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Miscibility of a liquid crystalline polyurethane with common segmented polyurethanes

M.-M. Pohl*, R. Dany, R. Mix and J. Gähde
Institute of Applied Chemistry, Rudower Chaussee 5, D-12484 Berlin-Adlershof, Germany

and G. Hinrichsen
Technical University of Berlin, Institute of Nonmetallic Materials, Englische Strasse 20, D-10587 Berlin, Germany
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The phase behaviour of blends of a liquid crystalline polyurethane A, based on 4,4′-bis(6-hydroxyhexoxy)-biphenyl (BHHBP) as the mesogenic diol and toluene 2,4-diisocyanate (TDI), with common segmented polyurethanes B (based on poly(tetramethylene adipate), methylene di-*p*-phenylene isocyanate (MDI) or toluene 2,4-diisocyanate (TDI) and 1,4-butanediol) with various segment lengths was studied by differential scanning calorimetry (d.s.c.) and electron microscopy. No miscibility of the polyurethane A and the hard segments of the different polyurethanes B, independent of the length of the hard segments and the type of diisocyanate used, was observed. With decreasing length of the soft segment an increasing amount of the liquid crystalline polymer (LCP) can be mixed with the amorphous phase of the soft segment in the case of the MDI-polyurethanes, whereas the TDI-polyurethanes B are completely immiscible with polyurethane A. Copyright © 1996 Elsevier Science Ltd.

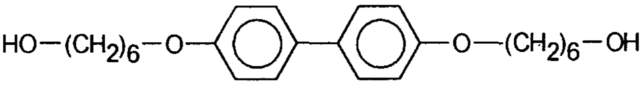
(Keywords: polymer blend; segmented polyurethane; liquid crystalline polyurethane)

INTRODUCTION

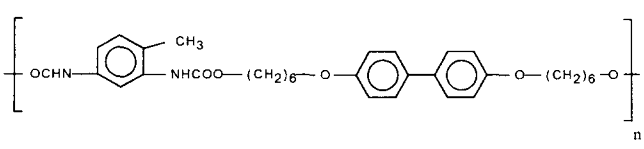
The motivation for blending liquid crystalline polymers (LCPs) is the same as that for blending any other polymer, namely the modification and improvement of properties. In general, polymer blends of two or more components are not miscible[1]. In the case of mixtures with liquid crystalline polymers a poor adhesion to other polymers is usually observed. To overcome this problem, partial miscibility of the components may be a possible way to achieve better interaction and dispersity between two chemically different polymers. Miscibility is determined by molecular interactions. When using copolymers, intramolecular repulsion may dominate intermolecular repulsion and may lead to miscibility. In this case, miscibility depends on the copolymer composition and segment-length distribution[2,3]. With polyurethanes it is easy to obtain variable segment lengths in order to modify the chemical structure of the components. Therefore, in this study, we have used mixtures of a liquid crystalline polyurethane and common segmented polyurethanes containing various segment lengths. The existing phases of both components can be characterized by thermal methods as well as by electron microscopy. The aim of this present work is to study, as a first step, the influence of polyurethane composition on the miscibility behaviour of blends containing an unsegmented liquid crystalline polyurethane.

EXPERIMENTAL

The liquid crystalline polyurethane (A) investigated in this paper is based on 4,4′-bis(6-hydroxyhexoxy)-



biphenyl(BHHBP):
and toluene 2,4-diisocyanate (TDI). The resulting poly-



urethane structure contains the following repeat unit:
The synthesis of this material has been described in detail by MacKnight and coworkers[4].

The blending partners (polyurethanes B) are based on poly(tetramethylene adipate) as the soft segments, with hard segments resulting from methylene di-*p*-phenylene isocyanate (MDI) or toluene 2,4-diisocyanate (TDI) as the diisocyanate species. 1,4-Butanediol was used as a chain extender in all of the syntheses. The molecular weights of the soft segments in polyurethanes B vary over the range from 2000 to 600 g mol^{-1} (BASF, molecular

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*To whom correspondence should be addressed

Table 1 S.e.c. data and transition temperatures of polyurethane A and the polyurethane B series

Polyurethane	Composition, soft segment/chain extender	M_n of soft segment (g mol^{-1})	M_n (g mol^{-1})	M_w (g mol^{-1})	M_w/M_n	T_g of BTDI and BMDI series, soft segment (°C)	T_m of BMDI series, hard segment (°C)
A	–	–	26 700	33 700	1.3	87	–
BTDI-1	1/1	2000	86 000	105 000	1.2	−41	
BTDI-2	1/1	600	48 700	79 000	1.6	1	–
BTDI-3	1/4	2000	48 200	72 000	1.5	−11	–
BTDI-4	1/4	600	74 700	150 000	2.0	34	–
BMDI-1	1/1	2000	25 400	39 500	1.6	−44	127
BMDI-2	1/1	600	42 500	86 000	2.0	−35	192
BMDI-3	1/4	2000	53 800	142 000	2.6	−43	195
BMDI-4	1/4	600	53 300	115 000	2.2	6	208

Table 2 D.s.c. data of BTDI/polyurethane A mixtures (2nd heating run)

Composition (wt% A)	Glass transition		Melting temperature, polyurethane A		Clearing temperature, polyurethane A	
	T (°C)	Δc_p (J g^{-1} K^{-1})	T (°C)	ΔH (J g^{-1})	T (°C)	ΔH (J g^{-1})
100	87	0.285	156	11.1	168	36.9
BTDI-1						
0	−41	0.496	–	–	–	–
20	−38	0.578	146	1.7	160	7.3
40	−39	0.305	148	4.7	164	10.4
60	−40	0.151	147	6.2	163	18.8
BTDI-2						
0	1	0.473	–	–	–	–
20	6	0.367	121	2.5	155	3.3
40	7	0.347	150	3.5	164	10.5
60	12	0.240	149	2.522	164	19.619
BTDI-3						
0	−11	0.390	–	–	–	–
20	−10	0.360	–	–	168	14.8
40	−6	0.220	160	1.6	170	22.7
60	−11	0.097	158	2.97	169	22.73
BTDI-4						
0	34	0.484	–	–	–	–
20	38	0.406	125	1.1	163	4.0
40	42	0.364	149	3.1	165	10.3
60	43	0.290	148	7.2	164	19.0

weights by end-group titration: 2110 and 650 g mol^{-1}), respectively, while the soft-segment/chain-extender ratio was kept at 1 : 1 or 1 : 4. The molecular weights (*Table 1*) of the polymers were determined by size exclusion chromatography (s.e.c.) with refractive index viscosity detection at 25°C in N,N'-dimethyl formamide (DMF) (1 ml s^{-1}), calibrated by polystyrene standards.

These polyurethanes were synthesized by a two-step process under a nitrogen atmosphere. The polyester and MDI (TDI) were reacted first for 30 min at 60°C with stirring. Dried dioxane was then added to the prepolymer melt, followed by dropwise addition of the 1,4-dissolved butanediol in dioxane. The solution that was obtained had a polyurethane content of 25 wt%. This second reaction (chain extending) was carried out with stirring, first for 20 h at 80°C and then for 1 h under reflux. To prepare the blends, the polymers were dissolved in a DMF/dioxane (20/80wt%) mixture containing 15 wt% polymer. The solutions were cast on glass plates and the films that were formed were then dried for 8 h at 100°C in a vacuum oven.

The d.s.c. measurements were carried out by using a Perkin-Elmer DSC-7 machine, at a heating rate of 20 K min^{-1}. The second heating run was performed after heating up the sample to 210°C (because of possible thermal degradation) and then quenching to −70°C. For the electron microscopy observations thin films were prepared by casting a 1 wt% solution on freshly cleaved rock salt surfaces; the films produced were dried for 1 h at 100°C. The samples were then stained with ruthenium tetroxide, following the procedure of Trent, in order to enhance the phase contrast[5–7]. For control of the morphology ultrathin cuts at −70°C were made; no morphological differences compared to the cast films were detected. Observations were carried out using a TESLA BS-500 transmission electron microscope operating at 90 kV.

RESULTS AND DISCUSSION

Polyurethane A is described in great detail in the literature[4,8–12]. It has been reported that this polymer forms a monotropic liquid crystal phase of the smectic C type[11,12], but with a strong tendency to crystallize. From the second d.s.c. heating run the following transitions were obtained: glass transition temperature (T_g) = 87°C,

Table 3 D.s.c. data of BMDI polyurethane A mixtures (2nd heating run)

Composition (wt% A)	Glass transition		Melting temperature, polyurethane A		Clearing temperature, polyurethane A		Hard-segment melting temperature, BMDI	
	T (°C)	Δc_p ($J g^{-1} K^{-1}$)	T (°C)	ΔH ($J g^{-1}$)	T (°C)	ΔH ($J g^{-1}$)	T (°C)	ΔH ($J g^{-1}$)
100	87	0.285	156	11.1	168	36.9	–	–
BMDI-1								
0	−44	0.381	–	–	–	–	127	4.9
20	−39	0.354	147	1.9	161	3.9	129	2.1
40	−37	0.278	147	4.8	163	10.8	126	1.0
60	−36	0.127	147	7.1	163	18.4	127	0.3
BMDI-2								
0	−35	0.180	–	–	–	–	192	10.5
20	−11	0.178	117	2.6	154	4.2	190	14.4
40	−6	0.131	–	–	166	13.5	186	2.6
60	22	0.361	127	5.7	158	14.9	–	–
BMDI-3								
0	−43	0.236	–	–	–	–	195	8.5
20	−38	0.166	150	2.2	161	3.6	192	11.0
40	−34	0.126	149	5.1	163	10.5	183	3.9
60	−41	0.087	149	8.4	163	19.2	–	–
BMDI-4								
0	6	0.084	–	–	–	–	208	8.0
20	17	0.304	–	–	166	5.28	–	–
40	50	0.221	–	–	167	14.76	–	–
60	52	0.369	126.6	1.5	160	16.2	–	–

melting temperature $T_m = 155°C$, and clearing temperature = 168°C. In accordance with ref. 4, a supercooling of the transition temperatures over a range of 40 K was observed in the cooling run.

The polyurethane B series, consisting of common segmented polyurethanes, is characterized by the transition temperatures (2nd heating run) listed in *Table 1*. Soft segments with a molecular weight of 2000 g mol^{-1} are crystallizable. The melting temperatures of the crystalline soft-segment phases are in the range from 40 to 45°C, which in most cases are observed only in the first d.s.c. heating run and by electron microscopy, due to the comparability of the state of the electron microscopy samples with that of the specimens in the first d.s.c. run. 2,4-TDI-containing polyurethanes (BTDI series) exhibit no phase separation[13]. They form soft/hard-segment mixtures with only a glass transition temperature, but no separated hard phase. This is the reason why the glass transition temperature in all cases is strongly influenced by the polyurethane composition. MDI-containing polyurethanes (BMDI series) are separated into two phases, i.e. a soft-segment and a hard-segment phase[14], but in the case of the short soft segment a part of the hard segment is incorporated into the soft phase. The result is a shift of the glass transition temperature for BMDI-2 and BMDI-4, but with a clearly visible hard-segment melting temperature. The higher glass transition of the MDI–butanediol hard segments, the larger amount of hard segments due to the molar mass of MDI, and the stiffer environment, lead to greater shifts in T_g when compared to the TDI-containing polyurethanes. The melting temperatures of the hard segments are in the range of 190–210°C, depending on the state of crystalline order.

Comparison of the temperature ranges of the transition data obtained from the second d.s.c. runs for the polyurethane B series and polyurethane A clearly shows that it is possible to follow changes of the phase separation of these similar mixtures by observing the glass transitions as well as the melting and clearing temperatures, which are sufficiently removed from each other.

For an examination of the possible mixed phases, the transitions of the polyurethane A, the soft-segment glass transition of the polyurethanes B, and the hard-segment melting temperature of the MDI-containing polyurethanes are of particular interest. *Table 2* shows the relevant d.s.c. data for mixtures containing the BTDI polyurethanes. In these mixtures no significant influence of the percentage content of polyurethane A on the transition temperatures of either component polymer is observed. These blends form multiphase systems, as previously observed for mixtures of polyurethane A with other polymers[12]. The glass transition temperatures of the BTDI polyurethanes within the mixtures remain constant. TDI-containing polyurethanes show no miscibility with polyurethane A, even for samples with the shortest soft segments. The glass transition temperature of the soft segments does not depend on the percentage of polyurethane A, nor on the chemical composition of the BTDI component (*Figure 1a*).

In the case of mixtures of polyurethane A with BMDI polyurethanes (*Table 3*) the hard-segment transition temperatures are unaffected by the percentage content of polyurethane A. There exists no indication of any miscibility of the two hard segments, but partial miscibility of the soft segment with polyurethane A takes place in some MDI-containing blends, with this behaviour being dependent on the length of the soft segments. This is observed with BMDI-2 and BMDI-4, which contain soft segments of the shortest length, but differ in hard-segment content. BMDI-1 and BMDI-3 mixtures, containing the longer soft segments, show no significant shift of glass transition, as observed for the TDI-containing polyurethanes. This behaviour is represented in *Figure 1b*. The glass transition temperature of the soft segment increases strongly with the percentage content of polyurethane A if the length of the soft

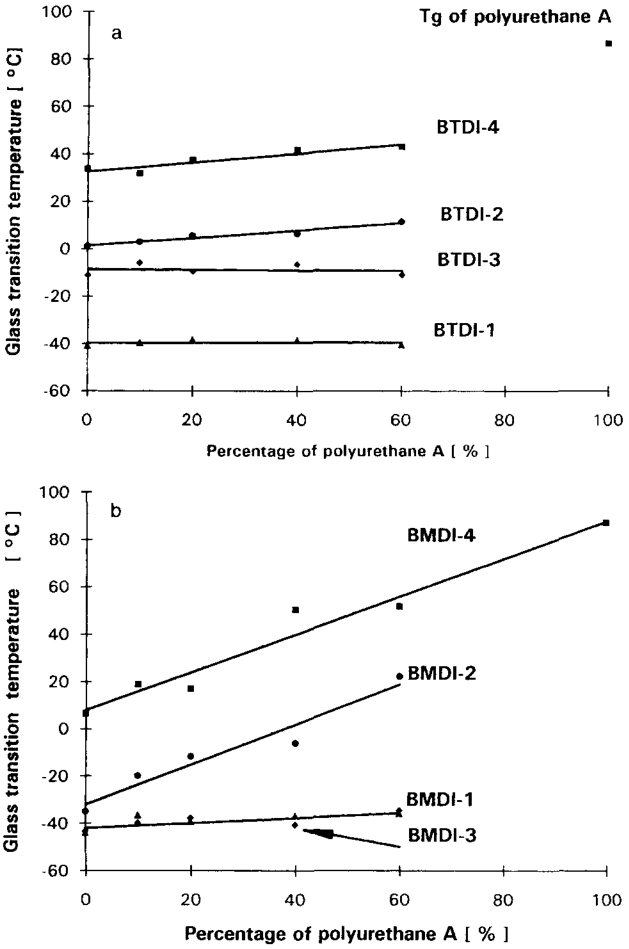

Figure 1 Variation in the soft-segment glass transition temperatures of mixtures of the liquid crystalline polyurethane A with conventional polyurethanes: (a) of the BTDI-type; (b) of the BMDI-type

segment is short. However, in all cases, even at the highest shift of the glass transition temperature, some remaining unperturbed polyurethane A can still be detected. This result is in accordance with electron microscopy observations, which show a pronounced phase separation in the cases of the BMDI-2 and BMDI-4 mixtures, when compared to those of BMDI-1, BMDI-3, and all of the BTDI mixtures. *Figure 2* shows representative micrographs of the BTDI-4 and BMDI-4 systems.

CONCLUSIONS

Blends of the liquid crystalline polyurethane A with common segmented polyurethanes form phase-separated systems. In these blends the polymer/polymer miscibility does not only depend on the chemical constitution of polyurethane B, but also on the segment length. In the case of mixtures with MDI-containing polyurethanes, partial miscibility of polyurethane A with the short soft segments was found, which is independent of the hard-segment content in the chain-extending range from 1 : 1 to 1 : 4. These studies will be continued by using infra-red spectroscopy and polarizing microscopy in order to obtain a more detailed understanding of the observed partial miscibility and the liquid crystal behaviour. Additional investigations on segmented liquid crystalline polyurethanes blended with common polyurethanes may open a route to obtaining soft-segment miscible blends with improved interactions between the phases and appropriate mechanical properties.

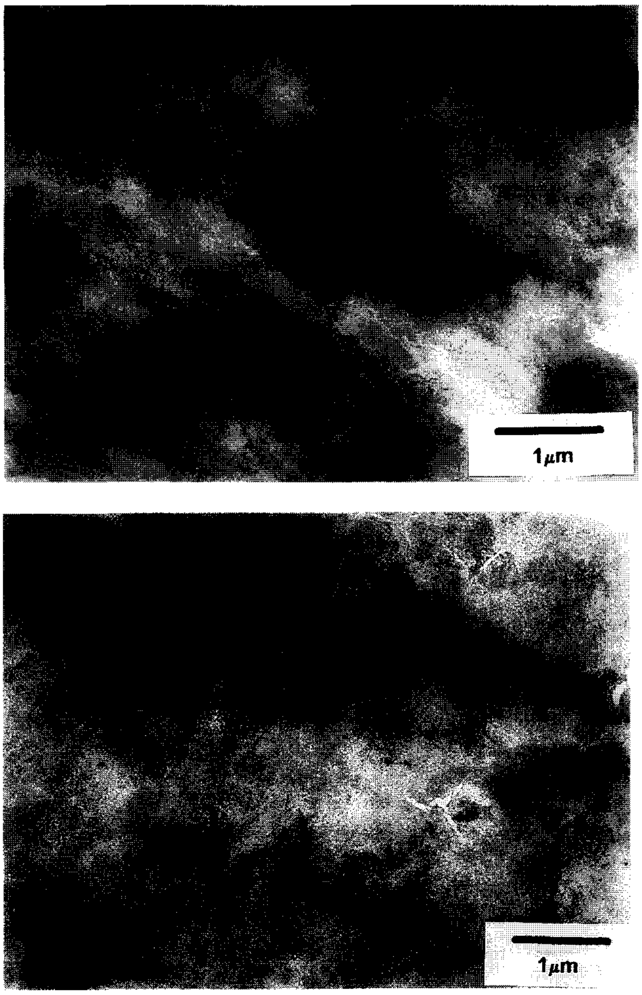

Figure 2 Transmission electron micrographs of polyurethane mixtures: (a) 60 wt% polyurethane A/40 wt% BTDI-4; (b) 60 wt% polyurethane A/40 wt% BMDI-4

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