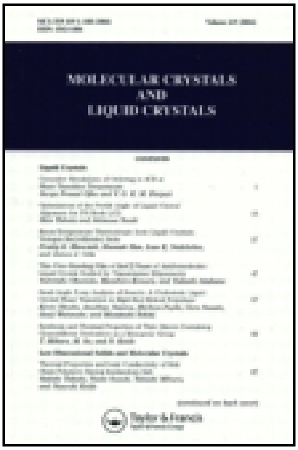

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Rigid rod Polymers With Flexible Side Chains 5. Structure and Phase Behavior of Thermotropic Poly (2-n-Alkyl-l, 4-Phenylene Terephthalate)S

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RIGID ROD POLYMERS WITH FLEXIBLE SIDE CHAINS
5. STRUCTURE AND PHASE BEHAVIOR OF THERMOTROPIC POLY(2-n-ALKYL-1,4-PHENYLENE TEREPHTHALATE)S

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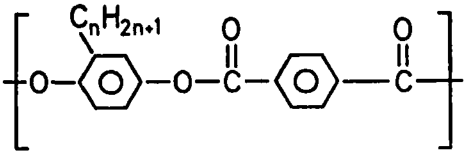
ABSTRACT

A series of poly(2-n-alkyl-1,4-phenylene terephthalate)s with n =3 to 18 has been investigated by DSC, optical microscopy and wide-angle x-ray analysis. The degree of crystallinity as inferred from x-ray analysis is rather low but increases upon annealing. None of the materials under consideration here exhibits a glass transition. If n $\leq$ 12 the polyesters form nematic melts, appending of longer side chains lead to the observation of a layered mesophase.

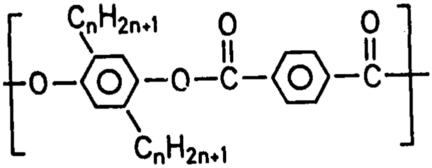
INTRODUCTION

Liquid crystalline polymers with mesogenic groups in the main chain have been studied extensively because of their capability to form high strength fibers. A serious problem encountered when investigating and processing these materials is their extremely low solubility and a melting temperature often being located above the limits of thermal stability. As shown by a number of previous investigations appending of flexible side chains to the rigid backbone can circumvent these difficulties in a well-defined manner. Thus, Majnusz, Catala and Lenz[1] were the first to demonstrate that the melting transition of the poly(1,4-phenylene terephthalate)s is lowered drastically by n-alkyl side chains.affixed to the hydroquinone moiety. This system bearing a wide variety of substituents has been studied in detail since[2-4]. Here we wish to present a systematic investigation of the poly(2-n-alkyl-1,4-phenylene terephthalate)s 1 where the number n of carbon atoms of the pendant hydrocarbon chains is varied between 3 and 18. For comparison with results obtained on similar but un-symmetrically substituted stiff-chain polyesters[5,6], polyamides[7] and polyimides[8] a polyester 2 prepared from terephthalic acid and 2,5-dioctadecyl hydroquinone was studied in addition to system 1. Special emphasis is laid on the determination of the order being present in the solid state as well as in the mesophases of polyesters 1 and 2. Based on the observation of the textures, Lenz and coworkers[1] suspected the polyesters 1 to form a smectic mesophase. Krigbaum, Hakemi and Kotek[2], however, concluded that this system only forms a nematic mesophase. Since optical textures do not allow an unambigous conclusion with regard to this question, wide-angle-x-ray studies together with thermal analysis (DSC) were carried out.



1

n = 3-18



2

n = 18

EXPERIMENTAL

Measurements

DSC analysis was carried out with a Perkin-Elmer DSC 7. Wide-angle-xray diffractograms were monitored using Ni-filtered Cu-K_α radiation in reflection mode. All diffractograms reported herein are uncorrected. HPLC analysis was performed using a Lichrosorb column (Merck) and methanol as the eluent at 1.5ml/min. Inherent viscosities were determined in p-chlorophenol at 50°C by means of an Ubbelohde viscometer.

The fatty acids needed for the synthesis of the monomer were purchased from Merck (zur Synthese) and used without further purification. Boron trifluoride was obtained from Linde and used directly.

Synthesis of the monomers

The 2-n-alkyl hydroquinones necessary for the synthesis of polyesters 1 can be obtained either directly by reaction of 1,4-benzoquinone with trialkylborane[9,10] or by acylation of hydroquinone and subsequent hydrogenation[11,12]. Here we chose the latter route which seems to be the easiest access to the required monomers with high purity. The acylation was done according to Armstrong et al.[11] using BF_3 as catalyst. The 2-n-akanoyl-hydroquinones resulting from this step with 70-90% yield were reduced by the Clemmensen method using the standard procedure given in reference /13/ (cf. also ref./12/). The yields of this step were between 60 and 80%. Alternatively, the hydrogenation can be done with H_2 in glacial acetic using a catalyst (Pd on a support) The raw monomers were recrystallized from ethanol/H_2O, $CHCl_3$, and from cyclohexane/ligroin. In case of short alkyl side chains column chromatography (Kieselgel 60, Merck, petrolether/ethyl acetate as eluent) had to precede recrystallization in order to achieve the required purity. All compounds were checked by elemental analysis, NMR, and HPLC. The following table summarizes the melting points of the 2-n-alkyl-hydroquinones.

Table I Melting points of the 2-n-alkyl-hydroquiones

n	3	6	10	11	12	14	16	17	18
T_m / °C	92	85	104	98	107	107	110	107	111

Synthesis of the 2,5-di-n-octadecyl hydroquinone

This compound was prepared according to Armstrong et al.[11] by acylation of 2-octadecyl hydroquinone in presence of BF_3. (Melting point of the 2-octadecyl-5- octadecyloyl hydroquinone : 101°C) The hydrogenation again is done most conveniently with the Clemmensen method. The final product (melting point: 111 °C) was purified by column chromatography and by recrystallization from ethanol and cyclohexane. NMR analysis unambigously demonstrated that no isomerization has taken place during acylation. In addition, the presence of a single signal of the phenyl protons seen in the NMR spectra of the final product proves substitution solely in 2,5 position.

Polymer synthesis

All polymers reported herein were either prepared by solution polycondensation in presence of pyridine (method A [1,5]) or by melt polycondensation (method B [1,5]) under an atmosphere of nitrogen. Since polyesters <u>1</u> with short side chains did not exhibit a sufficient solubility in common organic solvents, all inherent viscosities collected in table II were determined using p-chlorophenol at a concentration of 5g/l.

RESULTS AND DISCUSSION

Thermal Analysis and Optical Microscopy

All polyesters 1 exhibit a melting transition between 240 and 360 °C. Optical miscroscopy shows that the resulting melt is liquid crystalline. The DSC trace of the polyester 1 bearing a n-dodecyl chain (see fig.(1)) has a bimodal

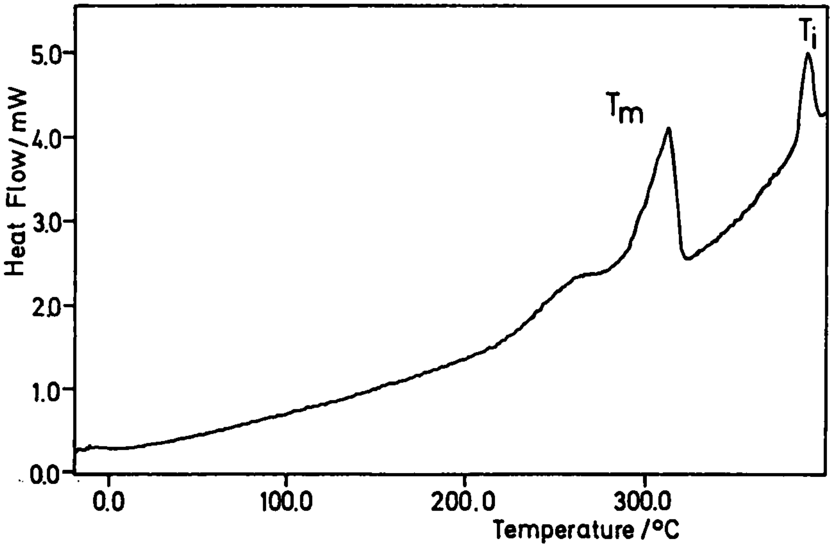


Fig.(1) DSC trace of polyester 1 (n=12) recorded at 20K/min.

Table II Inherent viscosities and transition temperatures of polyesters 1 and 2.

n	method	η_{inh} /dl g^{-1}	T_m/°C	T_i/°C	T_s/°C
3	A	0.86	340/360	-	-
3	B	1.10	360		
6	A	0.27	280/315	-	-
6	B	0.44	340	-	-
10	A	0.29	255/275	370	-
11	A	0.20	250/275	370	-
12	A	0.29	260/310	386	-
14	A	0.20	270	340	-
14	B	0.40	290/310	340	-
16	A	0.28	240/280	310	-
17	A	0.15	195/240	255	19
18	A	0.32	240	290	22
18	B	0.41	240	290	28
Polyester 2					
18	A	0.12	95/107	120	48

shape typical for the melting of polyesters[14]. The respective peak temperatures are gathered in the fourth column of table II. Additional DSC experiments showed that the melting range can be reduced considerably by annealing for ca. one hour. It is therefore concluded that the bimodal form of the DSC trace seen in Fig.(1) is not originated by an additional phase but by crystallites of different size or order present in the material (cf. ref./14/). The different molecular weights as measured by the inherent viscosities does not allow a quantitative conclusion with regard to the dependence of T_m on side chain length n. However, the data show that an increase of n is followed by a reduction of melting transition.

Careful attention has to be paid to frozen-in non equilibrium states. DSC traces taken from fresh polyester samples prepared by method A exhibited a number of small thermal events between 40 and 200 °C which disappeared upon annealing. In this context it is interesting to note that no sign of a glass transition could be detected for any of the polyesters 1 and 2 by the present DSC analysis. Dicke and Lenz[3] reported T_g values in the range of 202 to 267°C for polyesters in which hydroquinone was substituted with a cyclic or branched alkyl group. Majnusz et al.[1] did not find a glass transition in polyesters 1. This result was corroborated by Krigbaum et al.[2] who studied a sample of 1 bearing a hexyl side chain. By studying a number of mono- and disubstituted poly(1,4-phenylene terephthalate)s the latter authors found that a glass transition is only prominent in the heating curves if both phenyl groups of the repeating unit bear a substituent[2]. These results as well as the findings reported herein lead to the conclusion that the polyesters 1 do not exhibit a glass transition. However, it has to be noted that additional measurements are needed to confirm this result being solely based on thermal analysis.

For very long side chains (n=17, 18) the polyesters 1 as well as 2 show an additional transition in the region of low temperatures. The respective peak temperatures T_s are given in the 6th column of table II. In analogy to the polyesters and polyimides studied previously[5,8] this first order transition may be ascribed to the melting of the side chains.

The texture viewed between crossed polarizers for 1 with $n \leq 12$ appears to be of the nematic type (see below), materials with higher n exhibit a threaded texture which cannot be identified with known liquid crystalline structures. Optical microscopy demonstrates that the second peak in the DSC analysis (Fig.(1)) is the transition to an isotropic melt. At these high temperatures thermal decomposition becomes a serious problem for materials 1. From the present investigation any value located above 400^0C therefore seems to be of limited reliability. Hence, the fifth column of table II only gathers the values of isotropization temperature T_i for $n \geq 10$ where DSC runs can be performed with moderate heating rates (20 K min^{-1}).

The clearing temperatures for system 1 are located in the same range as the data reported by Dicke and Lenz /3/ for poly(1,4-phenylene terephthalate)s having cyclic or branched substituents. There is, however, a discrepancy of T_i reported in this work (column 5, table II) and the values given by Lenz et al.[1] In all cases where similar inherent viscosities allow a comparison of the clearing temperatures, the data shown herein are considerably higher than the ones given reference /1/. Despite these uncertainties the present findings indicate a decrease of T_i with increasing length of the side chains. This can be seen most clearly when comparing T_i of 1 (n=18) with the values given for 2 having two octadecyl side chains. The monotonous lowering of T_i with n is also in accordance with results obtained on the related poly(2,5-dialkoxy-1,4-phenylene terephthalate)s [5,6] and can be explained in good approximation by treating the side chains as a diluent[15]. In terms of this model an increasing volume fraction of flexible hydrocarbon chains dispersed as side chains in the system lower the steric interaction between the rigid main chains. In addition to this, the anisotropic dispersion forces operative between the cores are diluted and partially shielded off by the side chains. Both effects lead to the observed decrease of T_i (see reference /15/ for an extended discussion of this point).

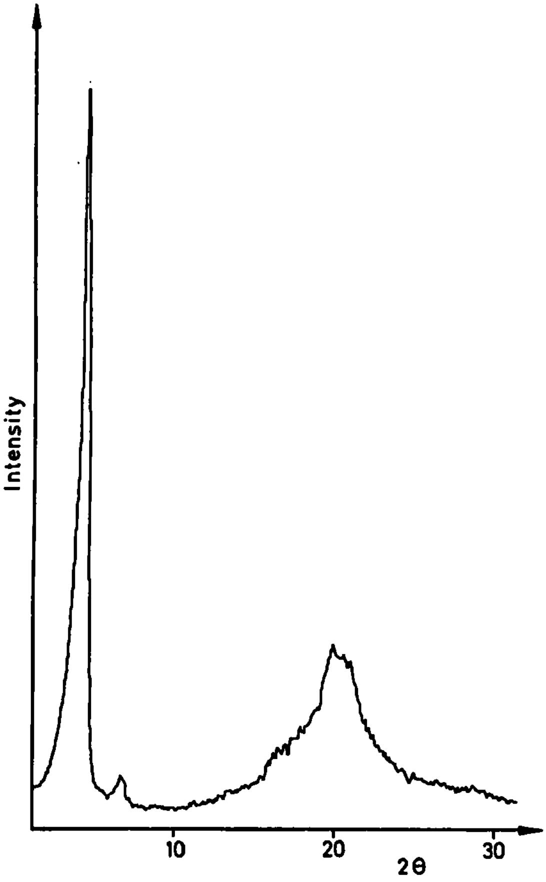


Fig.(2) X-ray diffractogram of polyester 1 (n=12) recorded at room temperature after annealing for 1 hour at 250 °C

X-ray measurements: solid state

Wide angle x-ray diffractograms recorded prior to annealing may be interpreted in terms of a low crystallinity for all polyesters 1 investigated here. Another common feature is a strong reflection in the region of low scattering angles ($2 \lesssim 2\theta \lesssim 6$). Annealing for several hours at temperatures located ca. 20°C below the melting point resulted in a sharpening of the low-angle reflection and to an increase in crystallinity as may be inferred from the appearance of broad peaks in the wide angle region. Fig.(2) shows a typical example for 1 with n=12 after being annealed for 1 hour at 250°C.

The strong Bragg reflection together with its second order unambigously demonstrates the material to crystallize within layers. Similar results have been obtained in the previous study of the poly(2,5-dialkoxy -1,4-phenylene terephthalate)s[6,7] and in an investigation of polyimides of similar structure[8]. Fig.(3) shows the layer spacings d for polyesters 1 at room temperature. The spacings for the unannealed samples (open triangles) are considerably higher than the d values after heat treatment (filled triangles), especially in case of propyl side chains. Here d of the melt condensate (open circle) and d after annealing coincide but the unannealed material has a much higher value. This again underscores the importance of a well-defined thermal history and the influence of frozen-in non equilibrium states (see above). As observed in references /6-8/ there is a linear relationship between d and the number n of carbon atoms in the side chains, at least for $n \geq 10$. The increment per CH_2 observed herein is

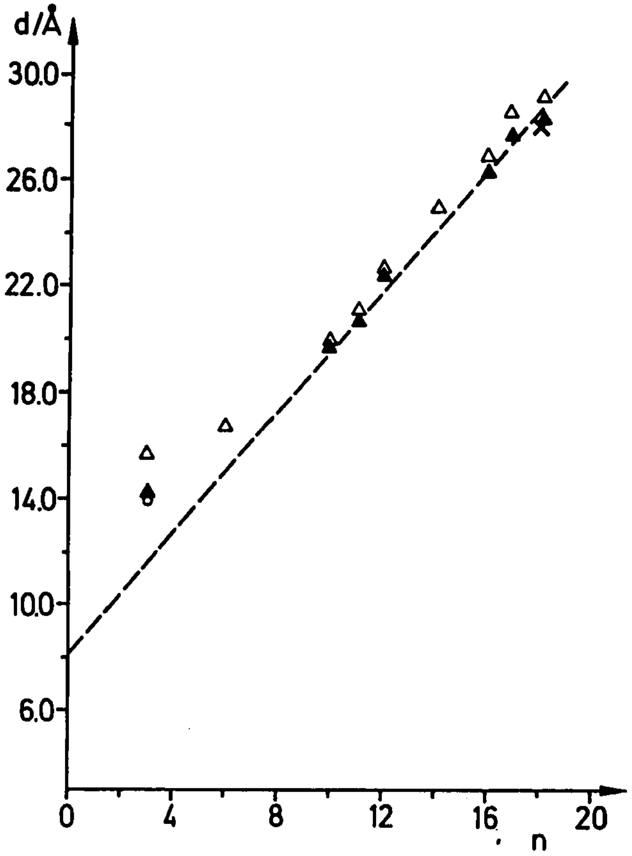


Fig.(3) Layer spacing calculated according to Bragg's law for the polyesters 1 (triangles, n=3-18) and 2 (cross, n=18))at room temperature. Filled symbols: annealed samples; open symbol: unannealed sample; open circle: unannealed sample of polyester 1 (n=3) prepared by melt condensation (method B).

slightly smaller than the value of 1.25Å found for the polyesters, polyamides and polyimides having two side chains per repeating unit[6-8]. But in contrast to these systems the intercept for polyesters 1 amounts to 8Å the uncertainties of the extrapolation in fig.(3) notwithstanding. This is distinctly higher than the diameter of one unsubstituted main chain found in the similar extrapolation for the poly(2,5-dialkoxy-1,4-phenylene terephthalate)s[6,7]. Hence, it may be conceivable that the side chains of a given main chain point all into one direction as shown schematically in fig.(4). By packing together two main chains a space-filling, i.e., intercalated arrangement of the side chains becomes possible.

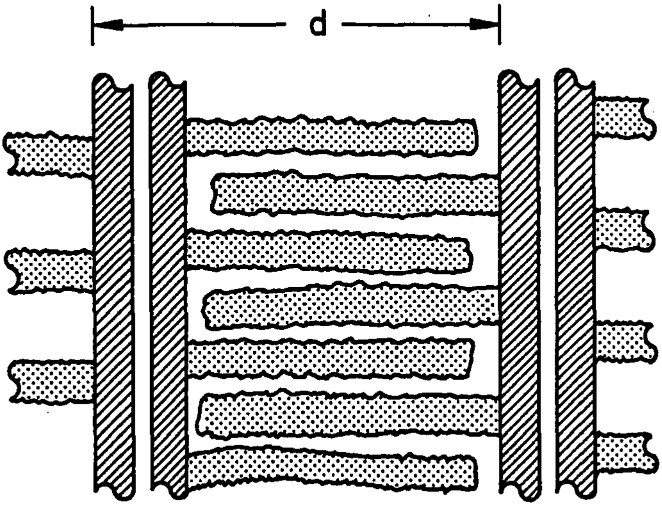


Fig.(4) Scheme of the molecular arrangement in the layers formed by polyesters 1.

X-ray investigations of the mesophases

As mentioned above, the textures of the mesophases do not allow a definite conclusion with the regard to the structure of the mesophase. High-temperature x-ray investigations of the melt are required to settle this question. The resulting diffractograms of 1 with n being located between 3 and 12 lead to the conclusion that the melts of these polyesters are nematic. This can be argued from the fact that besides two halos no additional feature typical for smectic phases can be seen in the wide-angle x-ray analysis. If n≥14, the diffractograms of the mesophase show a distinct reflection corresponding to a Bragg reflection slightly higher than the result obtained at room temperature (see fig.(3)). A typical example is seen in fig.(5). Similar to the diffractograms obtained for the mesophase of the poly(2,5-dialkoxy-1,4-phenylene terephthalate)s[7]. The strong Bragg reflection and its second order shows the liquid crystalline phase to be organized in layers. However, it has to be noted that the half-width of the reflection is broader than observed for systems being substituted symmetrically (cf. /7/). This points to a smaller number of layers organized in one

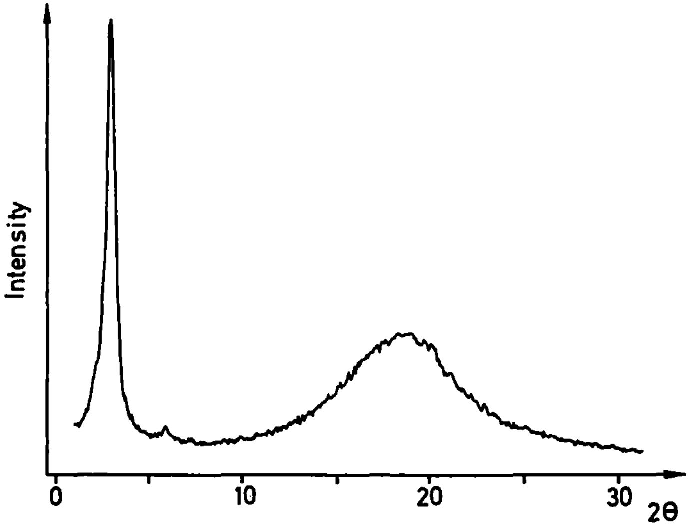


Fig.(5) X-ray diffractogram of the mesophase formed by polyester 1 (n=18) at 260°C.

domain. The broad halo in the wide-angle region is due to a liquid-like order on a short molecular scale. Raising the temperature above T_i leads to the disappearance of the layer reflection leaving behind a halo in the small-angle region (see Fig.(6)).

The diffractogram in Fig.(6) resembles very much the result obtained for an unoriented nematic phase of the polyesters 1 having side chains shorter than n=14.

The sample of polyester 2 having two octadecyl side groups exhibits a similar layered mesophase but with a half-width of the Bragg reflection much smaller than obtained for polyesters 1. In contrast to polyesters of type 1 the spacing obtained for the mesophase of 2 is smaller than the

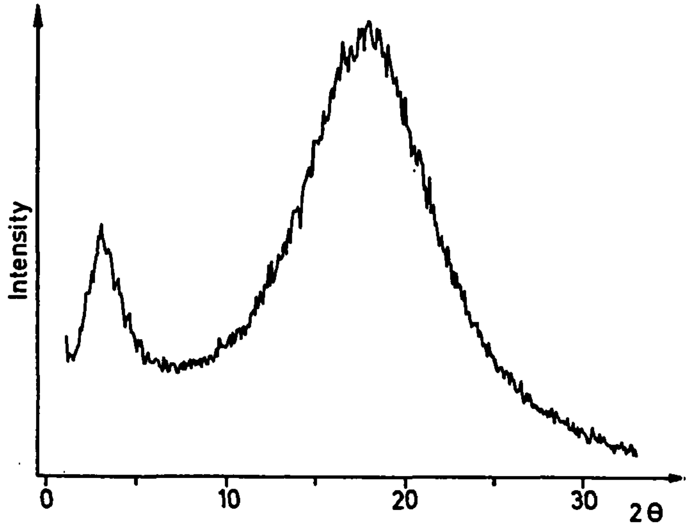


Fig.(6) X-ray diffractogram of the polyester 1 (n=18) in the isotropic phase at 300°C

corresponding value for the solid state.

In conclusion, the results obtained for the mesophase of 1 point to a arrangement of the polyester molecules as depicted in fig.(4). If the hydroquinone moiety is substituted twice, i.e., if the repeating units contains two alkyl chains instead of one as in the case of 1,.the packing of the molecules in the solid state as well as in the mesophase seems to resemble much the arrangement found for the poly(2,5-1,4-phenylene terephthalate)s[6,7].

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REFERENCES

/1/ J. Majnusz, J.M. Catala, R.W. Lenz, Europ.P.J. 19,1043(1983)
/2/ W.R. Krigbaum, H.Hakemi, R. Kotek, Macromolecules 1985, 18,965
/3/ H.-R. Dicke, R.W. Lenz, J.Pol.Sci.Pol.Phys.Ed. 21,2581 (1983)
/4/ H.-R. Dicke, R.W. Lenz, Angew.Makromol.Chem. 131,95 (1985)
/5/ M. Ballauff, Makromol.Chem. Rapid Comm. 1986, 7,407
/6/ M. Ballauff, G.F. Schmidt, Mol.Cryst.Liq.Cryst. 1987, 147,163
/7/ M. Ballauff, G.F. Schmidt, Makromol.Chem. Rapid Comm. 1987, 8,93
/8/ M. Wenzel, M. Ballauff, G. Wegner, Makromol.Chem., in press
/9/ M.F. Hawthorne, M. Reintjes, J.Amer.Chem.Soc. 87,4585 (1965)
/10/ J. Majnusz, R.W. Lenz, Europ.Pol.J. 21,565 (1985)
/11/ E.C. Armstrong, R.L. Bent, A. Loria, J.R. Thirtle, A. Weissberger, J.Amer.Chem.Soc. 82,1928 (1960)
/12/ W. Weissflog, D. Demus, Crystal Res. & Technol. 19,55 (1984)
/13/ W.H. Hartung, R. Simonoff, Org. Reactions 7,263 (1953)
/14/ G. Wegner, in " Polymere Werkstoffe", Ed. H. Batzer, Bd. 1, Thieme, Stuttgart 1985
/15/ M. Ballauff, Liquid Crystals 1987, 2,219