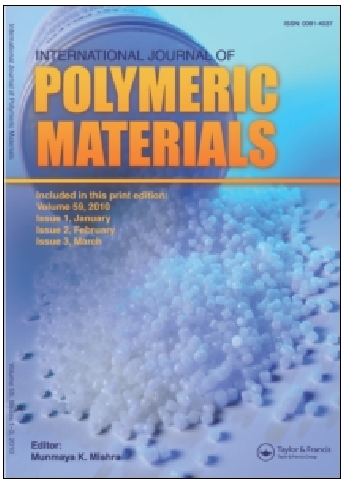

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Fluorescence studies on intermolecular interactions in laterally branched4, 4'-biphenyldicarboxylate polyesters

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FLUORESCENCE STUDIES ON INTERMOLECULAR INTERACTIONS IN LATERALLY BRANCHED 4, 4′-BIPHENYLDICARBOXYLATE POLYESTERS

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A series of polymers with rigid segments in the main-chain connected by short propylene spacers with systematically changed structure has been investigated utilizing the strong fluorescence emitted from biphenylene moieties. The polymer with the un-substituted spacer behaves differently in packing and overlap of the biphenylene groups. The temperature dependence of the fluorescence is able to indicate even small thermal transitions.

Keywords: biphenylene polyesters, liquid crystal, fluorescence

INTRODUCTION

Rigid-rod polymers are of particular interest for applications as mechanically strong materials or for special optical applications. Lyotropic and/or thermotropic mesophases are frequently observed. The draw back of these materials, however, is the low solubility in normal solvents and the usually high thermal transition temperatures causing problems in processing. There are several approaches to solve this problem, for example by introducing kinks in the linear chain [1],

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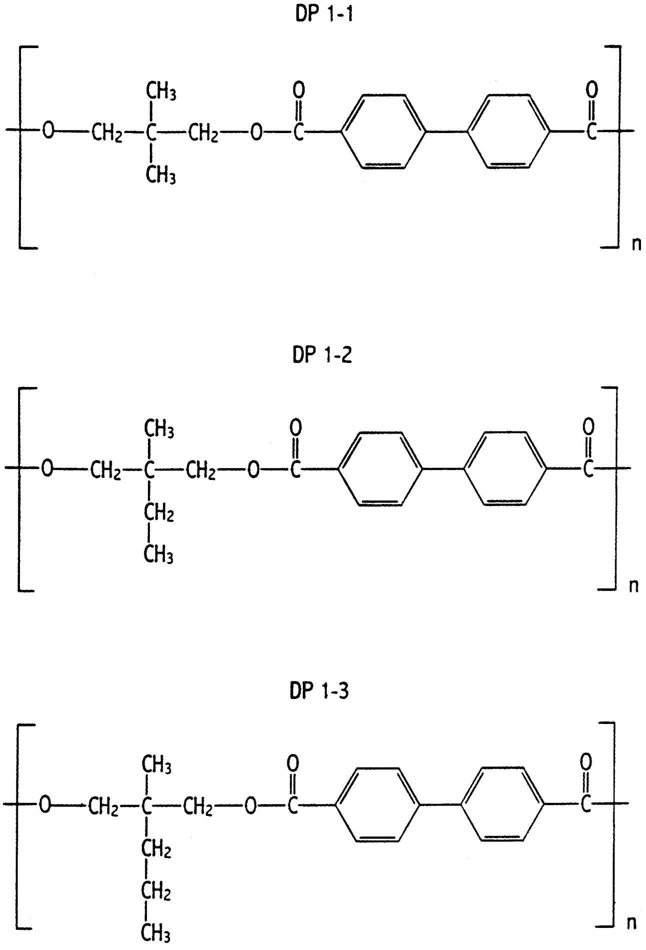
introduction of side-chains on the rigid segments [2], or by insertion of spacers between the rigid segments [3]. Depending on the length of the spacers odd–even effects can be observed. For a number of years we have concentrated on an alternative approach, by introducing short spacers like propylene or butylene, which carry laterally attached unsymmetrical side chains [4]. These side-chains disturb the chain packing and decrease the tendency of the polymers to obtain a liquid crystalline mesophase [5]. The mesophase formation in main-chain polymer liquid crystals is caused by anisotropic interactions between the rigid chain segments, which in the present study are 4, 4′-biphenylcarboxylic esters, see Figure 1.


DP 1-1

DP 1-2

DP 1-3

FIGURE 1 Structure of DP 1,1; 1,2; 1,3.

Fluorescent studies have become an important tool in the study of physical and dynamic behaviour of macromolecules [6–11]. Fluorescence reflects the energy levels of the microstructure of the polymers, and intermolecular interactions cause changes in wavelength or intensity corresponding to changes of the molecular environment. Fluorescence measurements provide a high sensitivity in the nanomolar concentration range of the radiating molecules so that intra- and intermolecular interactions between rigid aromatic segments can be analyzed. The intermolecular interactions between the rigid and frequently mesogenic moieties of rigid and semi-rigid moieties of polymers play a crucial role in determining the material's properties of these types of polymers. We have recently used the fluorescence technique to study changes in intermolecular interactions of main-chain polymer liquid crystals (LCPs) evidenced by changes in the electronic distribution of the systems, in particular interactions between the biphenyl moieties of the polymer chains.

To investigate the change of intermolecular interaction the fluorescence behaviour was studied using 4,4′-diacetoxybiphenyl and biphenyl as model compound. The biphenyl group is known to be a strong fluorophore so that the fluorescence behaviour could be used for the analysis of intermolecular interactions in these types of semi-rigid, respectively liquid crystalline polymers [12]. What makes these polymers in particular interesting is the fact that increasing the length of the alkyl side-chain on the (short) spacer decreases the tendency of the polymers to enter a mesophase state. DP 1,2 and DP 1,3, for example are monotropic or show weak liquid crystalline morphologies after long annealing [13, 14]. Packing effects appear to be responsible for this behaviour, and packing effects should be reflected by the fluorescence spectra.

Studies of dihydroxybiphenyl polyesters with linear spacers with different amounts of methylene groups showed that the main difference between the crystalline phase and the S_H mesophase is that the full overlap of the mesogenic biphenyl moieties changes to an only partial overlap in the mesophase [15]. Comparison of biphenyl dicarboxy acid polyesters with linear spacers with model compounds like biphenyl and 4,4′-diacetoxybiphenyl showed an intermolecular ground state complex of two completely overlapping biphenyl units in the crystalline state fluorescing at $\approx$360 nm, corresponding to the fluorescence emitted from the crystalline state of the LCP, as shown by Huang *et al.* [16] and Horie *et al.* [17].

It was found that the 343 nm fluorescence excited at 320 nm–400 nm is independent of the excitation wave lengths while the fluorescence at 365 nm–469 nm (excited between 320 nm–400 nm) strongly depends on the excitation wave length. Therefore it was concluded, that the fluorescence at 343 nm is due to the monomer since it is shows the same behaviour as the model component in dilute solution. The fluorescence of two fully overlapping biphenyl moieties is at about 360 nm, and it can be concluded that a fluorescence red shift can be attributed to a decreasing overlap of the biphenyl systems.

MATERIALS AND METHODS

The polymers were synthesised in a modified way as already described elsewhere [4]. Steady state fluorescence spectra were measured with a Hitachi 850 fluorescence spectrometer equipped with a Xe-lamp. The band passes were 5 nm for emission and excitation monochromators. The respective fluorescence excitation spectra of 10^{-4} M of the model compounds were measured using a quartz cell in side face detection. The PLCs were measured in a front face arrangement to minimize the self-absorption. The temperature was controlled by an Alfa Engineering Thermostat coupled with a control unit.

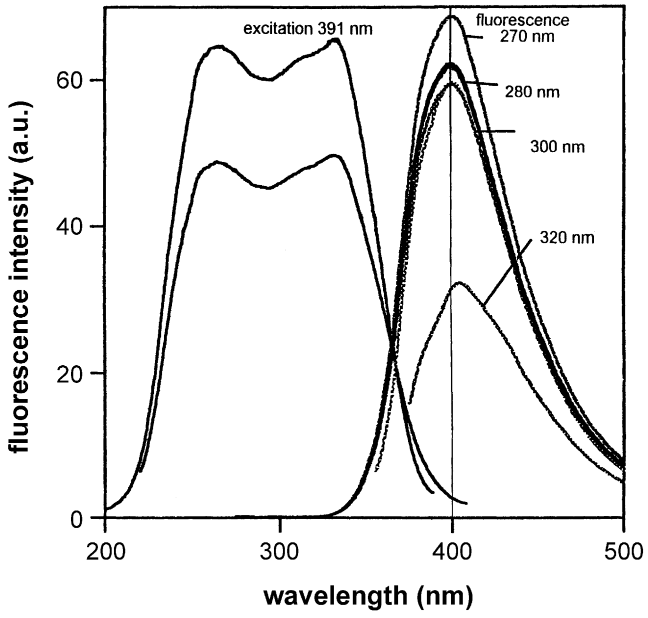


FIGURE 2 Excitation spectrum (left) and fluorescence spectrum (right) of DP 0,0 at room temperature.

RESULTS AND DISCUSSION

The excitation spectra and the fluorescence spectra of DP 0,0; DP 1,1 and DP 1,3 at room temperature are shown in Figures 2–5.

DP 0,0 is highly crystalline, no glass transition was detected calorimetrically. DP 1,1 is semi-crystalline (Tg ≈ 110°C) while DP 1,2 (Tg ≈ 100°C) and DP 1,3 (Tg ≈ 90°C) are usually amorphous, showing mesophases only on cooling (monotropic). The fluorescence maximum of all polymers lies clearly higher than 360 nm indicating incomplete interchain overlap of biphenyl units but a significant contribution of biphenyl-ester interactions. In analogy with Ref. [16, 17] the fluorescence maxima at 390 nm and 400 nm can be attributed to the formation of an intermolecular ground state complex with overlapping arrangement of biphenyl and carbonyl groups. The crystalline structure of the corresponding model compound dimethyl biphenyl-4,4′-dicarboxylate has been ascertained to be as discussed in Ref. [16, 17] as shown by Li and Brisse [18]. The unsubstituted, highly crystalline DP 0,0 with an emission maximum of 400 nm shows a longer fluorescence wavelength than the other polymers,

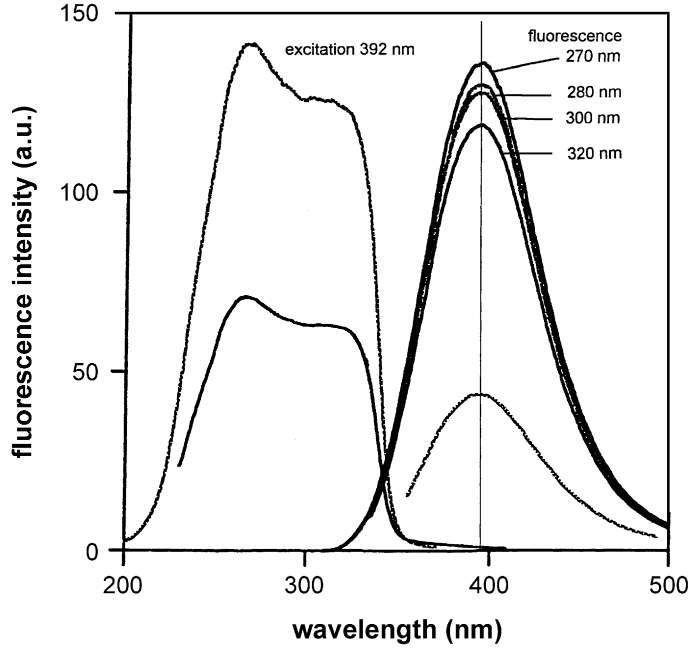


FIGURE 3 Excitation spectrum (left) and fluorescence spectrum (right) of DP 1,1 at room temperature.

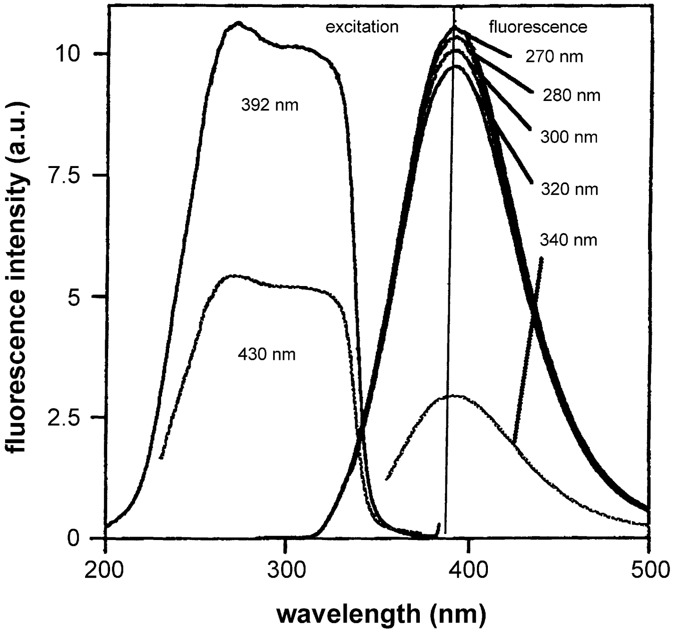


FIGURE 4 Excitation spectrum (left) and fluorescence spectrum (right) of DP 1,2 at room temperature.

which all have their emission maximum around 391 nm. This indicates that the presence of the side-chains on the propyl spacer causes certain packing effects which decrease the strong interchain interaction between the biphenyl and the carbonyl group of DP 0,0 and consequently do not support liquid crystalline ordering. The formation of a mesophase is disturbed by the curvature of the polymer chain caused by the odd number of spacer carbons. Steric effects of the side-chain probably lock the biphenyl moieties. It will be interesting to see if special interactions between the side-chains can force the biph enyls to a stronger interchain overlap. The shapes of the fluorescence curve of DP 1,1; DP 1,2 and DP 1,3 are very similar despite the steric effects which are to be expected by the growing side-chain. However, the symmetrically substituted DP 1,1 shows a stronger decrease of the fluorescence intensity with increasing excitation wave length and the emission caused by excitation at 320 nm shows a significant unsymmetry (tailing) which might indicate a distribution of populations with different overlap, see below.

There is only a weak dependence of the fluorescence on the excitation wave length in DP 0,0 and practically non in all other polymers

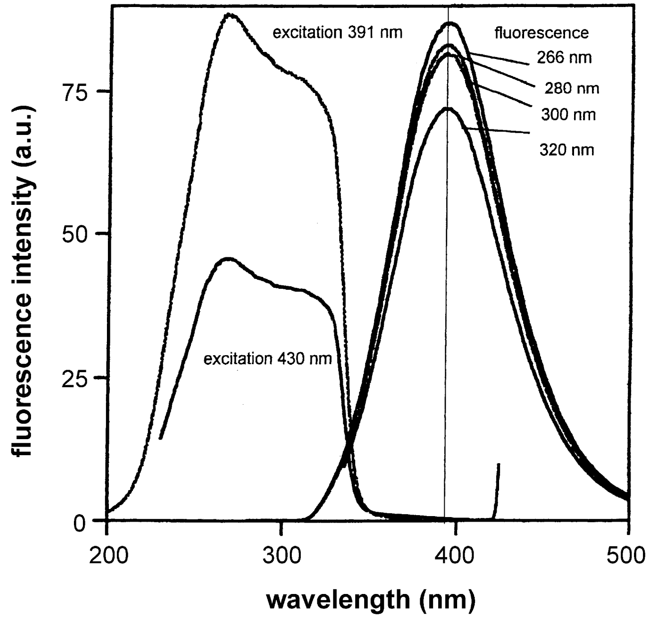


FIGURE 5 Excitation spectrum (left) and fluorescence spectrum (right) of DP 1,3 at room temperature.

investigated. Only at an excitation at 340 nm there is a red-shift of about 20 nm in DP 0,0 which might be due to the formation of disordered crystals [17]. In addition, the shape of the fluorescence peak of DP 0,0 is rather unsymmetrical indicating more than one component. This is particularly evident at the highest excitation wave length (320 nm) where a second component emitting at about 425 nm is indicated. Only a few papers have discussed the dependence of the fluorescence on the wave length of the excitation [19, 20] and it seems that fluorescence spectroscopy can distinguish aggregates differing in the degree of overlap.

The temperature dependence of the emission wave length differs significantly between DP 0,0 and the substituted polymers, see Figure 6.

There is a slight blue shift of the emission until 100°C (about 4 nm) in DP 0,0 remaining constant up to $\approx 260°C$. These effects seem to reflect the transition of small amounts of amorphous phases and the melting. The emission maxima of the other polymers remain practically constant up to the glass transition temperature where a blue shift of about 30 nm begins. A levelling out is observed in DP 1,1 and

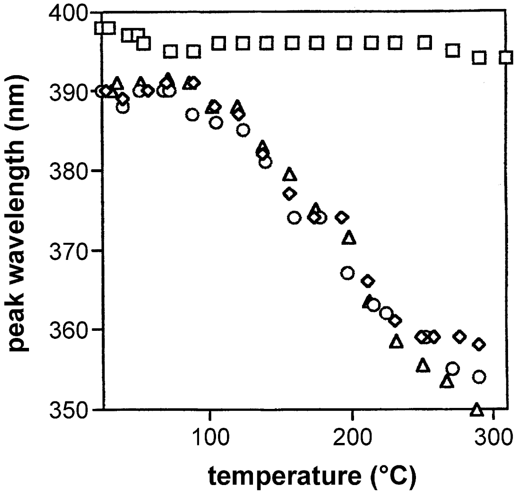


FIGURE 6 Temperature dependence of the emission maximum (excitation 320 nm). Symbols: rectangle: DP 0,0; lozenge: DP 1,1; circle: DP 1,2; triangle: DP 1,3.

DP 1,2 around 250°C where a weak first order mesophase transition is suspected, while DP 1,3 continues its blue shift beyond 280°C. The increasing temperature is obviously able to release the interlocked polymer chains allowing for a complete overlap of the biphenyl moieties in the molten state. This gradual blue shift of the fluorescence wavelength can be attributed to an increase in thermal wagging fluctuation of the mesogenic groups which weakens the interchain interaction between the mesogens, while the packing pattern remains almost unaltered during heating in the liquid crystalline state.

REFERENCES

[1] Calundann, G. W. and Jaffe, M. (1982). *Proc. Robert A. Welch Found. Conf. Chem. Res.*, **26**, 247.
[2] Ballauff, M. and Schmidt, G. F. (1987). *Mol. Cryst., Li. Cryst.*, **147**, 163.
[3] Lenz, R. W. (1985). *Faraday Disc. Chem. Soc.*, **79**, 21.
[4] Hess, M., Poersch, G. and Kosfeld, R. (1991). *Mat. Res. Soc. Symp. Proc.*, **183**, 123.
[5] Hess, M. and Pionteck, J., *Mater. Res. Innov.*, submitted.
[6] Lakowicz, J. R., *Principles in Fluorescence Spectroskopy*, Plenum Press, New York, 1986.
[7] Turro, N. J., *Modern Molecular Photochemisty*, University Science Books, New York, 1991.
[8] Winnik, M. A. (Ed.) Photophysical and Photochemical Tools in Polymer Science (Conformation, Dynamics, Morphology), *NATO ASI Series*, Reidl, 1986.

[9] Hole, C. E. and Torkelson, J. M. (Eds.), *Photophysics of Polymers* (ACS Symposium Series 358) American Chemical Society, Pittsburgh, 1987.

[10] Itagaki, H., Horie, K. and Mita, I. (1990). *Progr. in Polym. Sci.*, **15**, 361.

[11] Huang, H. W. and Horie, K. (1997). *Trends in Polymer Science*, **5**(12), 407.

[12] Huang, W. *et al*. (1996). *Macromolecules*, **29**, 3485.

[13] Hess, M., Woelke, R. and Pionteck, J., *Mater. Res. Innov.*, submitted.

[14] Hess, M., Woelke, R. and Jo, Byung-wook. (2001). *Int. J. Polym. Materials*, in press.

[15] Kriegbaum, W. R., Watanabe, J. and Ishikawa, T. (1983). *Macromolecules*, **16**, 1271.

[16] Huang, H.-W., Horie, K., Tokita, M. and Watanabe, J. (1998). *Macromol. Chem. Phys.*, **199**, 1851.

[17] Horie, K., Huang, H.-W., Shimada, M. in Morishida, Y., Norisuye, T. and Tashiro, K. (Eds.), Molecular Interactions and Time−Space Organization in Macromolecular Systems, *Proc. OUMS'98*, Osaka, Japan, Springer, Berlin, 1999.

[18] Li, X. and Brisse, F. (1994). *Macromolecules*, **27**, 2276.

[19] Al-Hassan, K. A. and El-Bayoumi, M. A. (1987). *J. Polym. Sci.*; *Polym. Phys.*, **25**, 495.

[20] Al-Hassan, K. A. and El-Bayoumi, M. A. (1998). *Chem. Phys. Lett.*, **150**, 344.