

## **4,4'-diisocyanatoazobenzene a mesogen for liquid crystalline polyurethanes?**

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### **Abstract**

The mesomorphic properties of 4,4'-diisocyanatoazobenzene were investigated by polarizing microscopy and DSC. It shows a nematic phase when thoroughly purified by distillation. The nematic range, however, is smaller than that of other liquid crystalline diisocyanates like 4,4'-diisocyanatophenyl benzoate. A number of binary hard segment type polyurethanes was made with several diols as chain extenders and in addition ternary copolyurethanes containing two different mesogenic diisocyanates. They are crystalline materials with poor solubility. The melt temperatures of these polyurethanes are higher than those of the corresponding polymers with 4,4'-diisocyanatophenyl benzoate. Liquid crystalline behaviour could not be observed in any of the polymers probably because of the high melting transitions and relatively lower isotropization temperatures which result from the higher rigidity and symmetry of the azobenzene structure.

### **Introduction**

Liquid crystalline polyurethanes obtained by step polyaddition reactions have been described or claimed in several recent papers(1-3). They were made from either a mesogenic diisocyanate and common chain extenders or a mesogenic diol and technical diisocyanates. A different approach is based on step polycondensation of bischloroformates and secondary diamines of the piperazine type(4,5).

In our investigation of liquid crystalline polyurethanes based on mesogenic diisocyanates we have shown that liquid crystalline polyurethanes from diad 4,4'-diisocyanatophenyl benzoates and normal diols cannot be obtained; only in the case of special chain extenders like 3-methyl-1,5-pentanediol monotropic nematic phases were observed(6). Enantiotropic phases resulted from mixtures of two diols with chainlength sufficiently different to suppress crystallisation. The clearing point, however, was still below the virtual melting temperature of the copolymer. Methyl substituents in various positions of the isocyanate gave a strong depression of isotropization temperatures and no mesomorphic phases could be observed in the corresponding polyurethanes(7).

We were interested to prove whether this behaviour is restricted to the diisocyanatoesters or a common feature of other liquid crystalline diisocyanates and the corresponding polyurethanes. Derivatives of 4,4' disubstituted azobenzene are known to have mesogenic properties; they have been widely used for low molecular weight liquid crystals(8) for side chain lc-polymers as well as for main chain lc-polymers like semirigid polyesters(9). 4,4'-Diisocyanatoazobenzene which has been used to make polyurethanes in very few cases up

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to now is of interest for various reasons: as a probe for the mobility of the local environment by the rate of *cis/trans* isomerization(10), as a sensor for the rate of polyurethane formation and finally as a way to compare isostructural rigid rod and coiled polymers having identical molecular weight.

The present investigation deals with the characterization of the mesogenic properties of diisocyanatoazobenzene as well as the synthesis and characterization of several binary and ternary polyurethanes.

## Experimental

**Methods of characterization:** IR spectra were recorded on a Bruker ISF48 FTIR spectrometer as films or nujol mulls between NaCl plates, <sup>1</sup>H-NMR spectra on a Bruker WP 80 in deuteriochloroform using TMS or CHCl<sub>3</sub> as internal standard. Viscometry was made with an Ubbelohde type viscosimeter. The thermal properties were investigated with a Mettler TA 4000 System, heating rates were 20 K/min unless otherwise stated. microscopy was made with a Leitz Laborlux polarizing microscope equipped with a Mettler FP 82 hot stage.

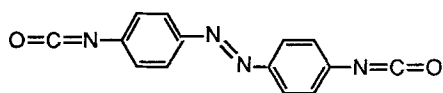
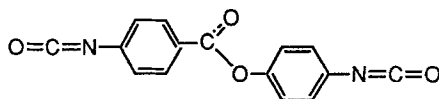
**Materials:** 1,4-Butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,10-decanediol from Bayer AG, Leverkusen, 3-methyl-1,5-pentanediol from BASF, Ludwigshafen, and diethylene-glycol from Bayer were distilled in vacuo before use. N,N-Dimethylformamide (DMF) and N,N-dimethylacetamide (DMA) were dried by distillation from phosphorous oxide. 4,4'-Diisocyanatophenyl benzoate was prepared as previously described(6). All reactions were made in flame dried glass equipment in an argon atmosphere.

**Poly(urethane)s (3-11) (general procedure).** To 7 ml DMA containing 5 % LiCl were added 5 mmol of the mesogenic diisocyanate **1** or **2** and the equivalent amount of a diol chain extender. The mixture was stirred and heated to 100 °C for 30 - 45 min and finally to 150 °C for 5 min. until the reaction was complete (IR-control). The polymers were precipitated in methanol, purified by reprecipitation, and dried in vacuo at 80 °C. Satisfactory micro analyses were obtained from all polymers. For m.p., yields,  $\eta_{inh}$  cf. Tab. 2.

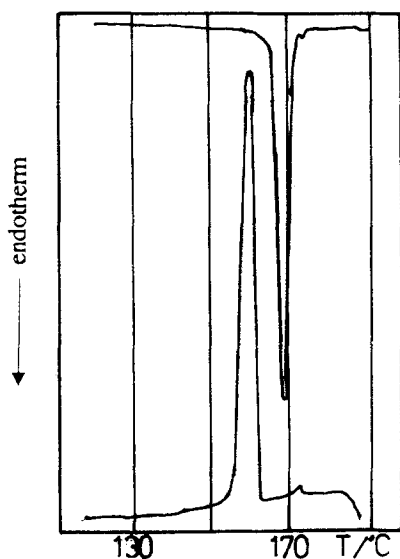
## Results and discussion

### 4,4'-diisocyanatoazobenzene

4,4'-Diisocyanatoazobenzene has been described for the first time in a paper by Siefken (11) and later by Shinde and coworkers(12). It is normally made by phosgenation of 4,4'-diaminoazobenzene. The reported melting point is 160 °C (12) The sample used in the present investigation was made by the same technique and obtained as a gift from Bayer AG. The crude product had a melting point of 165 °C and showed liquid crystalline properties though a clearing point could not be observed by DSC. It was further purified by short path distillation in a Kugelrohr apparatus which raised the melting point to 169.0 and the clearing point to 176 °C (Tab.1, Fig.1). A second distillation under identical conditions did not improve these values any further. The enantiotropic phase was identified as nematic from polarizing microscopy. The observed value of the enthalpy of isotropization is well within the range of nematic liquid crystals (13). As reported for other liquid crystalline diisocyanates the clearing transition decreases during the observation in the lc phase due to the high reactivity of the isocyanate moieties at these temperatures.

4,4'-diisocyanatoazobenzene **1**4,4'-diisocyanatophenylbenzoate **2****Tab. I:** Thermal transitions of mesogenic diisocyanates

Isocyanate	M.p. °C	T <sub>i</sub> °C	$\Delta H_{cn}$ kJ/mole	$\Delta H_{ni}$ kJ/mole
4,4'-diisocyanatoazobenzene	169.0	n 176	37.2	0.21
4,4'-diisocyanatophenyl benzoate	118.0	n 148	34.2	0.82

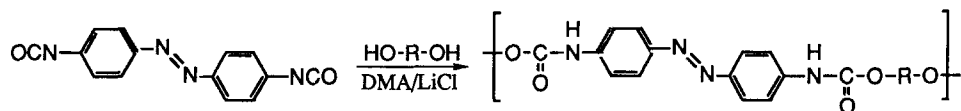
**Fig. 1:** DSC curve of 4,4'-diisocyanatoazobenzene **1** (upper curve heating, lower curve cooling, heating rate 5K/min).

The transition temperatures of 4,4'-diisocyanatoazobenzene are higher than those of the corresponding ester **2** the nematic range, however, is smaller due to the high melt transition of the former. The reason for this may be either the hindered rotation around the N=N double bond or the higher symmetry of the azo compared to the ester linking group. The latter, in addition, imparts different reactivity to both isocyanate moieties due to the electron withdrawing effect of the oxycarbonyl and the electron donating effect of the carbonyloxy group. From other low molecular weight azobenzene mesogens similar behaviour has been reported in comparison with less rigid mesogens.

### Polyurethanes

The polyurethanes described in this paper were made by step polyaddition in solution. In order to obtain reasonable molecular weight (inherent viscosities) DMA/5% LiCl was used as

solvent since the polymers had a limited solubility in DMA alone and precipitated from the reaction mixture in a rather early state of reaction. The reaction proceeded rapidly at 100 °C without the need of a catalyst. The polyurethanes were precipitated in methanol and purified by reprecipitation with the same solvent non solvent system.



We used a number of common diols as chain extenders with the aim to evaluate the influence of the chain length (number of carbon atoms in the spacer): 1,4-butanediol, 1,5-pentane-1,5-diol, 1,6-hexanediol, and 1,10-decanediol and the influence of substitution or hetero-atoms: 1,5-pentane-1,3-diol, 3-methyl-1,5-pentane-1,5-diol, and 3-oxa-1,5-pentane-1,5-diol (diethylene-glycol). In addition to the binary polyurethanes a ternary copolyurethane was prepared having equimolar amounts of the two mesogenic diisocyanates 1 and 2. The properties of the polyurethanes are listed in Tab. 2.

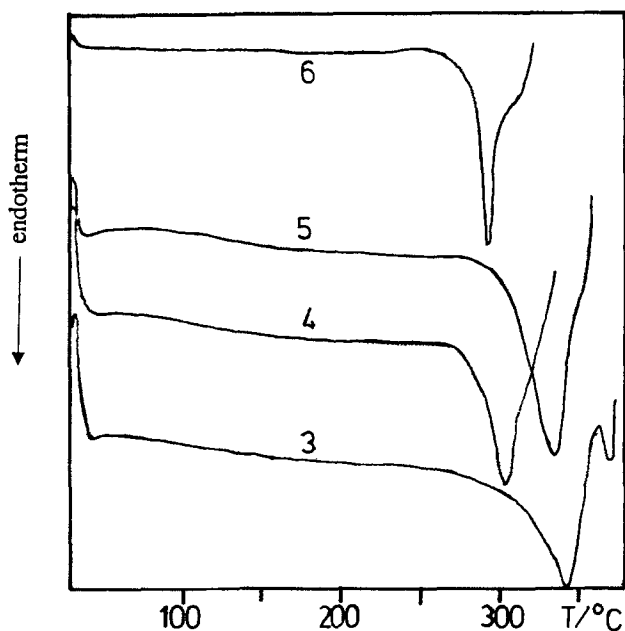


Fig. 2:  
DSC traces of polyurethanes  
3, 4, 5, and 6 (cf. Tab.2)

The inherent viscosities of the polyurethanes depend on the conditions of preparation: in the poorer solvent DMA lower viscosities result due to the precipitation of rather low molecular weight oligomers whereas high viscosities result after addition of 5 % LiCl. A further reason for the high values of the viscosity observed should also be the more rigid character of the azobenzene moiety in 1 as compared to the phenylbenzoate skeleton in 2 which is less rigid due to the single bonds connecting the two phenyl rings.

All polymers based on diisocyanate **1** are crystalline materials with very high melting points. The influence of the chain extender is as to be expected. It decreases with increasing chain length and there seems to be an odd even effect (Entries 3 -6, Tab. 2). Introduction of an oxygen in the 3-position of 1,5-pentanediol reduces the melting point further though a more pronounced effect is observed with an ethylidene moiety in the same position (**7**).

**Tab. 2:** Properties of polyurethanes from 4,4'-diisocyanatoazobenzene

No.	R	1)	Yield in %	M.p. <sup>2)</sup> in °C	$\eta_{inh}^3)$ in dl/g	M.p. <sup>2)</sup> PUR based on <b>2</b>
3	-(CH <sub>2</sub> ) <sub>4</sub> -	a	80	342 (dec.)	0.27	343(dec.)
		b	99	dec.	1.02	
4	-(CH <sub>2</sub> ) <sub>5</sub> -	a	70	300 (dec.)	0.24	328(dec.)
		b	96	302 (dec.)	1.05	
5	-(CH <sub>2</sub> ) <sub>6</sub> -	a	75	326 (dec.)	0.43	
6	-(CH <sub>2</sub> ) <sub>10</sub> -	a	98	298	--	281(dec.)
7	-(CH <sub>2</sub> ) <sub>2</sub> -CH(CH <sub>3</sub> )-(CH <sub>2</sub> ) <sub>2</sub> -	a	77	263	0.25	259
		b	96	277	1.20	
8	-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -	a	92	292	0.32	236
9 <sup>4)</sup>	-(CH <sub>2</sub> ) <sub>2</sub> -CH(CH <sub>3</sub> )-(CH <sub>2</sub> ) <sub>2</sub> -		94	242	0.30	
10 <sup>5)</sup>	-(CH <sub>2</sub> ) <sub>2</sub> -CH(CH <sub>3</sub> )-(CH <sub>2</sub> ) <sub>2</sub> -		88	254	0.28	

1) a in DMA without added LiCl, b in DMA with 5 % LiCl

2) Peak maxima from DSC

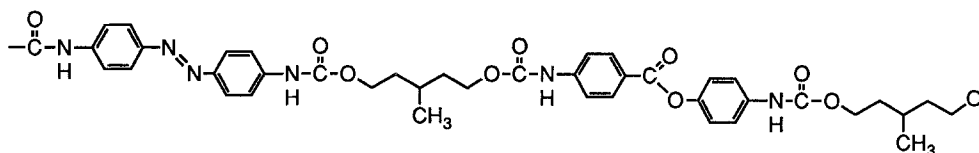
3) in DMA/5% LiCl, 25°C, 0.3 g/ dl

4) Isocyanates **1** and **2** in a molar ration 20 : 80

5) Isocyanates **1** and **2** in a molar ratio 50 : 50

The DSC traces of these compounds (cf. Fig. 2) show melting endotherms accompanied or followed by decomposition. It is somewhat speculative to assign true melting points to these endotherms since it is unknown to what extent decomposition (reverse reaction of the urethane groups) influences the liquification of these polyurethanes. Decomposition in terms of weight loss as determined by thermogravimetric analysis is in the same order as with isocyanate **2** though it reflects mainly evaporization of the diols used. Polyurethane **7** has a 5 % weight loss at 305 and the onset at 315 °C. The values of the corresponding polyurethane based on **2** are 10 °C higher The melting temperatures of the polyurethanes (**6**, **7** and **8**) from **1** which do not decompose immediately after melting are higher than those of the corresponding polymers based on **2** (**5**). This can be explained with the higher rigidity and symmetry of **1** as compared with **2**. The ester group of the latter can be randomly distributed in the polymer which in addition may contribute to the lower melting points of this series.

None of the binary polyurethanes showed liquid crystalline properties upon investigation by DSC and polarizing microscopy. In order to get an idea on the range of the virtual isotropization temperature copolymers were prepared having both diisocyanates (**1** and **2**) in different ratios and 3-methyl-1,5-pentanediol as chain extender. The corresponding unipolymer from **2** has a monotropic nematic phase and from the influence of **1** on the isotropization temperature the value for polyurethane **7** could be obtained by extrapolation.



**9, 10**

Two polyurethanes having 20 and 50 mole % of **1** were synthesized and investigated (entries No. **9** and **10** Tab. 2). The melting temperatures could be slightly lowered but again no liquid crystallinity was observed. Obviously the azobenzene group gives rise to polyurethanes in which the melting points are higher than those of polyurethanes from less symmetric diisocyanates like **2**. The clearing points of the polyurethanes based on **1**, however, are probably lower than those based on **2** because of the dipole moment of the latter which stabilizes the nematic phase and brings the isotropization temperature closer to the melting point.

## Conclusions

It has been shown in the present investigation that polyurethanes from the diaromatic mesogenic diisocyanato azobenzene **1** do not have liquid crystalline phases. The melting points of these polyurethanes are higher whereas the isotropization temperatures are lower than those of similar compounds based on diisocyanatophenyl benzoate. Obviously diaromatic mesogens have to low an aspect ratio to exhibit enantiotropic mesophases in hydrogen bond forming polymers.

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