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Mobility and Orientation of Semi-Rigid Polyesters*

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Summary: Mobility and orientational behavior of semi-flexible polyesters from diphenyl-dicarbonic acid and some branched propyl-and butyl spacers have been investigated using static NMR techniques. Increasing molar mass of the polymers was found to influence the mobility of the rigid parts of the polymer chain while the spacer remains almost unaffected by the degree of polymerization. The mobility of the spacer carbons depends, however, on the length of the side chains. Even a magnetic field of 7 Tesla was not able to cause a reasonable macroscopic orientation in most of the samples, probably hindered by the high viscosity of the melts.

Introduction

Polymer liquid crystals (PLC's) are of growing technological interest since they combine the properties of macromolecules with those of monomer liquid crystalline materials (MLC's)$^{1)}$ giving rise to high performance non-metallic high-strength materials$^{2)}$. This is especially true for longitudinal PLC's rather than for other types. For a classification of PLCs see for example$^{3, 2)}$. Along with a

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* Dedicated to Prof. Dr. E. A. Hemmer, Duisburg, on the occasion of his 70th birthday

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mechanically strong polymer usually comes a low solubility and high melting points of the material resulting in many processing problems, caused by the stiffness the constitutional units have to provide for the polymer chains. Different attempts have been made to overcome these problems[2)], one of them is to connect rigid chain segments by short, branched spacers to control solubility and manipulate thermal transition temperatures[4, 5)]. During the recent years we have prepared a series of semi-rigid branched polymers (Fig. 1), the properties of which we are studying by systematical variation of the structure. This means changing the groups R_1 and R_2 in Fig.1. One effect caused by our modifications is an improved solubility and more moderate transition temperatures. There is still little known about other molecular properties.

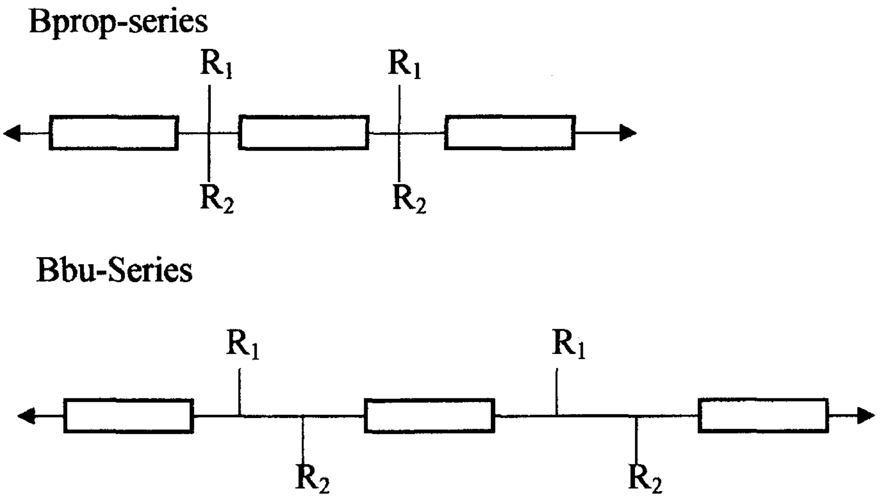


Fig. 1: General structure of semi-rigid polymers with branched spacer.

NMR-spectroscopy is a very powerful technique to study the behavior and interactions between organic groups in solid or molten polymers on nm scale[6, 7, 8)]. We have started to investigate the influence of molecular structure on mobility and order in these semi-rigid. The most important possible molecular motions in mesophases are:

- **internal motions**, e. g.: local intra-molecular reorientations as ring flips or trans-gauche rearrangements[9)]

- **collective motions of several chain segments or complete chains** in the MHz-range which comprise rotation around the chain axis and reorientation processes of the axis itself[10)]
- the most important motions, which are exclusively present in mesophases, are collective motions of larger molecular ensembles[11)], known as **director fluctuations**, characterized by a broad distribution of correlation times contributing to the longitudinal relaxation of magnetization in the MHz range

Consequently, one part of this investigation will analyse NMR relaxation to identify rigid and flexible parts of the polymer chain. Information about orientational effects can be derived from the anisotropy of the chemical shift (CSA), see for example Komoroski[7)]. A complete determination of orientation distribution functions[12, 13,14, 15, 16)] however, is not under the scope of this investigation and is supposed to be subject of subsequent publications.

Theory[6 - 8, 17 ,18 ,19)]

High resolution ^{13}C-CP-MAS NMR is a frequently used technique to study polymers.

In the absence of magic angle spinning (MAS) the proton decoupled ^{13}CNMR spectrum can be used to study in a qualitative way the molecular order. In general, the chemical shift is an anisotropic quantity described by a second rank tensor $\overline{\overline{\sigma}}$:

$$\overline{\overline{\sigma}}=\begin{pmatrix} \sigma 11 & 0 & 0 \\ 0 & \sigma 22 & 0 \\ 0 & 0 & \sigma 33 \end{pmatrix} \quad (1)$$

where σ_{11}, σ_{22} and σ_{33} are the principal elements of $\overline{\overline{\sigma}}$. In a liquid fast tumbling of the molecules averages $\overline{\overline{\sigma}}$ to the isotropic value σ_{iso}:

$$\sigma_{iso}=\frac{1}{3}\left(\sigma 11+\sigma 22+\sigma 33\right) \quad (2)$$

In a solid the chemical shift anisotropy (CSA) causes the resonance frequency ω of a spin to be dependent on the orientation of the molecule with respect to the external magnetic field $\mathbf{B_0}$. This orientation dependence of ω can be shown by defining the orientation of $\mathbf{B_0}$ in the principle axis system (PAS) of the chemical shift tensor by the polar angles Φ and θ.

In an axis system with the z-coordinate parallel to $\mathbf{B_0}$, the laboratory frame, $\overline{\overline{\sigma}}$ becomes:

$$\overline{\overline{\sigma}}=\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \quad (3)$$

and the resonance frequency ω:

$$\omega=\gamma B_0(1-\sigma_{zz})=\gamma B_0-\gamma B_0(\sigma_{11}\sin^2\theta\cos^2\Phi+\sigma_{22}\sin^2\theta\sin^2\Phi+\sigma_{33}\cos^2\theta) \quad (4)$$

γ is the magnetogyric ratio

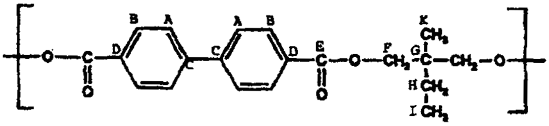
For a powdered solid eq. 4 leads to the familiar CSA powder patterns. For oriented samples the resonance frequency ω can be anywhere between $\gamma\mathbf{B_0}(1-\sigma_{11})$ and $\gamma\mathbf{B_0}(1-\sigma_{33})$, see eq. 4, depending on θ and ϕ of the oriented molecule. For liquid crystalline samples fast molecular large amplitude motions can partly average $\overline{\overline{\sigma}}$, yielding new averaged principal elements $\overline{\sigma_{11}}$, $\overline{\sigma_{22}}$ and $\overline{\sigma_{33}}$. The transition of a liquid crystalline sample between the isotropic and a mesophase is evidenced by the sudden change of the NMR line position from $\gamma\mathbf{B_0}(1-\sigma_{iso})$ to $\gamma\mathbf{B_0}(1-x)$ where x, depending on the orientation of the director can be any value between $\overline{\sigma_{11}}$ and $\overline{\sigma_{33}}$.

Materials and Methods

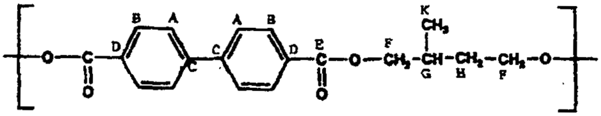
Polymers

The following polymers – Fig. 2 – were synthesized according to standard procedures described earlier⁴⁾. In contrast to the unsubstituted polymers, all samples – except Bbu 0, 1 – were soluble in THF. Bbu 0, 1 was soluble in trifluoro acetic acid. The molar mass distribution was analyzed by size exclusion chromatography coupled with multi angle light scattering. In general $\langle M_w \rangle / \langle M_n \rangle \cong 2$ was found.

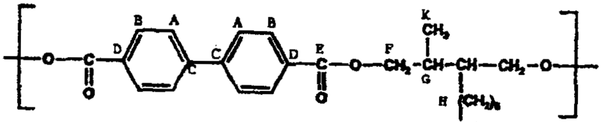
Melt viscosity of the polymers was in the order of magnitude of 1,500 Pa·s at 225°C and a shear rate of 0.1 s^{-1}.



Bprop 1, 2



Bbu 0, 1



Bbu 1, 6

Fig. 2: Polymer structures, identification of the carbons, and abbreviations.

NMR Experiments

Temperature depending HPDEC (High Power Proton Decoupling) were measured on a BRUKER CXP 300 Spectrometer with a B-VT 1000 temperature control unit Usually 2,000 – 5,000 scans were accumulated. In general, the samples were heated into the isotropic state and measured on a cooling run. The thermal treatment of the sample in the magnetic field of the spectrometer is given in Fig. 3.

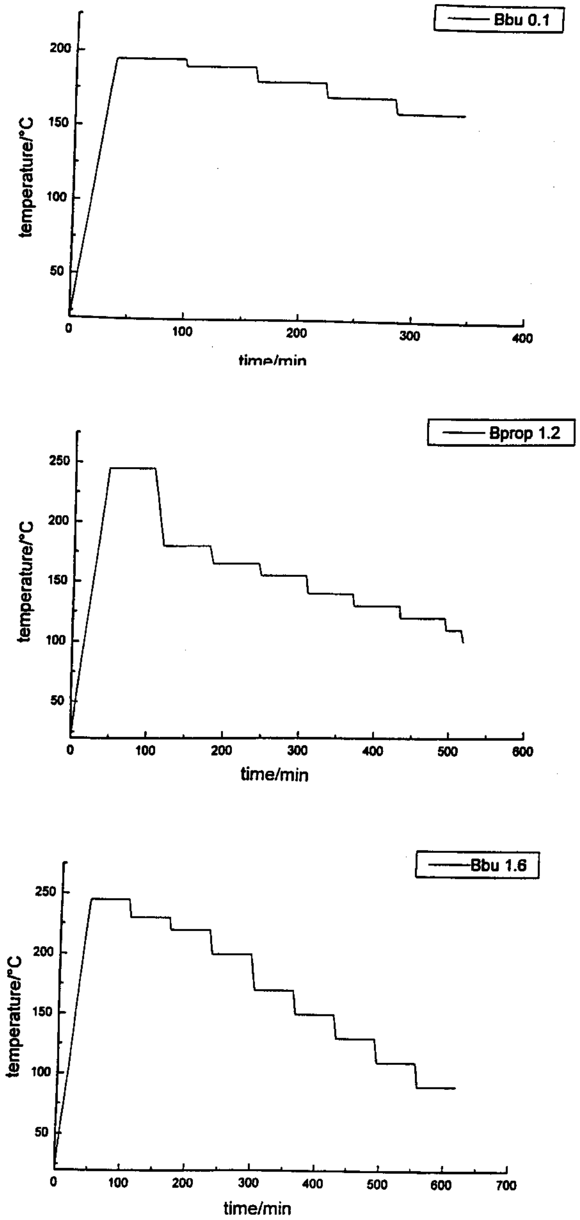


Fig. 3: Temperature depending HPDEC measurements of Bprop 1, 2

Calorimetry

All experiments were done with 5 mg – 10 mg sample weight at a heating/cooling rate of 20 K/min in a Perkin- Elmer DSC 7, calibrated with Sn and In.

Polarization Microscopy

A LEITZ Orthoplan® equipped with a LEITZ 350 hot stage controlled by a JULABO LC1 was used.

X-Ray Scattering

Scattering experiments were carried out on the Polymer Beam Line at the DESY (Hamburg) if not otherwise indicated. The Cu Kα line was used. The samples were heated up with 40 K/min into the isotropic phase and cooled down with 10 K/min.

Bulk Viscosity

Temperature and shear dependent measurements of the bulk viskosity were performed on a Rheometrics dynamic-mechanical tester with cone-plate geometry [a].

Results and Discussion

Bprop 1, 2

Polarisation microscopy could not provide unequivocal information about Bprop 1,2 ($\langle M_w \rangle$ 25,000 g/mol) since the viscosity of the specimens was quite high - 1,500 Pa·s at 225 °C, respectively 130 Pa·s at 25°C (shear rate 0.1 s^{-1}) - and structures formed only very slowly with an unspecific texture, Fig. 4.

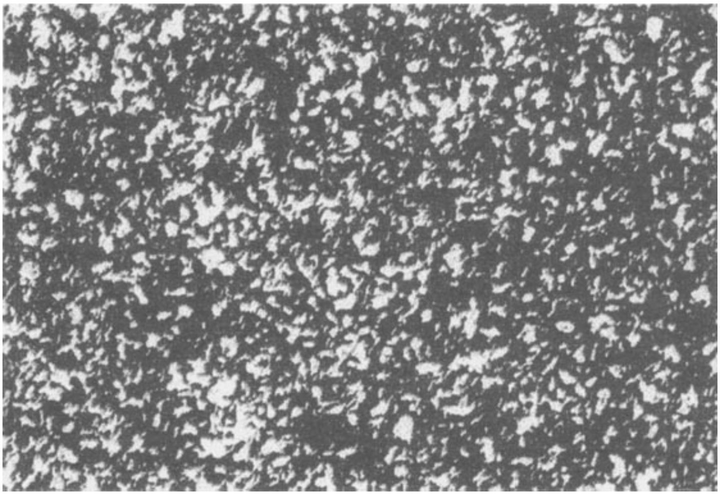


Fig. 4: Bprop 1, 2: texture of the mesophase at 220°C

glass-87°C-melt-(131°C-LC1-170°C-LC2)[b]-239-i

The glass transition temperature depends on the molar mass: 104°C ($\langle M_w \rangle \cong 25{,}000$ g/mol) or 88°C ($\langle M_w \rangle \cong 7{,}500$ g/mol), respectively. The results of the conventional DSC were confirmed by ODSC (Oscillating DSC)[c]. They identify the transition above 120°C clearly as "kinetic processes" in terms of ODSC which means 1st order transitions.

Their intensity depends on annealing conditions and develops only slowly. X-ray diffraction investigations [d], Fig. 5, show the development of a smectic reflex at about 180°C in a cooling run which corresponds to a spacing of about 2.5 nm. Above 240 °C the material is amorphous. These results suggest the existence of smectic structures up to about 180°C, possibly changing to a nematic phase. The isotropic phase becomes stable above 240°C.

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[a] kindly provided by Prof. B. A. Wolf. Department of Physical Chemistry, Johannes-Gutenberg-University.

[b] unequivocally only in samples with a molar mass of ca. 6.000g/mol

[c] measurements performed by Bryan Bilyeu, Laboratory of Polymers and Composites, Materials Science Department, University of North Texas, Denton.

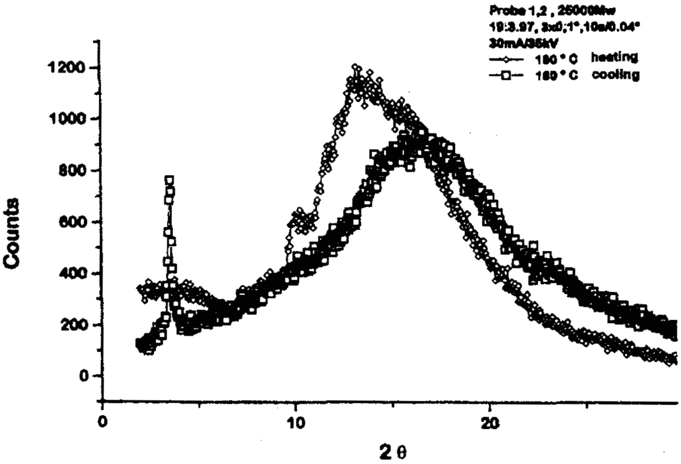

Fig. 5: Bprop 1, 2: development of a smectic reflex on cooling at 180°C

The possible existence of mesophases were investigated by temperature dependent HPDEC measurements. The results are shown in Fig. 6

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[d] by Manfred Stamm, Max-Planck-Institute for Polymer Research, Mainz, Germany

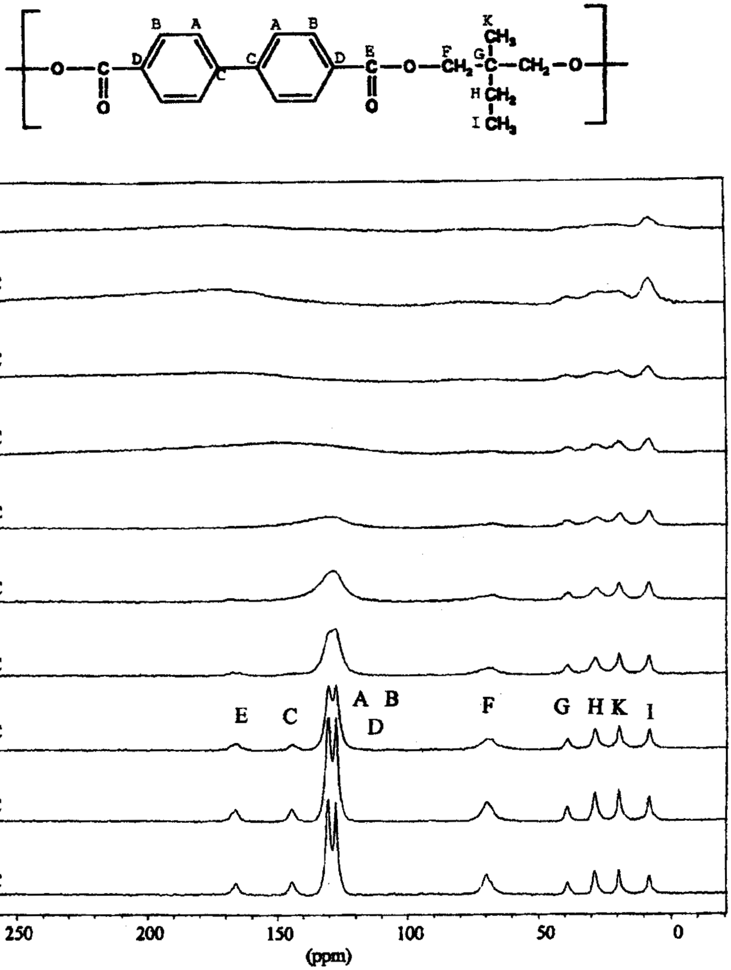


Fig. 6: Temperature depending HPDEC measurements of Bprop 1, 2

Around 130°C there is a change in chemical shift and shape of the phenyl carbons A, B, D. This can be correlated with the glass transition temperature – determined to be at about 104°C in calorimetric experiments. From investigations by Lauprêtre[20)] it is known that glass transition temperatures determined by DSC can differ from NMR results up to 50 K. The phenyl carbons

A, B, and D split up into a high field and a low field resonance: in a low molar mass sample ($\langle M_w \rangle \cong 7{,}500$ g/mol) the splitting was observed first at about 167°C, in a high molar mass sample at about 177°C. It can be understood by assuming a larger number of interacting sites per chain in polymers with a higher degree of polymerization. There is no such difference in the mobility of the spacer carbons F-K. This makes clear that the interchenar interactions are localized in the rigid parts of the chains. The existence of mesophases, however, were not proven by the NMR results since no chemical shift change, as discussed above, was detected in the corresponding temperature range. It was reported by Lauprêtre26), Ballauff21), and Noël22) that even in strong magnetic fields it can happen that no macroscopic orientation in liquid crystalline material is detected. High viscosities of the thermotropic melts seem to be responsible for this behavior, and its influence is larger than that of the molar mass22).

Fig. 7 shows the analysis of the chemical shift of the individual carbons depending on temperature. All chemical shifts of aromatic carbons (A-D) and the carbonyl carbon (E) go down-field with increasing temperature starting around the glass transition temperature. After that no significant changes occur except for the splitting of the ring carbons ABD at about 150°C. In contrast, the chemical shift of the spacer carbons G-K is almost temperature independent. Only the carbon F which is closest to the ester linkage, shows the same characteristics as the ring carbons, however, not as pronounced. This shows that the influence of the rigid biphenyl structure proceeds through the ester linkage at least to the first carbon of the spacer.

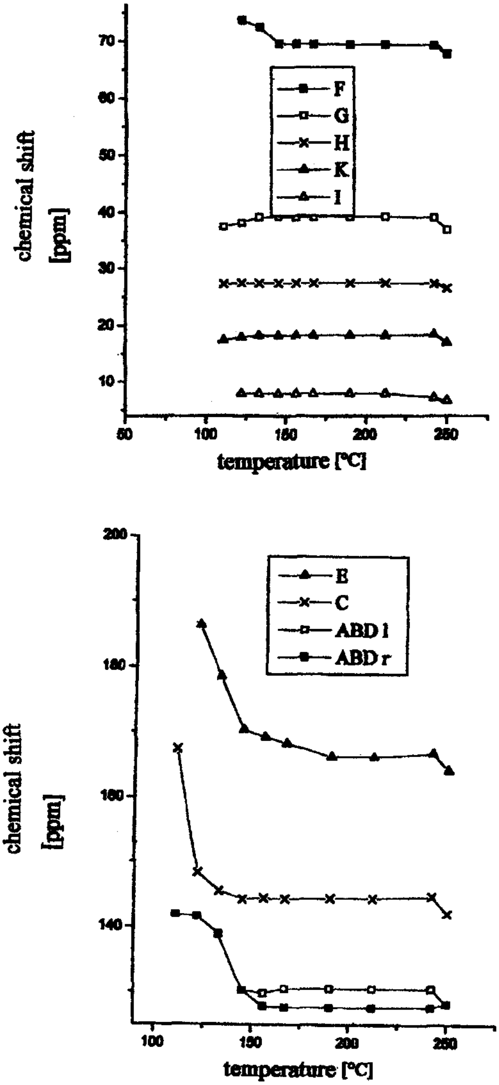


Fig. 7: Chemical shift of the individual carbons of Bprop ($\langle M_w \rangle \cong 25{,}000$ g/mol)as a function of the temperature. The notation “l” and “r” in the lower figure corresponds to the left (high-field) respectively right (low-field) of the two ABD-resonances which occur beyond 150°C. Identification of the nuclei as in Fig. 2.

The mobility of the nuclei were investigated by analyzing the peak width at ½ peak height. In case of the aromatic carbons A, B, and D the resonance peaks were deconvoluted. The results are shown in Fig. 8, indicating an increasing chain mobility in all parts with temperature. The high molar mass polymer shows only minor differences in the line width of the constituents of the phenyl resonances. For the low molar mass polymer, however, there are significant differences: the high field resonance is narrower than that of the low field line. This behavior can be explained by more interacting sites per chain in the high molar mass polymer. The splitting of the phenyl resonances may be due to the unsymmetric substitution of the side chain on the spacer.

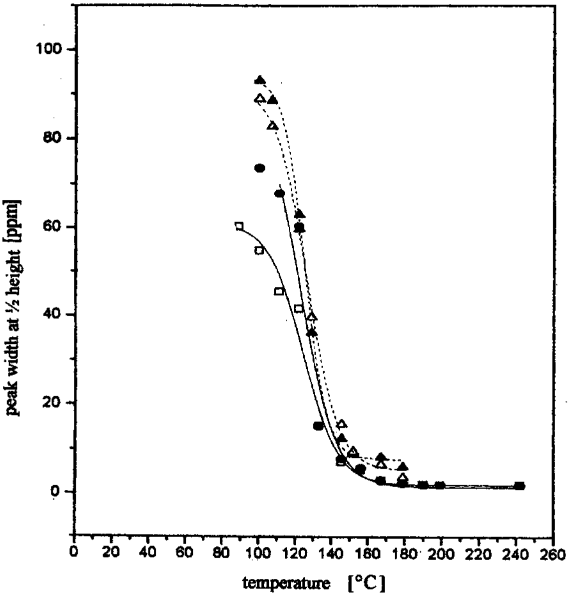


Fig 8: Peak width at ½ peak height of the resonance of the aromatic carbons A, B, and D calculated from temperature dependent HPDEC spectra. Bprop 1, 2 $\langle M_w \rangle$ 25,000 g/mol (-----): The carbon resonances were deconvoluted to two peaks. The open triangles indicate the high-field peak, the filled triangles the low-field peak. Correspondingly, Bprop 1, 2 $\langle M_w \rangle$ 7,500 g/mol (——): the open squares indicate the low-field and the filled circles the low-field contribution of the deconvoluted resonance. Not

only the phenyl resonances but all peaks show corresponding behavior. Identification of the nuclei as in Fig. 2. Temperature program see Fig. 3.

The change of chemical shift and peak width with temperature between 100°C and 140°C are due to the glass transitions. Since there seem to be no further changes in chemical shift or line width with temperature any mesophases are not apparent. There is definitely one strong process which can be identified with the glass transition.

Bbu 1,6

Calorimetric analysis, polarization microscopy and X-ray scattering experiments clearly show that this polyester ($\langle M_w \rangle$ 6,200 g/mol) is liquid crystalline. The melt is turbid and birefringent, the clearing point, however, could not be unequivocally identified by light microscopy but was concluded from DSC and X-ray scattering. Because of the long time of exposure no microphotographs were optained. DSC shows the following transitions:

Glass-81°C-(cryst 90°C)-143°C-s(?)-160°C-n-230°C-i

There is some evidence from X-ray scattering that these events are due to the melting to a smectic phase, followed by the transition to a nematic phase and the isotropic transition, respectively. Fig. 9 shows the static HPDEC spectra.

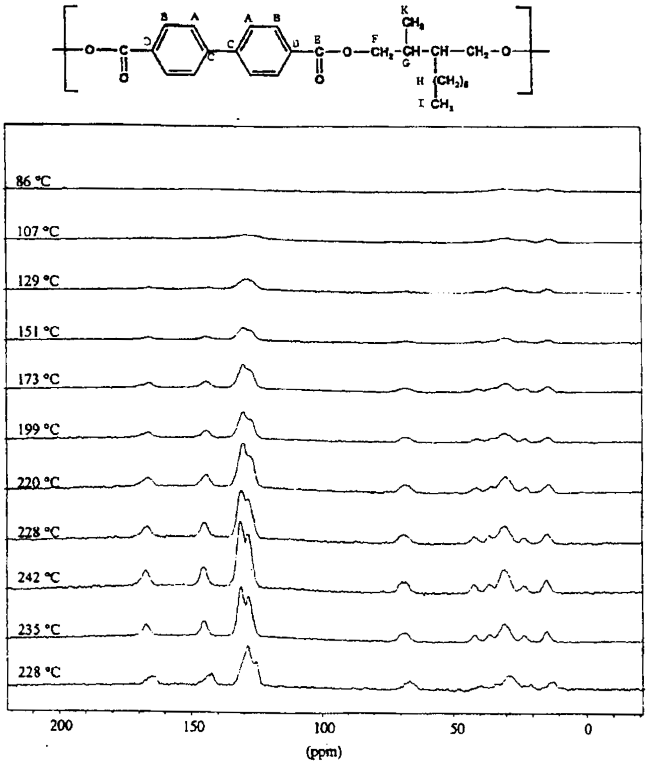


Fig. 9: Temperature depending HPDEC measurements of Bbu 1, 6.
Temperature program see Fig. 3

Almost all motions are frozen below the glass transition temperature so that there is almost no residual signal intensity in the spectrum. Only minor activities are observed in the region of the spacer resonances. At higher temperatures there is again the splitting of the phenyl resonances which had also been observed in Bprop 1, 2. There is no significant temperature dependent chemical shift of the carbonyl-or phenyl resonances in the melt, therefore no indication of thermal transitions other than the glass transition, see Fig. 10.

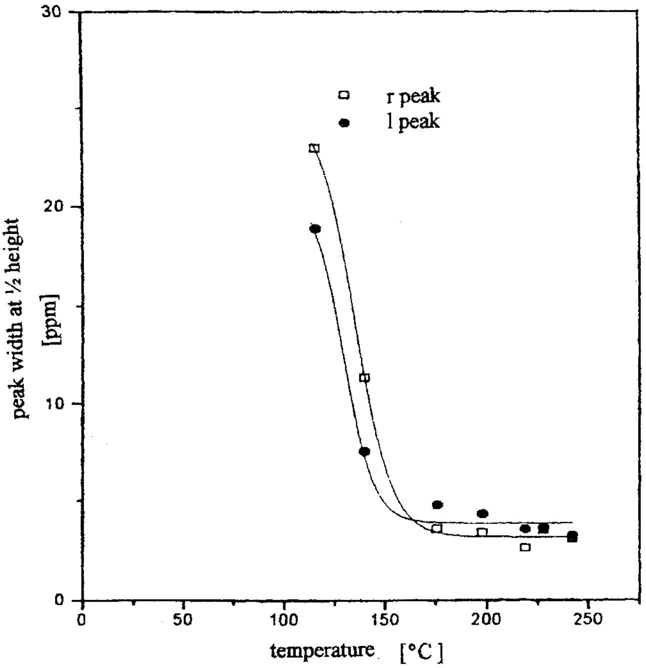


Fig. 10: Peak width at ½ peak height of the resonance of the aromatic carbons A, B, and D calculated from temperature dependent HPDEC spectra. Bbu 1, 6 $\langle M_w \rangle$ 6,500 g/mol. Peak identification as in Fig. 2. The carbon resonances were deconvoluted to two peaks, the high-field contribution (l) and the low-field contribution (r). Temperature program see Fig. 3.

Compared with Bprop 1, 2 of comparable molar mass (Fig.8), the peak width of Bbu 1, 6 is smaller at the same temperature and drops within a smaller temperature difference to the value of the isotropic phase. This means that the mobility of the aromatic carbons in Bbu 1, 6 below and above the glass transition temperature is higher than in Bprop 1, 2. This behavior can be explained in terms of the free volume created by the longer side chains of Bbu 1,6. Further investigations have to confirm this hypothesis. Yoshizawa[23)] and coworkers have found changes of the chemical shift of nearly 80 ppm for the ester carbonyl resonance caused by orientation of the molecules in the melt. This, however, was found in monomer liquid crystals of low viscosity. Highly viscous material may take quite long to orient under the influence of external fields: Moore and Strupp[24)], for example found in thermotropic polyesters of comparable molar mass that orientation kinetics were strongly temperature dependent, obviously because of the temperature dependence of the viscosity. There may be many small domains with a preferred orientation in the sample, of which the individual directors **n**, however, are randomly distributed and the applied field is too weak to achieve a reasonable macroscopic overall orientation on short terms. Also it is important that the applied field is appropriate for the desired orientation. A shear flow, for example, usually does not destroy the domains, an extensional flow is necessary to achieve this[25)].

Bbu 0, 1

Because of the poor solubility it was not possible to analyze the distribution of the molar mass of this polyester. Microscopic investigations clearly revealed mesophases, probably smectic and nematic, Fig. 11. At least one smectic and the nematic phase were confirmed by X-ray scattering.

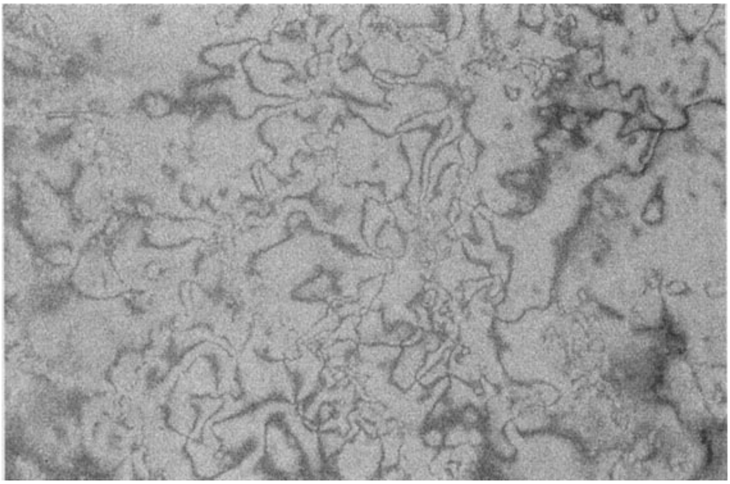
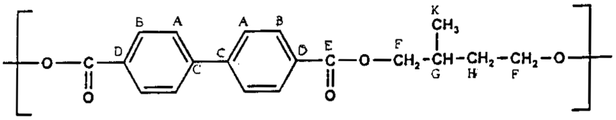


Fig. 11:Schlieren texture of a mesophase of Bbu 1,0 at 220°C.

glass-68°C-cryst.-175°C-s(?)-195°C-n-210°C-i

The temperature dependent HPDEC spectra - Fig. 12 – show that at 107°C at least one strong new line at 155 ppm occurs.



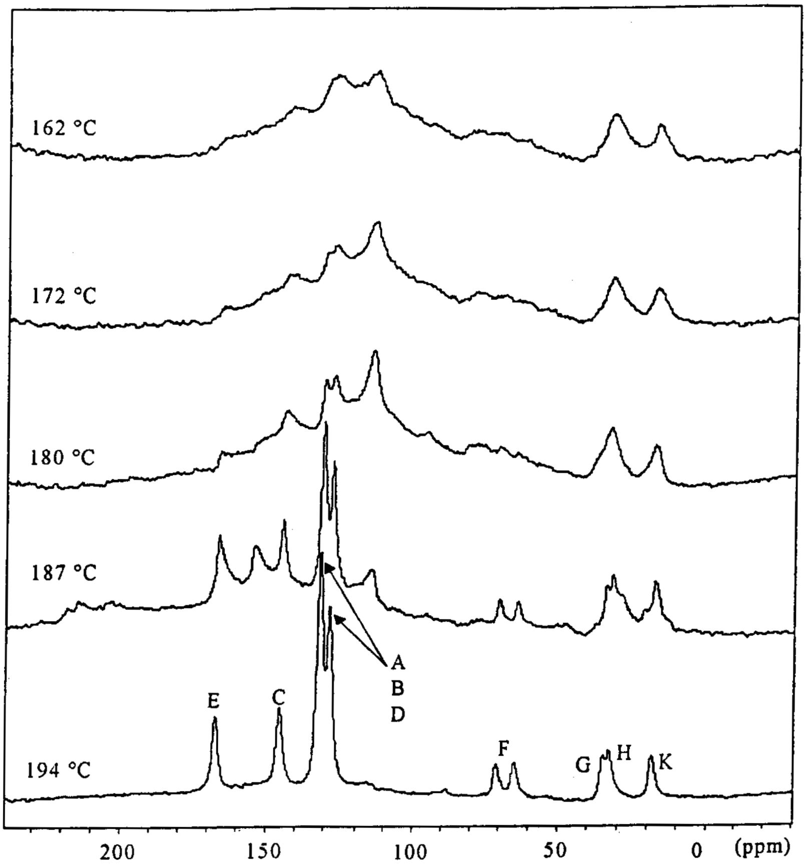


Fig. 12: Temperature depending HPDEC measurements of Bbu 0, 1
Temperature program see Fig. 3.

This is the first possible sign from the NMR-spectra that a mesophase exists, also because it is gone in the isotropic phase. The intensity and position suggests that this line is due to protonated ring carbons. When we assume – as usual[26] – that the protonated ring carbon σ_{11} // C-H and $\sigma_{33} \perp$ the ring plane, we can calculate the chemical shift in case of a perfect orientational ordering. When the director, the long axis of the biphenyl fragment, would be oriented parallel to $\mathbf{B}_0$ then the angles ϕ and θ in eq. 4 have the values $\theta = 90°$ (while $\sigma_{33} \perp \mathbf{B}_0$) and $\phi = \pm 60°$. Then eq. 4 yields:

$$\sigma_{22} = \sigma_{11}\cos^2\phi + \sigma_{22}\sin^2\phi = \tfrac{1}{4}\,\sigma_{33} + \tfrac{3}{4}\,\sigma_{33} \qquad (5)$$

When we take the σ-values of the solid benzene at low temperature (where no ring rotation occurs) σ_{11} = 234 ppm and σ_{22} = 146 ppm[27], we obtain σ_{zz} = 168 ppm, which is not far from 155 ppm, the value of the new line mentioned above, certainly when we take into account that the principal values for benzene do not apply for the biphenyl unit. This would mean that at least in some domains in the temperature range at 187°C molecules are approximately oriented with their long axis parallel to $\mathbf{B}_0$. This is supported by the weak lines around 210 ppm, because the non-protonated ring carbons in the oriented molecules have their σ_{11}-axis parallel to $\mathbf{B}_0$, and using eq. 5 with $\theta = 90°$ and $\phi = 0°$ we find $\sigma_{zz} = \sigma_{11}$. Again σ_{11} for this molecule is not known but should be between 200ppm and 233 ppm.

Concluding Remarks

The results of this study show that static magnetic fields are able to orient polymer liquid crystals. The viscosity, which is strongly depending on the molecular shape and the molecular mass strongly influences the orientability of the molecules. Butyl spacers with their even number of carbons atoms in the chain seem to form mesophases more easily than the three membered chain of propyl spacer which introduces a bend in the polymer chain. The power of relatively simple NMR techniques in analyzing molecular mobility and orientation could be demonstrated. Further experiments with different substituents and symmetry are in progress and studies about the free volume are in preparation. Other interesting questions to be solved are e. g.: which is the conformation of the side chain? There is some evidence from X-ray studies that beyond a critical chain length the spacer becomes parallel with the polymer backbone[4)]. In which way is the mobility of individual nuclei of the molecule influenced by structural features of the rigid part or the spacer? There are many interesting questions of principal nature which can be solved with further more sophisticated NMR experiments, e. g.: multidimensional NMR and relaxation time studies. The present study also shows the importance of redundant studies with different techniques. It seems that butyl spacers are better suited to stabilize mesophases than propyl spacers with their odd number of chain carbons. In the latter, a bend sequence is formed while a spacer with an even number of chain carbons allows a more straight conformation of the back bone.

Acknowledgement

ODSC-measurements on Bprop 1,2: Bryan Bilyeu, Laboratory of Polymers and Composites, Materials Science Department, University of North Texas, Denton, TX. Some of the X-ray scattering experiments were carried out by Dr. Manfred Stamm, Max-Planck-Institute for Polymer Research, Mainz, Germany, others were carried out at the Polymer Beam Line of HASYLAB at DESY, Hamburg, and we thank the crew of the late Professor Zachmann for their helpful assistance. We are indepted Prof. B. A. Wolf, Department of Physical Chemistry, Johannes-Gutenberg-University, Mainz, Germany, and his coworkers – especially Dipl. chem. Axel Hinrichs for the opportunity to use their equipment and their hospitality. The Deutsche Forschungsgemeinschaft (DFG), Bonn, is greatly acknowledged for their financial support.

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