is true for PU/LCP (PPG-300) blends of 1% and 10%: $71/103 \cong (2\times 36)/(3\times 36) = 2/3$.

It can be seen from *Figure 1* that the 50% composition of PU/LCP (PPG-300) is characterized by phase separation. The diffraction peak position corresponds to

6.4 nm of periodicity, and the position of the diffuse maximum defines the interdomain distance of 9.7 nm.

Conclusions

The compositions investigated are molecularly compatible up to a content of 10% LCP admixture. Despite the structural similarity of flexible moieties of the components, the trapping of LCP rigid fragments into rigid domains is the dominating factor of supramolecular structure formation. Microphase separation involves the incorporation of each third (or fourth) LCP rigid fragment into rigid domains of PU, thus the interdomain distance of PU supramolecular structure is defined by the length of the periodicity of the LCP chain.

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