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Synthesis and thermal properties of diurethanes containing various mesogenic units

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Five homologous series of diurethanes containing mesogenic moieties were synthesized by addition reactions of ω-alkenols to aromatic diisocyanates. The thermal behaviour of the compounds was studied by differential scanning calorimetry and on the hot stage of a polarizing microscope. Thermotropic liquid crystal behaviour was found for the diurethanes having a central core of more than two aromatic rings. Smectic C mesophases were observed for the derivatives of 4,4″-*p*-terphenylene and nematic mesophases for the diurethanes containing a di(4-phenylene)terephthalate unit. The compounds of both series possess high transition temperatures and narrow mesomorphic ranges.

1. Introduction

In spite of the great variety in chemical structure of liquid-crystalline compounds, few urethanes (carbamates) displaying mesomorphic behaviour have so far been synthesized and investigated. For low molar mass substances there are mainly reports on the preparation of liquid-crystalline steroidal urethanes [1]. Verbit and Lorenzo [2] have investigated 25 systems containing a central urethane linkage, but none was mesogenic. In the polymer field liquid-crystalline polyurethanes have received attention in recent years. A review on thermotropic liquid crystal main chain polyurethanes has been given by Sati [3]. However, in comparison with liquid-crystalline polyesters which have been examined extensively, only little is known about the specific features of this class of polymers.

In the present paper we report the synthesis and thermal properties of five homologous series of diurethanes which serve as model compounds for liquid crystal polyurethanes. The substances, obtained by addition reactions of ω-alkenols to aromatic diisocyanates, have the general formula

$$CH_2{=}CH{-}(CH_2)_n{-}O{-}CO{-}NH{-}R{-}NH{-}CO{-}O{-}(CH_2)_n{-}CH{=}CH_2$$

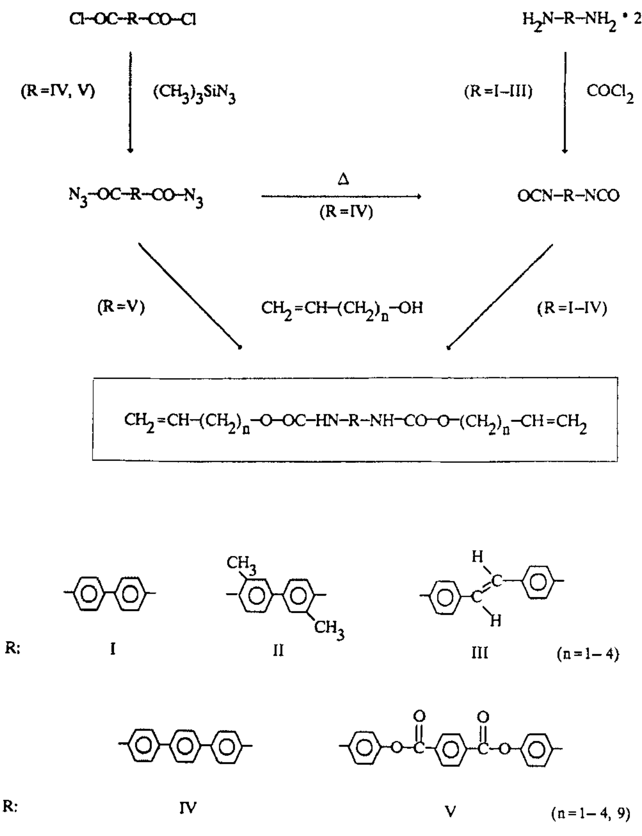
R= 4,4′-biphenylene (**I**), 3,3′-dimethyl-4,4′-biphenylene (**II**),
trans-stilbene-4,4′-diyl (**III**), $n = 1$–4;

R= 4,4″-*p*-terphenylene (**IV**), di(4-phenylene)terephthalate (**V**),
$n = 1$–4, 9.

The central cores (**I**)–(**V**) were selected for two reasons. First they can be prepared as diisocyanato derivatives and, secondly, they have been incorporated as mesogenic fragments in both liquid crystal polymers [4] and monomers [1, 5].

2. Synthesis of the diurethanes

The various synthetic routes used for the preparation of the diurethanes are shown in scheme 1. The diisocyanato derivatives of the mesogenic units were synthesized by two different methods. 4,4′-Diisocyanato-biphenyl [6], 3,3′-dimethyl-4,4′-diisocyanato-biphenyl [6] and 4,4′-diisocyanato-*trans*-stilbene [7] were obtained by phosgenation of the appropriate diamines. The diisocyanato derivatives of (**IV**) and (**V**) were made by a Curtius degradation based upon a method of Kricheldorf [8]. Thus, the 4,4″-diisocyanato-*p*-terphenyl was prepared from 4,4″-dichloroformyl- *p*-terphenyl and azidotrimethylsilane followed by thermal decomposition of the diazido compound formed. It is noteworthy that this diisocyanate already exhibits mesomorphic behaviour.



Scheme 1.

For the preparation of di(4-isocyanatophenyl)terephthalate we followed the same route. However, we could not obtain the product by thermal decomposition of di(4-azidoformylphenyl)terephthalate with sufficient purity. Nevertheless, heating the diazido derivative in the presence of the ω-alkenols afforded the diurethanes in good yields and purities.

In all other cases the desired products were obtained by a simple addition reaction of the ω-alkenols to the diisocyanates.

3. Results and discussion

The thermal properties of the homologous series were studied by differential scanning calorimetry and on the hot stage of a polarizing microscope. The results of these investigations are summarized in the table. Although the diurethanes were designed according to the building principles for liquid crystals (rigid central core and terminal groups in the long axis of the molecule) [9], only compounds of series (**IV**) and (**V**) containing an aromatic triad as the central unit exhibit mesomorphic behaviour. Obviously, a mesophase is only formed if the mesogenic group is sufficiently elongated. In general, symmetrically disubstituted *p*-terphenyl [10] and di(4-phenylene)-terephthalate [11] derivatives have a greater tendency to form a liquid-crystalline phase than comparable biphenyl [10] and stilbene [12] derivatives. The mesophase ranges of the diurethanes (**IV**) and (**V**) are small and the transition temperatures are high compared with the corresponding diesters [13]. This may be attributed to the additional NH-group which enables the diurethanes to form hydrogen bonds. It is likely that the increase in molecular interaction causes both the higher melting points and the lower thermal stability of the mesophases.

Thermal properties of the diurethanes.

Compound	*n*	Phase transition temperatures/°C (*a*)	Liquid crystal–isotropic transition enthalpies/kJ mol^{-1}
Ia	1	C 220 I	
Ib	2	C 213 I	
Ic	3	C 199 I	
Id	4	C 192 I	
IIa	1	C 174 I	
IIb	2	C 158 I	
IIc	3	C 126 I	
IId	4	C 117 I	
IIIa	1	C 248 I	
IIIb	2	C 242 I	
IIIc	3	C 230 I	
IIId	4	C 215 I	
IVa	1	C 291 S_C 332 I	11(*d*)
IVb	2	C 282 S_C 322 I	14(*d*)
IVc	3	C 269 S_C 312 I	15(*d*)
IVd	4	C 262 S_C 269 I	13(*d*)
IVe	9	C 235 S_C 243 I	21·5
Va	1	C 275 N 290 I	1·3
Vb	2	C 246 N 275 I	1·2
Vc	3	C 263 I (240 N) (*b*)	1·5
Vd	4	C 248 I (236 N) (*b*)	1·3
Ve	9	C 229 I (222 N) (*b*, *c*)	—

(*a*) C, crystalline; S_C, smectic C; N, nematic; I, isotropic; peak onset of the differential scanning calorimetry endotherms.

(*b*) Monotropic transition; I–N transition temperature and transition enthalpy destinated from the differential scanning calorimetry exotherms.

(*c*) The N–I transition temperature could only be detected by optical microscopy.

(*d*) Due to decomposition, deviations of 10 per cent were observed for successive measurements.

3.1. *Thermal properties of the 4,4″-di(ω-alkenyloxycarbonylamino)-p-terphenyls*

It was found that thermal decomposition of the *p*-terphenyl derivatives (**IVa**)–(**IVe**) occurs within the mesophase region. Therefore observation of textures and phase changes of the compounds with short terminal alkenyl groups ((**IVa**)–(**IVc**)) cannot be achieved by hot stage microscopy. Differential scanning calorimetry traces show two endothermic peaks on the first heating runs which are attributed to the melting and clearing points (figure 1). On cooling no corresponding transitions were observed. Due to lower transition temperatures the mesomorphic properties of the diurethanes with longer alkenyl chains ((**IVd**) and (**IVe**)) can be studied before decomposition. The textures observed are similar to the textures of smectic C mesophases [14]. Moreover, the clearing enthalpies of the diurethanes (**IVa**)–(**IVe**) between 11 and 21·5 kJ mol^{-1} are consistent with values determined for S_C–I transitions of other compounds [15]. Thus, the mesophase formed by the diurethanes (**IV**) is designated as smectic C.

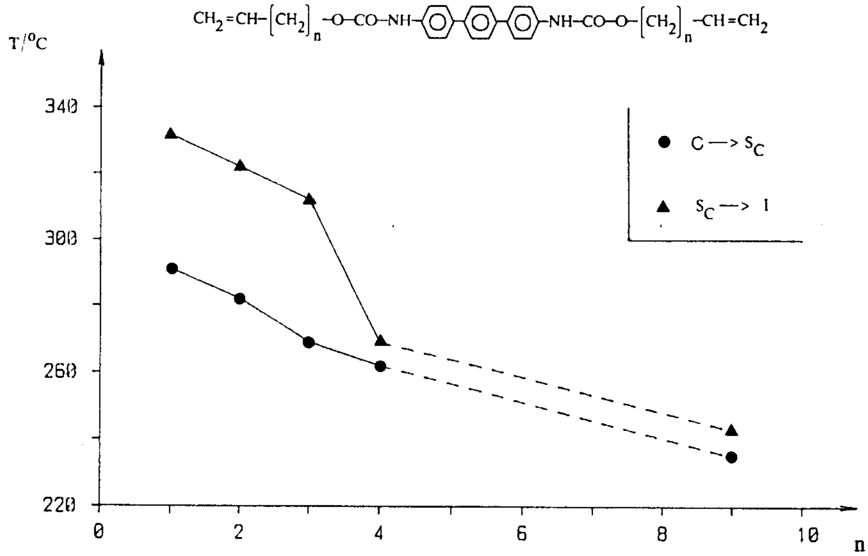


Figure 1. Plots of transition temperature versus *n* for 4,4″-di(ω-alkenyloxycarbonylamino)-*p*-terphenyl homologues.

3.2. *Thermal properties of the di[4-(ω-alkenyloxycarbonylamino)phenyl]terephthalates*

Despite decomposition it is possible to investigate the mesomorphic properties of series (**V**). The members with short terminal alkenyl groups ((**Va**) and (**Vb**)) show enantiotropic mesomorphism with relatively high melting and clearing points. Increasing the chain length of the alkenyl fragment (n = 3, 4 and 9) causes the clearing points to drop markedly while only a weak decrease of the alternating melting points occurs (see figure 2). In consequence monotropic mesophases are observed for the higher members of this series. All of the compounds show typical nematic textures [16]. The values of $\Delta H_{N\text{-}I}$ of between 1·2 and 1·5 kJ mol^{-1} are in the range found for nematic–isotropic transitions [15].

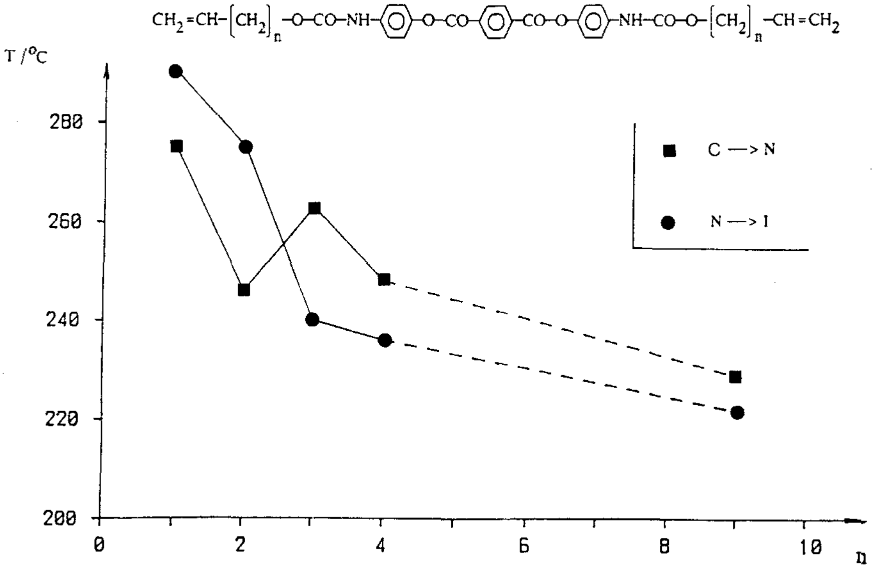


Figure 2. Plots of transition temperature versus *n* for di[4-(ω-alkenyloxycarbonylamino)-phenyl]terephthalate homologues.

4. Experimental

4.1. *Starting materials*

4,4″-Dicarboxy-*p*-terphenyl was prepared by a Friedel–Crafts acylation. For conversion to the diacidchloride the crude dicarboxylic acid was treated with thionylchloride in the presence of pyridine [17]. Di(4-chloroformylphenyl)terephthalate was synthesized according to a procedure given by Galli *et al.* [18]. The product was purified by recrystallization from tetrahydrofuran (THF). 4,4′-Diisocyanato-biphenyl, 3,3′-dimethyl-4,4′-diisocyanato-biphenyl and 4,4-diisocyanato-*trans*-stilbene were made by phosgenation of the corresponding diamines [6, 7]. 4-Penten-1-ol and 5-hexen-1-ol were prepared by ring cleavage of 2-(chloromethyl)tetrahydrofuran [19] and 2-(chloromethyl)tetrahydropyran [20], respectively. All other substances used were commercial products. The solvents were purified by standard methods and stored over molecular sieves.

4.2. *Preparation of 4,4″-diisocyanato-p-terphenyl*

(*a*) A mixture of 26 g (74·3 mmol) 4,4″-dichloroformyl-*p*-terphenyl and 28·5 g (0·25 mol) azidotrimethylsilane was stirred in 350 ml THF at 60°C for 13 h. The 4,4″-diazidoformyl-*p*-terphenyl formed was filtered off and air-dried. I.R. (KBr), 2180, 2140 $\mathrm{cm^{-1}}$ (N_3); 1685 $\mathrm{cm^{-1}}$ (CO).

(*b*) The crude diazido compound (18·9 g) was suspended in 260 ml toluene. The mixture was heated on an oil bath, and decomposition started at approximately 100°C. After the evolution of nitrogen had stopped, the mixture was stirred for a further 30 min. The resultant hot solution was filtered to remove any insoluble impurities and the pale yellow product crystallized on cooling. The diisocyanate was collected on a filter, washed with toluene and dried *in vacuo*. Yield, 12 g (51·7 per cent); T_m, 184°C. A mesophase observed could not be identified because rapid decomposition occurred after melting. I.R. (KBr), 2280 $\mathrm{cm^{-1}}$ (NCO).

4.3. *Preparation of di(4-azidoformylphenyl)terephthalate*

A saturated solution of 4 g (9 mmol) di(4-chloroformylphenyl)terephthalate in 40 ml THF was prepared by heating under reflux for 30 min. The bath temperature was reduced to 60°C and 3 ml (23 mmol) azidotrimethylsilane was added. After stirring for 18 h the mixture was cooled to room temperature. The white solid formed was filtered off, washed with THF and dried *in vacuo*. Yield, 2·8 g (68 per cent). I.R. (KBr), 2150, 2180 $\mathrm{cm^{-1}}$ (N_3); 1740 $\mathrm{cm^{-1}}$ (CO-ester); 1695 $\mathrm{cm^{-1}}$ (CO-azide).

4.4. *Preparation of the diurethanes*

(*a*) The following method was used for the preparation of the homologous series (**I**)–(**IV**). 10 mmol of the diisocyanate was dissolved in carbon tetrachloride ((**I**)–(**III**)) or toluene (**IV**) and the solution was filtered to remove any insoluble matter. An excess of the ω-alkenol was added and the mixture was heated under reflux. The product began to separate after approximately 15 min. Refluxing was continued overnight, and after cooling to room temperature the precipitate was filtered off and washed with carbon tetrachloride and toluene, respectively. The diurethanes of series (**I**) and (**II**) were recrystallized from methanol and of series (**III**) from acetone. In the case of the diurethanes of series (**IV**) recrystallization was carried out first with a mixture of THF and acetone and then with dimethylsulphoxide (DMSO). To remove the remaining DMSO the substances were stirred in acetone.

(*b*) For the preparation of the diurethanes (**Va**)–(**Ve**), 2·5 g di(4-azidoformylphenyl)terephthalate and a tenfold excess of the appropriate ω-alkenol were heated under reflux in 100 ml *o*-xylene. After stirring for 10 min a clear solution resulted, indicating the end of the decomposition of the diazido derivative. The solution was stirred for a further 50 min. On cooling to room temperature the diurethane precipitated and the mixture became somewhat gelatinous. It was then poured into 200 ml of acetone (except (**Ve**) which was poured into ethanol), stirred for 15 min and the white solid was isolated by filtration. The crude products (**Va**)–(**Vd**) were purified by dissolution in dimethylformamide, filtration and precipitation in water, followed by recrystallization from a mixture of THF and acetone. Product (**Ve**) was recrystallized twice, from THF and DMSO.

4.5. *Characterization methods*

The purities of the diurethanes were established by elemental analyses. The proposed structures all agree with I.R., and ^{1}H and ^{13}C N.M.R. spectra. In the case of the compounds (**Va**)–(**Vd**) only I.R. and ^{1}H N.M.R. spectra and in the case of compounds (**IVe**) and (**Ve**) only I.R. spectra were recorded, because of the low solubility of the compounds in common deuterated solvents used for N.M.R. spectroscopy.

The thermal behaviour of the compounds was investigated using a Perkin Elmer differential scanning calorimeter, model DSC-2. Scanning rates between 10 and 40 K $\mathrm{min^{-1}}$ were used and samples ranged from 5 to 15 mg in weight. For the evaluation of transition enthalpies an indium sample was used as a reference standard. Observation of the textures and checks on transition temperatures as far as possible were made using a Leitz Orthoplan polarizing microscope equipped with a Leitz hotstage, model 350.

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References

[1] DEMUS, D., and ZASCHKE, H., 1984, *Flüssige Kristalle in Tabellen* (VEB Deutscher Verlag für Grundstoffindustrie), Vol. II.

[2] VERBIT, L., and LORENZO, G. A., 1975, *Molec. Crystals liq. Crystals*, **30**, 87.

[3] SATI, M., 1985, *Porima daijesuto*, **37** (6), 10.

[4] BLUMSTEIN, A., ASRAR, J., and BLUMSTEIN, R. B., 1984, *Liquid Crystals and Ordered Fluids*, Vol. 4, edited by A. C. Griffin and J. F. Johnson (Plenum Press), p. 311.

[5] DEMUS, D., and ZASCHKF, H., 1976, *Flüssige Kristalle in Tabellen* (VEB Deutscher Verlag für Grundstoffindustrie).

[6] LIESER, T., and NISCHK, G., 1950, *Liebigs Annln Chem.*, **569**, 59.

[7] BERTSCH, H., ULSPERGER, E., and BOCK, M., 1960, *J. prakt. Chem.*, **11** (4), 227.

[8] KRICHELDORF, H. R., 1972, *Synthesis*, 551.

[9] KELKER, H., and HATZ, R., 1980, *Handbook of Liquid Crystals* (Verlag Chemie), Chap. 2.

[10] SCHUBERT, H., and DEHNE, H., 1972, *Z. Chem.*, **12** (7), 241.

[11] DEWAR, M. J. S., and GOLDBERG, R. S., 1970, *J. org. Chem.*, **35**, 2711.

[12] YOUNG, W. R., AVIRAM, A., and COX, R. J., 1972, *J. Am. chem. Soc.*, **94**, 3976.

[13] BRAUN, F., WILLNER, L., HEß, M., and KOSFELD, R., (in preparation).

[14] GRAY, G. W., and GOODBY, J. W., 1984, *Smectic Liquid Crystals* (Leonhard Hill).

[15] MARZOTKO, D., and DEMUS, D., 1976, *Liquid Crystals, Proceedings of the International Conference, Bangalore*, edited by S. Chandrasekhar (Indian Academy of Science), p. 189.

[16] DEMUS, D., and RICHTER, L., 1978, *Textures of Liquid Crystals* (Verlag Chemie).

[17] CAMPBELL, T. W., 1960, *J. Am. chem. Soc.*, **82**, 3126.

[18] GALLI, G., CHIELLINI, E., OBER, C. K., and LENZ, R. W., 1982, *Makromolek. Chem.*, **183**, 2693.

[19] BROOKS, L. K., and SNYDER, H. R., 1955, *Org. Synth. Coll.*, **3**, 698.

[20] BUTLER, G. B., and PRICE, G. D., 1959, *J. org. Chem.*, **24**, 1092.