Polymers from Multifunctional Isocyanates. 5.[†] Synthesis of Liquid-Crystalline Polyurethanes from Methyl-Substituted Diisocyanato-Substituted Benzoates

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Received March 29, 1990

ABSTRACT: A number of new aromatic or cycloaliphatic diisocyanato-substituted benzoates: 4-isocyanatophenyl 4-isocyanatobenzoate, *trans*-4-isocyanatocyclohexyl 4-isocyanatobenzoate, and several derivatives with lateral methyl substituents were synthesized by the reaction of appropriate (trimethylsiloxy)phenyl or cyclohexyl isocyanates and isocyanatobenzoyl chlorides. They were reacted with 3-methyl-1,5-pentanediol and mixtures of two different diols to give hard-segment type polyurethanes. The influence of the substituents on the thermal behavior of the polyurethanes was studied and compared to the parent isocyanates. Monotropic nematic liquid-crystalline phases could be observed with polyurethanes from the unsubstituted 4-isocyanatophenyl 4-isocyanatobenzoate. In the case of the other polyurethanes, the melting points could be lowered, but this decrease was accompanied by the loss of liquid-crystalline properties.

Introduction

Synthesis and investigation of liquid-crystalline main-chain polymers are mainly directed to high-strength fibers, high-modulus thermoplastic materials, and self-reinforcing polymers, which in addition should have a better high-temperature performance and resistance to thermal degradation. Polyurethanes made by step polycondensation from secondary amines and bischloroformates, recently described by Kricheldorf and co-workers, fit into this pattern.[1,2] Their synthesis by interfacial polymerization resembles that of polycarbonates whereas they are nitrogen analogous polyesters with regard to their properties.

Polyurethanes obtained by step polyaddition from diisocyanates and diols—the only technology of commercial importance—have the disadvantage of moderate thermostability and high melting enthalpy if they have a regular sequence of building blocks. Liquid-crystalline polyurethanes of this type published in the literature so far have been made from technical diisocyanates and mesogenic diols,[3,4] in one case from a mesogenic diisocyanate (3,3′-dimethyl-4,4′-diisocyanatobiphenyl).[5] The choice of mesogens seems to be governed by accessibility rather than systematic considerations. With one exception, the resulting mesophases have not been characterized or identified.

Despite the drawback of moderate thermostability, we thought it worthwhile to systematically investigate main-chain liquid-crystalline polyurethanes for several reasons: The drawbacks mentioned above could not prevent polyurethane elastomers and fibers from becoming important commercial products. The ease of synthesis and the variability in composition make them suitable substrates to investigate the influence of hydrogen bonding on the thermal behavior.

We restrict ourselves to mesogenic diisocyanates with the main emphasis on those having ester linking groups, since semirigid polyesters are supposedly the best investigated class of liquid-crystalline main-chain polymers.[6] A general synthesis of an ester group containing isocyanates starting from monoisocyanate precursors enables us to design isocyanates within this framework, to introduce substituents in various positions of the mesogens, and to study their influence on the mesomorphic properties.[7] Diad and triad para-linked aromatic diisocyanato esters, which have been described in a previous paper of this series, show liquid-crystalline properties.[8] However, they give polyurethanes, which are not stable enough to allow the investigation of their phase behavior due to their high melting points.

In continuation of our work on liquid-crystalline polyurethanes, we have been looking for a way to lower the transition temperatures of polyurethanes made from liquid-crystalline diisocyanates below their decomposition temperatures. One approach to realizing this goal was thought to be the controlled introduction of substituents in the isocyanates to produce unsymmetrical polyurethanes without changing the rodlike character of the mesogens. Substituents in the ortho position of the isocyanate may also prevent or diminish the formation of hydrogen bonds in the polyurethanes.

Therefore, we were interested in mesogenic diisocyanates having methyl substituents in various positions of the aromatic rings. The central core of the molecules used in this study was chosen to consist of 1,4-phenylene or *trans*-1,4-cyclohexanediyl rings with an ester bridging group.[6]

Results and Discussion

Synthesis of Mesogenic Diisocyanato Esters. The diisocyanato esters were obtained by reaction of appropriate 4-isocyanatobenzoyl chlorides with 4-(trimethylsiloxy)phenyl or cyclohexyl isocyanates as outlined in Scheme I.

Trimethylsiloxy group containing isocyanates were synthesized from suitable amino hydroxy compounds **1a**–**6a** (phenols, cyclohexanol, aminobenzoic acids), which were converted into the (trimethylsiloxy)amines **1b**–**6b** by reaction with hexamethyldisilazane.[9] Since silylation of the amino group requires more drastic conditions, the desired compounds were obtained in almost quantitative yields when hexamethyldisilazane was used in an amount sufficient for silylation of the hydroxyl groups. The (trimethylsiloxy)phenyl isocyanates or cyclohexyl isocyanate are liquids or low melting solids [(trimethylsilyl) 4-aminobenzoate)]. The properties are given in Table I.

The amino trimethylsiloxy compounds were reacted with excess high boiling isocyanate (4,4′-diisocyanatodiphenyl-

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[†] Part 4: Mormann, W.; Hohn, E. *Makromol. Chem.* 1989, *190*, 1919.

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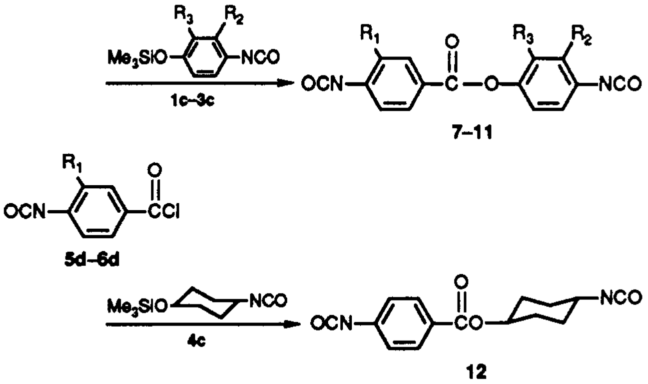
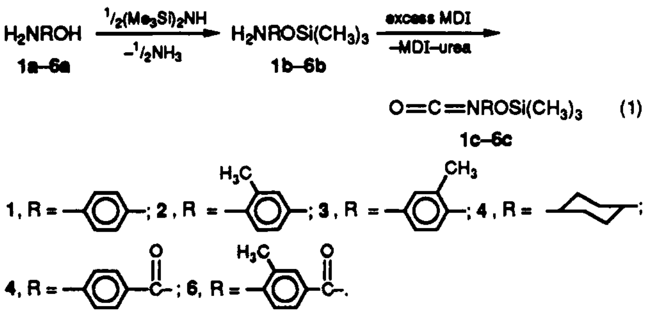
Scheme I[a]



[a] 7: $R_1 = H, R_2 = H, R_3 = H$.
8: $R_1 = CH_3, R_2 = H, R_3 = H$.
9: $R_1 = H, R_2 = CH_3, R_3 = H$.
10: $R_1 = H, R_2 = H, R_3 = CH_3$.
11: $R_1 = CH_3, R_2 = CH_3, R_3 = H$.

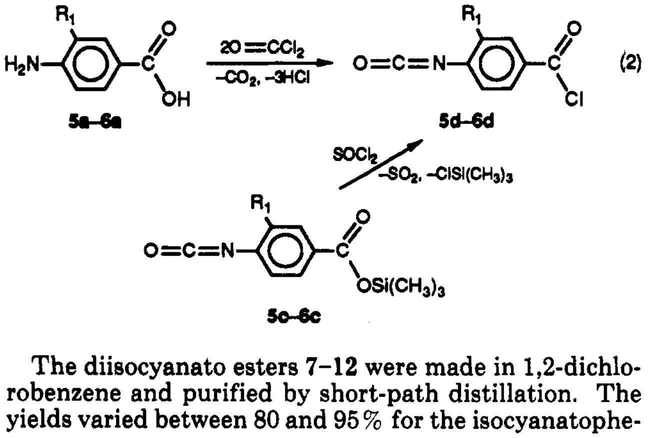
methane, MDI) to give the desired trimethylsiloxy isocyanates (eq 1 and Table II).[10] This synthesis involves



$$\underset{\mathbf{1a-6a}}{H_2NROH} \xrightarrow[-1/2 NH_3]{1/2 (Me_3Si)_2NH} \underset{\mathbf{1b-6b}}{H_2NROSi(CH_3)_3} \xrightarrow[-MDI-urea]{excess\ MDI} \underset{\mathbf{1c-6c}}{O{=}C{=}NROSi(CH_3)_3} \quad (1)$$

formation and cleavage of ureas, and the equilibrium is shifted toward the desired products by continuous distillation. Therefore, the limiting feature of this reaction is the boiling point of the target isocyanate, which has to be lower than that of the "high boiling isocyanate". The presence of hexamethyldisilazane from the previous step may cause trimerization and carbodiimide formation leading to cross-linking and evolution of carbon dioxide.[11]

Isocyanatobenzoyl chlorides were obtained from the corresponding amino acids either by phosgenation[12] or by reaction of the isocyanato silyl ester with thionyl chloride. The latter is a convenient laboratory alternative to the treatment with carbonyl chloride, especially as the yields are comparable or even better. The crude amino acid silyl esters may be used to make the isocyanato silyl esters, and these can be transformed into the isocyanato acid chlorides without further purification (eq 2, Table II).



The diisocyanato esters 7-12 were made in 1,2-dichlorobenzene and purified by short-path distillation. The yields varied between 80 and 95% for the isocyanatophenyl isocyanatobenzoates; that of the cyclohexyloxy group containing diisocyanato ester was markedly lower. Elimination, obviously, becomes an important side reaction for the secondary aliphatic trimethylsiloxy compound, especially in the presence of acidic catalysts.

Kricheldorf found that the reaction of the chloroformyl group with (trimethylsiloxy)arenes does not proceed even at high temperatures if very pure starting materials are used. He showed that chloride ions, either present in the reaction mixture or deliberately added, act as a catalyst (base catalysis).[13] We used proton and Lewis acids as well as bases [4-(dimethylamino)pyridine] for this purpose without investigating the mechanism of catalysis.

The diisocyanato esters are crystalline at room temperature. They show the characteristic absorptions of the isocyanate, ester carbonyl group, and aromatic double bonds. The properties of the diad diisocyanato esters are given in Table III. The unsubstituted 4-isocyanatophenyl 4-isocyanatobenzoate (7) has been described previously.[8]

A ^{13}C NMR spectrum of the cycloaliphatic compound was recorded in order to ensure that no isomerization of the desired trans isomers occurred during the reactions. Figure 1 shows the ^{13}C NMR spectrum of 12. The purity was estimated from the chemical shifts of the carbon atoms in the cyclohexyl ring as reported by Kricheldorf.[14] The presence of the cis isomer would be indicated by additional signals about 1-2 ppm downfield from the absorptions of the corresponding carbon atoms in the trans configuration.

The mesomorphic properties of the diisocyanato esters, the influence of the structure on the transition temperatures, and the effect of [2 + 2] cycloaddition (formation of 1,3-diazetidine-2,4-diones) have been discussed elsewhere.[15]

Poly(ester urethane)s. Poly(ester urethane)s 13-18 were made from the diisocyanates described above to study the influence of substituents on the thermal transitions. From the results obtained in an investigation of polyurethanes from the unsubstituted isocyanatophenyl isocyanatobenzoate and a series of different short-chain diols,[8] 3-methyl-1,5-pentanediol was chosen as the most able chain extender. Step polyadditions were made in *N,N*-dimethylacetamide (DMA) at 80-100 °C with no added catalyst. The reactivities of the diisocyanato esters are rather high; the isocyanate absorption had already disappeared when the mixture reached the final reaction temperature. The polyurethanes were precipitated in methanol and purified by dissolution in DMA and reprecipitation in methanol. A series of polyurethanes with different molecular weights (viscosities) was made from 4-isocyanatophenyl 4-isocyanatobenzoate by variation of the stoichiometry (excess of diol) in order to investigate the dependence of the thermal properties on molecular weight (13-13c). The polyurethanes were characterized by infrared spectroscopy, elemental analyses, GPC, and inherent viscosities. Composition, reaction conditions, and properties of the polyurethanes are summarized in Table IV.

The inherent viscosity of the polyurethanes varies from 0.4 to 0.8 dL/g for the aromatic diisocyanato esters. It is lower (0.2) for the cyclohexyl compound 18. Side reactions may occur due to the longer reaction time and the introduction of humidity during the removal of aliquots for reaction control by IR spectra. GPC results are in agreement with the viscosity data; they proved the absence of low or high molecular weight tails (Figures 2 and 3). In the series of polymers 13 with different molecular weights, GPC investigation in addition shows that there are no

Table I
Properties of (Trimethylsiloxy)amines

no.	mol formula (MW)	yield, %	bp, °C (mbar)	^{1}H NMR, ppm	IR absorptions, cm^{-1}	elem anal., %	C	H	N
2b	$C_{10}H_{17}NOSi$ (195.33)	97	121 (15)	6.5 (m, 3 H); 3.3 (s, 2 H); 2.07 (s, 3 H); 0.21 (s, 9 H)	3460, 3380, 1610, 850	calc found	61.5 61.3	8.77 8.60	7.17 6.96
3b	$C_{10}H_{17}NOSi$ (195.33)	98	54 (0.07)	6.7–6.3 (m, 3 H); 3.4 (s, 2 H); 2.14 (s, 3 H); 0.25 (s, 9 H)	3460, 3380, 1600, 850	calc found	61.5 61.5	8.77 8.80	7.17 7.30
4b	$C_9H_{21}NOSi$ (187.35)	88	82 (15)	3.4 (m, 1 H); 2.5 (m, 1 H); 1.9–0.8 (m, 10 H); 0 (s, 9 H)	3370, 3280, 1100, 840	calc found	57.7 55.6	11.3 11.1	7.48 7.55
6b	$C_{11}H_{17}NO_2Si$ (223.34)	94	120 (0.03) (mp 68 °C)	8.0–6.5 (m, 3 H); 4.2 (s, 2 H); 2.14 (s, 3 H); 0.38 (s, 9 H)	3480, 3370, 1670, 1600, 850	calc found	59.2 59.0	7.67 7.40	6.27 6.00

Table II
Properties of Trimethylsiloxy Isocyanates and Isocyanatobenzoyl Chlorides[a]

no.	mol formula (MW)	yield, %	bp, °C (mbar)	^{1}H NMR, ppm	n^{20}_D	elem anal., % C calc	C found	H calc	H found	N calc	N found
2c	$C_{11}H_{15}NO_2Si$ (221.34)	93	67 (0.06)	7.0–6.5 (m, 3 H); 2.21 (s, 3 H); 0.24 (s, 9 H)	1.5056	59.7	59.8	6.9	6.9	6.3	6.4
3c	$C_{11}H_{15}NO_2Si$ (221.34)	90	120 (15)	7.1–6.6 (m, 3 H); 2.18 (s, 3 H); 0.3 (s, 9 H)	1.5069	59.8	60.3	6.9	6.8	6.3	6.6
4c	$C_{10}H_{19}NO_2Si$ (213.35)	71	96 (15)	3.9–3.2 (m, 2 H); 2.2–1.1 (m, 8 H); 0.13 (s, 9 H)	1.4492	56.3	56.1	9.0	9.0	6.6	6.5
6c	$C_{12}H_{15}NO_3Si$ (249.34)	85	77 (0.03) (mp 52 °C)	7.9–7.0 (m, 3 H); 2.35 (s, 3 H); 0.39 (s, 9 H)		57.8	57.6	6.1	5.9	5.6	5.5
6d	$C_9H_6NO_2Cl$ (196.61)	78	66 (0.07)	8.0–7.0 (m, 3 H); 2.39 (s, 3 H)	1.5952	55.0	55.3	3.6	3.5	7.1	7.2

[a] IR absorptions: 2280 (N=C=O), 1775 + 1755 (C=O acid chloride), 1685 (C=O silyl ester), 1600 cm^{-1} (C=C). ^{13}C NMR of **4c**: 122.4 (NCO); 68.7 (CO); 52.5 (CN); 32.6 + 31.8 ppm (CH$_2$).

Table III
Properties of Diisocyanato-Substituted Benzoates[a]

no.	yield, %	bp,[b] °C	^{1}H NMR, ppm	mol formula (MW)	elem anal., % C calc	C found	H calc	H found	N calc	N found
7	90	190	7.09 (s, 4 H); 7.0–8.2 (AA′XX′, 4 H)	$C_{15}H_8N_2O_4$ (280.23)	64.3	64.4	2.9	2.9	10.0	10.0
8	95	180	2.41 (s, 3 H); 7.15 (s, 4 H); 7.1–8.1 (m, 3 H)	$C_{16}H_{10}N_2O_4$ (294.26)	65.31	65.5	3.43	3.6	9.52	9.6
9	92	180	2.33 (s, 3 H); 6.9–7.1 (m, 3 H); 7.1–8.2 (AA′XX′, 4 H)	$C_{16}H_{10}N_2O_4$ (294.26)	65.31	65.7	3.43	3.4	9.52	9.7
10	80	190	2.15 (s, 3 H); 6.9–7.1 (m, 3 H); 7.1–8.3 (AA′XX′, 4 H)	$C_{16}H_{10}N_2O_4$ (294.26)	65.31	65.25	3.43	3.6	9.52	9.6
11	90	195	2.36 (s, 3 H); 2.42 (s, 3 H); 6.9–8.1 (m, 6 H)	$C_{17}H_{12}N_2O_4$ (308.28)	66.23	66.4	3.92	4.0	9.08	9.2
12	20	160	1.5–2.3 (m, 8 H); 3.62 (m, 1 H); 5.04 (m, 1 H); 7.0–8.1 (AA′XX′, 4 H)	$C_{15}H_{14}N_2O_4$ (286.28)	62.93	63.1	4.93	5.2	9.78	9.85

[a] IR absorptions: 2300–2280 (N=C=O), 1745–1710 cm^{-1} (C=O). ^{13}C NMR of **12**: 164.8 (COO), 137.9 (C4), 131 (C3, C5), 127.9 (C1), 125.5 (N=C=O at C4), 124.6 (C2, C6), 122.4 (N=C=O at C4′), 71.2 (C1′), 51.9 (C4′), 31.1 + 28.1 ppm (C2′, C3′, C5′, C6′). [b] Temperature of heating cylinder of the glass tube oven.

figl

x = 240q; y = 132q

Figure 1. ^{13}C NMR spectrum of *trans*-4-isocyanatocyclohexyl 4-isocyanatobenzoate (**12**).

irregularities; i.e., increasing viscosity corresponds to increasing molecular weight from GPC. However, we believe it to be misleading to assign molecular weights to the polyurethanes by comparison to the polystyrene standards normally used for calibration in GPC, since these numbers are far too high to be of any real significance.

The thermal behavior of the polyurethanes was studied by polarized light microscopy and differential scanning calorimetry. The results are shown in Table IV. The transition temperatures of the isocyanates and the corresponding polyurethanes are also given for reasons of comparison.

In the diisocyanato esters lateral methyl substituents in the ortho position to either (**8**, **9**) or both of the isocyanate groups (**11**) lower the melting points by 40–50 °C with regard to the parent compound. A methyl group in the 2 (meta) position (**10**) lowers it less (15 °C). The strongest decrease is found for the cyclohexyl derivative (**12**) (almost 60 °C). The clearing temperatures are lowered even more, with the result that monotropic liquid-crystalline compounds are obtained except for **11**, which has no liquid-crystalline properties.

The melting points of the corresponding polyurethanes (**13**–**18**) do not change in the same way. The results can be explained best by taking into account the symmetry of the repeat unit and the steric hindrance of hydrogen bond formation by ortho methyl substituents. The unsubstituted compound (**13**) melts at 259 °C. The strongest decrease is observed with one methyl group in the 3 or 3′ position (**14**, **15**), causing disturbance of hydrogen bonding as well as dissymmetry. It is smaller with a 2′-methyl

Table IV
Properties of Polyurethanes

no.	isocyanate[a] no.	isocyanate[a] phase behavior[d]	diol[b]	yield, %	η_{inh},[c] dL/g	thermal and phase behavior[d]	TG, °C onset	TG, °C 5% loss
13	7	118 n (148 i)	MPD	85	0.72	k 259 n (242 i)	320	316
13a	7		MPD	86	0.45	k 259 n (236 i)	312	306
13b	7		MPD	59	0.35	k 258 n (222 i)	358	347
13c	7		MPD	75	0.16	k 252 n (<225 i)	325	315
14	8	83 n (74 i)	MPD	76	0.33	k 170 i	323	306
15	9	73 n (72 i)	MPD	76	0.37	k 164 i	319	298
16	10	103 a (56 i)	MPD	87	0.71	k 216 i	310	290
17	11	70 i	MPD	78	0.86	k 221 i	322	306
18	12	60 a (14 i)	MPD	55	0.21	k 247 i	299	277
19	7		MPD + TEG[e]	64	0.64	k 243 a (222 i)	310	320
20	7		MPD + BUD[e]	80	0.78	k 265 a (258[f] i)	308	315
21	7 + 9[g]		MPD	65	0.65	k 233 i	306	320

[a] Cf. Table I. [b] MPD, 3-methyl-1,5-pentanediol; TEG, triethylene glycol; BUD, 1,4-butanediol. [c] Inherent viscosity in DMA at 25 °C at a concentration of 0.3 g/dL. [d] k, crystalline; n, nematic; a, anisotropic; i, isotropic. [e] Molar ratio 75:25. [f] Observed by microscopy. [g] Molar ratio 70:30.

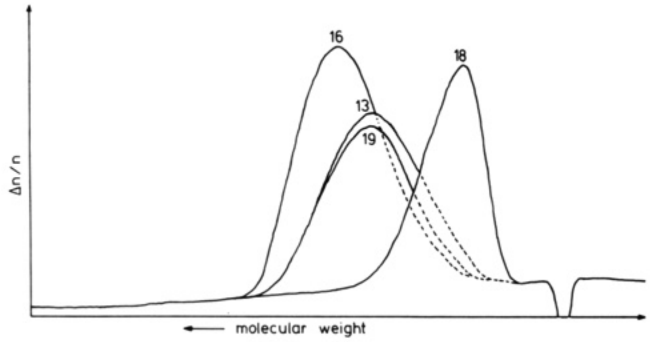


Figure 2. GPC curves of polyurethanes **13**, **16**, **18**, and **19**.

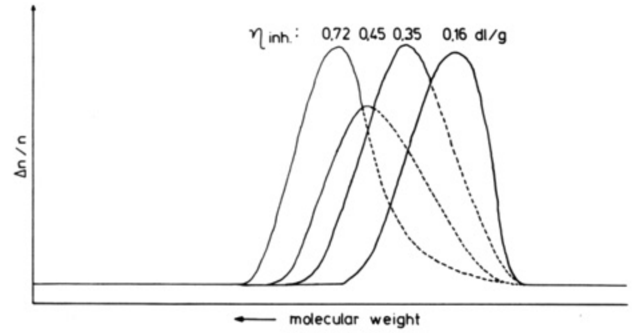


Figure 3. GPC curves of polyurethanes **13**–**13c**.

group (**16**), less for the 3,3′-dimethyl compound (**17**) resulting in a symmetric repeat unit, and almost zero for the cyclohexyl benzoate (**18**). This is rather surprising and is in contrast to the strong decreasing effect of the *trans*-1,4-cyclohexanediyl moiety in the parent isocyanate.

A liquid-crystalline phase was observed only for polyurethanes **13** from the unsubstituted isocyanatophenyl isocyanatobenzoate. When heated to melting, a nematic texture can be seen on cooling under the microscope. Figure 4 shows a micrograph of **13a** taken after cooling the sample below the clearing transition, which exhibits nematic droplets and schlieren. It must be mentioned however that it is difficult to obtain characteristic textures because of the high tendency of the polyurethanes to crystallize, which does not allow us to keep the samples in the liquid-crystalline phase over longer periods in order to develop better textures. DSC studies of **13a** in the cooling mode further supported the existence of a nematic mesophase. An exotherm is found at 236 °C for the isotropic–nematic transition and at 216 °C for recrystallization, as can be seen from Figure 5. None of the other binary polyurethanes showed mesomorphic properties.

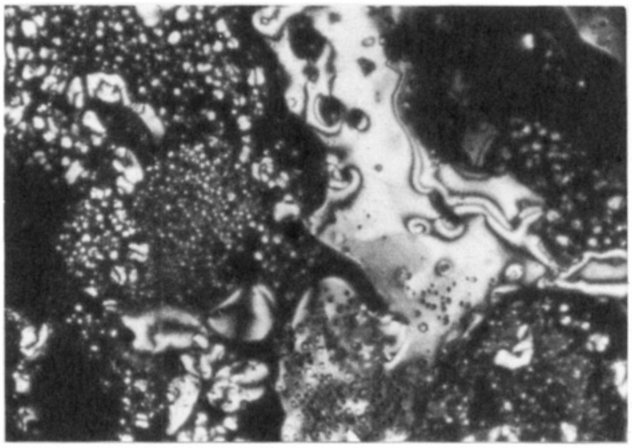


Figure 4. Optical micrograph of polyurethane **13a** at 230 °C showing nematic droplets and schlieren (original magnification 130×).

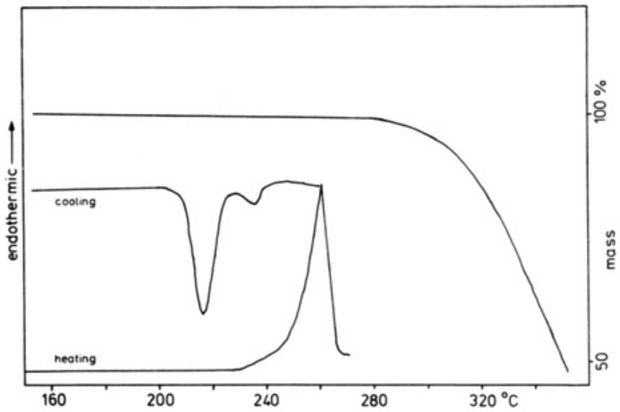


Figure 5. DSC and thermogravimetry curves of polyurethane **13a** (heating and cooling rates 20 K/min).

In addition to the binary polyurethanes, ternary copolyurethanes from mixtures of one diisocyanate with two diols and of two diisocyanates with one diol were made (Table IV, entries **19**–**21**). The diols were used in a molar ratio 3:1 (3-methyl-pentanediol–1,4-butanediol or triethylene glycol). The polyurethanes from two diols had liquid-crystalline properties as can be seen for **19** in Figure 6, whereas the methyl group in the isocyanate mixture was sufficient to suppress liquid crystallinity. The melting temperatures of the copolymers change toward those of the corresponding homopolymer from the added diol and isocyanatophenyl isocyanatobenzoate, which have been described earlier.[8]

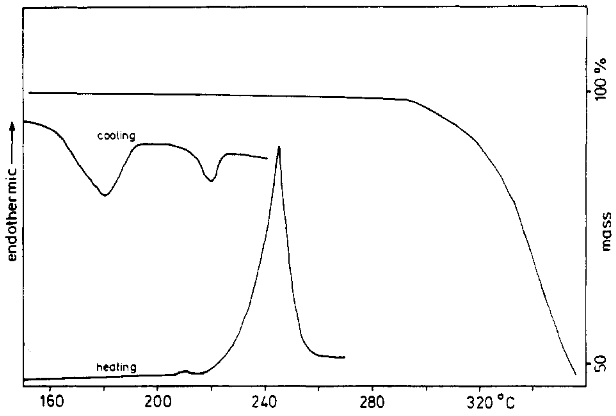


Figure 6. DSC and thermogravimetry curves of polyurethane **19** (heating and cooling rates 20 K/min).

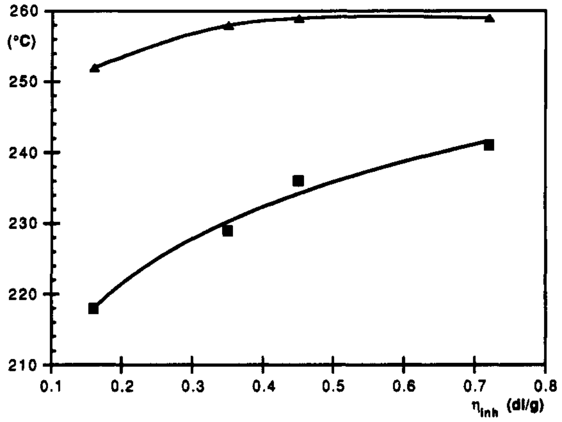


Figure 7. Dependence of thermal transitions of polyurethanes **13** from inherent viscosity (molecular weight): upper curve, crystalline melting; lower curve, nematic–isotropic transitions.

Phase transitions of polyurethanes occurring at temperatures above 200 °C may be influenced by decomposition due to the reverse reaction. We have investigated the effect of molecular weight (inherent viscosity) on the melting and isotropization temperatures of polyurethanes **13**. These data are presented in Figure 7, which shows the expected increase of both transition temperatures with molecular weight. The molecular weight represented by an inherent viscosity of 0.7 dL/g seems to be well in the range where the transitions are independent of molecular weight. The clearing transition is lowered by 6–10 °C after keeping the sample for 15 min in the nematic phase, and this means that the inherent viscosity (molecular weight) decreases by a factor of less than 2. Thus a certain extent of cleavage of urethane groups has to be assumed at these temperatures. However, FT-IR spectroscopy of a glassy nematic polyurethane up to 230 °C, which is above its clearing temperature, shows only a very weak isocyanate absorption, which is significantly weaker than that of a similar polyurethane in the isotropic phase at the same temperature.[16] This further proves that the polyurethanes are in an equilibrium with the reverse products, which can be regarded as stable during the time of observation. Thermogravimetric analysis as shown in Figures 5 and 6 for polyurethanes **13a** and **19** shows an onset of weight loss at 30–50 °C above the melting temperature of the polyurethanes, which is 80–100 °C higher than the boiling temperature of the chain extenders. Significant decomposition, therefore, should be accompanied by a noticeable weight loss.

Conclusions

It has been shown by us[15] that isocyanate groups have a strong stabilizing effect on the liquid-crystalline range of mesogenic compounds as compared to other terminal groups with a chain of three atoms. In contrast to the stabilizing effect of the isocyanate moiety in the isocyanatophenyl isocyanatobenzoates, transformation into the urethane group reduces the ability to obtain mesophases because of the high melting points resulting from hydrogen bond formation.

It is possible to lower the melting points of the polyurethanes by systematic introduction of methyl substituents in various positions of the isocyanate and to investigate the effect of substitution and substitution pattern. The influence of substitution on clearing temperatures is even stronger with the result that liquid-crystalline phases cannot be observed in polyurethanes from substituted diisocyanato-substituted benzoates. Diad mesogenic diisocyanates obviously have too small an aspect ratio to overcome this effect, since similar results have been found with other compounds, e.g., 4,4′-diisocyanatobiphenyl and 4,4′-diisocyanato-*trans*-stilbene based diurethanes, which have been published recently,[17] and polyurethanes from 4-isocyanatoazobenzene.[18]

Our further efforts will be devoted to triad diisocyanato esters, which have a more favorable aspect ratio and therefore higher clearing temperatures.[16] The introduction of lateral substituents will probably allow a reduction of the melting points without losing the enantiotropic liquid-crystalline properties.

Experimental Part

Materials. 4-Hydroxyaniline, 4-hydroxy-3-methylaniline, 4-hydroxy-2-methylaniline, 4-aminobenzoic acid, and 3-methyl-4-aminobenzoic acid were purchased from Janssen. *trans*-4-Aminocyclohexanol was purchased from Aldrich. The diols were distilled in vacuo before use.

Methods of Characterization. IR spectra were recorded on a Bruker IFS48 FT-IR spectrometer using films or Nujol mulls between NaCl plates. ^1H NMR spectra were obtained on a Bruker WP 80 and ^{13}C NMR spectra on a Bruker WH 400 (100 MHz) in deuteriochloroform using tetramethylsilane (TMS) or $CHCl_3$ as internal standard. Viscometry was performed with an Ubbelohde type viscometer. The thermal properties were investigated with a Mettler TA 4000 system with DSC 30 and TG 50 equipment. Heating rates were 20 K/min. The birefringent textures were observed with a Leitz Ortholux 12 polarizing microscope equipped with an FP 82 hot stage (Mettler).

All reactions were made in flame-dried glass equipment in an argon atmosphere.

(Trimethylsiloxy)amines 1b–6b. General Procedure. A total of 0.3 mol of the amino hydroxy compound, 0.15 mol of hexamethyldisilazane, and 0.5 mol % saccharin were heated slowly (to control the evolution of ammonia) to 140 °C where a clear solution was obtained and stirred for 2 h at this temperature. The (trimethylsiloxy)amines were purified by vacuum distillation. For yields and properties see Table I.

Trimethylsiloxy Isocyanates 1c–6c. General Procedure. A total of 200 g of 4,4′-diisocyanatodiphenylmethane (MDI) was heated to 100 °C, 0.3 mol of (trimethylsiloxy)amine was added, the mixture was heated to 180–195 °C, and the volatile compounds (trimethylsiloxy isocyanate) were distilled off in vacuo (0.5 mbar) until the boiling point reached that of MDI (160 °C). The crude isocyanates were purified by redistillation. For yields and properties see Table II.

3-Methyl-4-isocyanatobenzoyl chloride (6d) was obtained from the reaction of 0.2 mol of **6b** with 0.6 mol of thionyl chloride and purified by vacuum distillation.

Diisocyanato Esters 7–12. General Procedure. A total of 25 mmol of a 4-isocyanatobenzoyl chloride (**5d** or **6d**) and of a 4-(trimethylsiloxy)phenyl isocyanate (**1c**–**4c**) together with 20 mg of catalyst (sulfuric acid for **7**–**11**, DMAP in the case of **12**) in 6 mL of 1,2-dichlorobenzene were heated to 165 °C while trimethylchlorosilane was removed at 500 mbar. The reactions were monitored by IR spectroscopy and stopped when the absorption of the chloroformyl group had disappeared (6–9 h). The reaction of **4c** and **5d** to give **12** was stopped after 30 min to reduce elimination. The resulting ester diisocyanates were purified by short-path distillation in a Büchi glass tube oven. For boiling and melting points, yields, IR absorptions, and elemental analyses, see Tables III and IV.

Poly(ester urethane)s (13–21). A total of 2.5 mmol of the ester diisocyanate and the equivalent amount of the appropriate diol were diluted with 5 mL of dimethylacetamide, stirred, and heated to 90 °C for 2 h (10 h at 110 °C for **18**). The polymers were precipitated in methanol, filtered off, and dried in vacuo. Yields and properties are given in Table IV.

Acknowledgment. We are indebted to the Deutsche Forschungsgemeinschaft and to Bayer AG, Leverkusen, for financial support and a generous gift of chemicals.

References and Notes

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Registry No. **2b**, 122993-90-2; **2c**, 122993-92-4; **3b**, 131457-68-6; **3c**, 131513-80-9; **4b**, 122993-89-9; **4c**, 122993-91-3; **6b**, 131457-69-7; **6c**, 131457-70-0; **6d**, 131457-71-1; **7**, 92429-58-8; **8**, 121565-67-1; **9**, 121565-68-2; **10**, 121565-69-3; **11**, 121565-70-6; **12**, 131457-72-2; **13a** (copolymer), 121178-01-6; **14** (copolymer), 131457-83-5; **15** (copolymer), 131457-84-6; **16** (copolymer), 131457-85-7; **17** (copolymer), 131489-31-1; **18** (copolymer), 131489-32-2; **19** (copolymer), 131457-86-8; **20** (copolymer), 131457-87-9; **21** (copolymer), 131457-88-0.