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Poly(3,6-carbazolylmethylene)s with flourinated and nonflourinated tapered building side groups

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Summary

The syntheses of two different poly(3,6-carbazolylmethylene)s are described. The polycondensation reaction proceeds without any crosslinking and the obtained polymers were characterised by elemental analysis ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR. DSC studies evidenced that one of the obtained polymers, i.e. poly[N-(3,4,5-tris(4-perflouro-octylbutyl-1-yloxy)benzyl)carbazole] shows liquid crystalline behaviour and X-ray analysis pointed to a hexagonal columnar mesophase.

Introduction

Since Bruck (1) first reported on the syntheses of poly(3,6-carbazolylmethylene)s by polycondensation of N-alkyl carbazoles with formaldehyde or by acid catalysed polycondensation of N-ethyl-3-hydroxymethylcarbazole there have been published several papers concerning the synthesis of poly(3,6-carbazolylmethylene)s (2),(3),(4),(5) mainly concentrating on the polycondensation with formaldehyde. These polymers gained interest in different areas due to their remarkable properties for redox systems, electrochromism and Langmuir-Blodgett films.Most of the cited authors obtained, however, crosslinked materials from which they extracted the soluble portion. These polymers were characterized by their ^{1}H-NMR, ^{13}C-NMR, UV, IR and fluorescense spectra. Only in two of the papers are presented informations concerning the thermal characteristics or phase transitions of the obtained polymers. Bruck (1) reported for an amorphous poly(N-ethylcarbazolylmethylene) (DP=9) a "melting point" (probable the beginning of degradation) of 164°C, whereas Watarari (2) indicated 158°C for the same polymer beside the values for four other polymers with longer alkyl chains. But both authors do not indicate experimental details concerning the thermal characterization. Jeneke et al. (3), on the other hand, reported glass transition temperatures for poly(N-methylcarbazolylmethylene)s situated between 100°C (DP=13) and 150°C (DP=25).

It seemed to be of interest to combine the unique electrochemical properties of poly(3,6-carbazolylmethylene)s with liquid crystalline behaviour. Taking into account that some authors suggested the decreasing tendency towards crosslinking with an increasing bulkiness of the substituent on the carbazole nitrogen, the approach of Percec et al. (6) of using tapered building sideblocks to realize self assembled supramolecular architectures seemed to be well worth to be tested, because it should be possible to reach by this way simultaneous both goals, i.e. to avoid crosslinking and to induce mesomorphic behaviour.

Experimental

A. Materials

Commercial methylgallate (97%; Fluka) was recrystallized from methanol. (4-perfluoro-octyl)butane-1-ol was synthesized according to literature (7). The synthesis of para-toluenesulfonic-acid (4-perfluoro-octyl)butyl-1-ester will be described elsewhere.(8)

All other starting materials and solvents are commercially available and were used as received.

B. Techniques

^1H-NMR (300MHz) as well as ^{13}C-NMR (75,4MHz) and ^{19}F-NMR (282MHz) where recorded on a Bruker IFS88 spectrometer at 20°C in $CDCl_3$. Hexafluorbenzene was used as an internal standard for the ^{19}F-NMR and the respective chemical shifts are reported assuming $CFCl_3$ as zero point of the scale. Thermal transitions where measured on a Perkin Elmer DSC-7. First order transitions temperatures where attributed to the minima or maxima of the endothermic and exothermic peaks, respectively, observed during the second heating and cooling scanes. Tg values refer to the temperature of half c_p increase. Rates were 10°C min^{-1} in all cases. The melting points of the intermediate compounds were determined vizual on the Büchi 510 Melting Point Determinator. GPC measurements were carried out in $CHCl_3$ using polystyrene standards for calibration.

C. Syntheses of the monomers

The synthesis routes are outlined in scheme 1. Etherification of methylgallate with the corresponding alkylbromide or tosylate results in 3,4,5-tris(4-perfluoro-octylbutyl-1-yloxy)methylbenzoate and 3,4,5-tris(n-dodecane-1-yloxy)methylbenzoate, respectively.

Reduction with $LiAlH_4$ in THF and subsequent chlorination with $SOCl_2$ in CH_2Cl_2 or CF_3CCl_3, using DMF as catalyst, gives 3,4,5-tris(4-perfluoro-octylbutyl -1-yloxy)benzyl-chloride respective 3,4,5-tris(n-dodecane-1-yloxy)benzylchloride. The subsequent alkylation of carbazole was executed in the two phase system benzene / 50% NaOH (10). The N-alkylated carbazoles were formylated with a tenfold ecxess of DMF / $POCl_3$ at 90 °C. The obtained aldehydes were reduced with $NaBH_4$ in 2-propanol to the desired N-(3,4,5-tris(4-perfluoro-octylbutyl-1-yloxy)benzyl)- and N-(3,4,5-tris(n-dodecane-1-yloxy)benzyl)-3-hydroxymethylcarbazoles. For polymerization several solvents and catalysts have been tested. Best results were obtained by heating the monomer solution in THF / trifluoroacetic anhydride with $ZnCl_2$.

1) 3,4,5-tris(4-perfluoro-octylbutyl-1-yloxy)methylbenzoate (1a) and 3,4,5-tris(n-dodecane-1-yloxy)methylbenzoate (1b)

3,6g (19,5 mmol) methylgallate, 41,6g (64,4-mmol) p-toluenesulfonic-acid(4-perfluoro-octyl)butane-1-ester (or bromo-n-dodecane) and 20g (145 mmol) K_2CO_3 were suspended in 250 ml DMF and stirred under N_2 over night at 70°C. The reaction mixture was poured into water. A THF-solution of the product was filtered over basic Al_2O_3 and then recrystallized from EtOH.Yield : 28g (90%)

3,4,5-tris(4-perflouro-octylbutyl-1-yloxy)methylbenzoate,
mp (vizual) = 60-63,5°C; (Lit (7): 59-63,5°C)

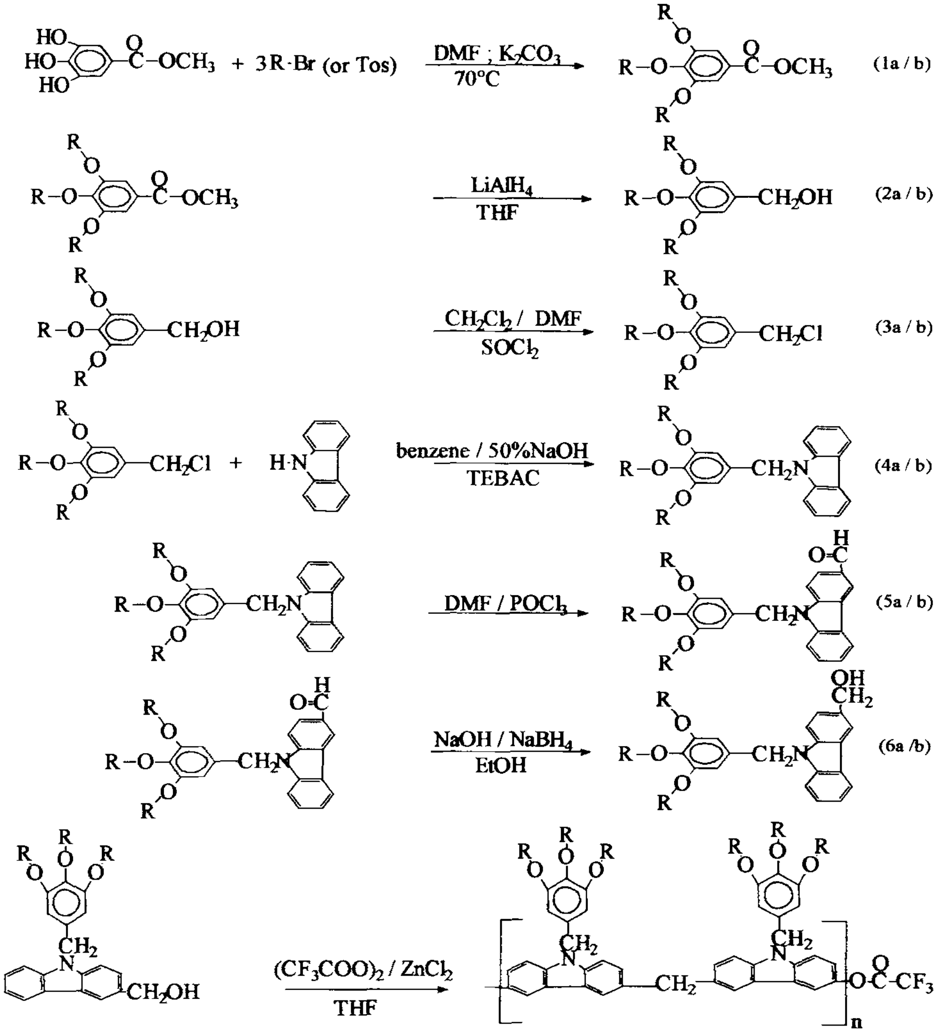
^1H-NMR : 7,3 (s; aromat.; 2H) ,4.1 (2t; $O\text{-}CH_2$; 6H), 3,9 (s; $O\text{-}CH_3$; 3H), 2,3-2,0 (m ; CH_2CF_2; 6H), 2,0-1,7 (m; $O\text{-}CH_2\underline{CH_2CH_2}CH_2CF_2$; 12H);

3,4,5-tris(n-dodecane-1-yloxy)methylbenzoate; mp (vizual) = 42°C; (Lit (9): 43°C)

^1H-NMR : 7,3 (s; aromat.; 2H), 4.1 (2t; $O\text{-}CH_2$; 6H), 3,9 (s; $O\text{-}CH_3$; 3H), 1,9-1,2 (m ; CH_2; 60H), 0.9 (t; CH_3; 9H)

R = $CF_3(CF_2)_7(CH_2)_4$ (a) or $CH_3(CH_2)_{11}$(b)

scheme 1



2) 3,4,5-tris(4-perfluoro-octylbutyl-1-yloxy)benzylalcohol (2a) and 3,4,5-tris(n-dodecane-1-yloxy)benzylalcohol (2b)

These compounds were obtained by reduction of the corresponding methylesters with $LiAlH_4$ in THF. Excess $LiAlH_4$ was quenched with H_2O /NaOH, the inorganic salts being then filtered. The solvent was removed and the products were used without further purification.

3,4,5-tris(4-perfluoro-octylbutyl-1-yloxy)benzylalcohol; mp (vizual) = 94°C

^{1}**H-NMR:** 6,6 (s; aromat.; 2H) , 4.6 (d; CH_2OH; 2H), 4,1 (t; O-CH_2 ortho; 4H), 3,9 (t; O-CH_2 para; 2H), 2,3-2,0 (m ; CH_2CF_2; 6H), 2,0-1,7 (m; O-$CH_2CH_2CH_2CH_2CF_2$; 12H)

3,4,5-tris(n-dodecane-1-yloxy)benzylalcohol ; mp (vizual) = 48-50°C

^{1}H-NMR : 6,5 (s; aromat.; 2H), 4.6 (CH_2OH), 4,0 (2t; O-CH_2; 6H), 1,9-1,2 (m ; CH_2; 60H), 0.9 (t; CH_3; 9H)

^{13}C-NMR : 152,8 (gallate 3), 136,9 (gallate 4), 136,0 (gallate 1), 104,9 (gallate 2), 73,1 (para -OCH_2), 68,7 (ortho -OCH_2), 65,0 (CH_2OH), 32-22,3 (CH_2), 13,8 (CH_3)

3) 3,4,5-tris(4-perfluoro-octylbutyl-1-yloxy)benzylchloride (3a) and 3,4,5-tris(n-dodecane-1-yloxy)benzylchloride (3b)

The benzylalcohols were dissolved in CH_2Cl_2 or CF_3CCl_3 together with a catalytic amount of DMF. Then $SOCl_2$ was added dropwise and the reaction mixture was stirred for 1h. Subsequently the reaction mixtures were concentrated and precipitated into methanol. The products were after that filtered and dried under vacuum.

3,4,5-tris(4-perfluoro-octylbutyl-1-yloxy)benzylchloride; mp (vizual) = 94°C

^{1}H-NMR: 6,7 (s; aromat.; 2H) , 4.5 (s; CH_2Cl; 2H), 4,1 (t; O-CH_2 ortho; 4H), 3,9 (t; O-CH_2 para; 2H), 2,3-2,0 (m ; CH_2CF_2; 6H), 2,0-1,7 (m; O-$CH_2CH_2CH_2CH_2CF_2$; 12H)

3,4,5-tris(n-dodecane-1-yloxy)benzylchloride; mp (vizual) = 45-47°C

^{1}H-NMR : 6,7(s; aromat.; 2H), 4.5 (s; CH_2Cl; 2H), 4,1 (t; O-CH_2 ortho; 4H), 3,9 (t; O-CH_2 para; 2H), 1,9-1,2 (m ; CH_2; 60H), 0.9 (t; CH_3; 9H)

4) N-(3,4,5-tris(4-perfluoro-octylbutyl-1-yloxy)benzylcarbazole (4a) and N- (3,4,5-tris(n-dodecane-1-yloxy)benzylcarbazole (4b) (10)

To a two phase system consisting of 100 ml benzene and 100 ml 50% NaOH, were added succesivly 0,7 g (0,12 mol) carbazole, 0,8 g TEBAC, and 4,75 g (0,12 mol) 3,4,5-tris(4-perfluoro-octylbutyl-1-yloxy)- respective 3,4,5-tris(n-dodecane-l-yloxy)benzylchloride. The reaction mixture was refluxed for 3h and then diluted with 100 ml benzene. The organic phase was seperated, washed with water, dried over $MgSO_4$ and filtered over acidic Al_2O_3. Benzene was removed. The crude products were recrystallized from 2-propanol.

N-(3,4,5-tris(4-perfluoro-octylbutyl-1-yloxy)benzyl)carbazole; mp (by DSC) = 109,8°C

^{1}H-NMR : 8,1 (d; carbazole 4,5; 2H), 7,4 (m; carbazole 1,2,7,8; 4H), 7.25 (m; carbazole ; 2H), 6,3 (s; aromat. gallate; 2H), 5,4 (s; N-CH_2 ; 2H), 3.9 (t; para -OCH_2 ;2H; ^{3}J=6,5Hz), 3,8 (t;ortho -OCH_2; 4H), 2,3-2,0 (m; CH_2CF_2 ; 6H), 1,9 -1,4 (m; CH_2 ; 12H)

^{19}F-NMR: -82,1 (s; CF_3; 9F), -115,5 (t; CH_2CF_2; ortho, 4F; J= 14,1Hz), -115,7 (s; CH_2CF_2;para,2F); -123,0 (s CF_2; 18F), -123,9 (s CF_2; 6F), -124,5 (s; ortho CF_2; 4F), -124,6 (s; para CF_2; 2F), -127,3 (s CF_2; 6F)

N- (3,4,5-tris(n-dodecane-1-yloxy)benzyl)carbazole; mp (byDSC) = 56,12°C

^{1}H-NMR : 8,1 (d; carbazole 4,5; 2H), 7,4 (m; carbazole 1,2,7,8; 4H), 7.25 (m; carbazole ; 2H), 6,3 (s; aromat. gallate; 2H), 5,4 (s; N-CH_2 ; 2H), 3.9 (t; para -OCH_2 ;2H), 3,8(t;ortho -OCH_2; 4H), 1,9-1,2 (m; CH_2 ; 60H), 0,9 (t; CH_3 ; 9H)

^{13}C-NMR : 153,0 (gallate 3), 140,9 (carbazole 9a and 8a), 137,3 (gallate 4), 132,1 (gallate 1), 125,8 (carbazole 2 and 7), 123,0 (carbazole 4a and 4b), 120,3 (carbazole 4 and 5), 119,1 (carbazole 3 and 6), 109,5 (carbazole 1 and 8), 104,7 (gallate 2), 73,1 (para -OCH_2), 68,8 (ortho -OCH_2), 48,5 (NCH_2), 32-22,3 (CH_2), 13,9 (CH_3)

5) N-(3,4,5-tris(4-perfluoro-octylbutyl-1-yloxy)benzyl)-3-carboxycarbazole (5a) and N- (3,4,5-tris(n-dodecane-1 yloxy)benzyl)-3-carboxycarbazole (5b)

3,91 g (25,5 mmol) $POCl_3$ were added dropwise under stirring to 1,95 g (26,67 mmol) DMF. After that 4,2 g (2,4 mmol) N-(3,4,5-tris(4-perfluoro-octylbutyl- (resp. n-dodecane)-1-yloxy)-benzyl)carbazole were added once. The reaction mixture was stirred for

6h between 90 - 100°C. The viscous reaction mixture was poured into a sodium acetate buffer and stirred over night. The product was filtered and again stirred in fresh sodium acetate buffer for one day. Then the product was filtered once more and dried under vacuum. The crude products were recrystallized from acetone.

N-(3,4,5-tris(4-perfluoro-octylbutyl-1-yloxy)benzyl)-3-carboxycarbazole

^{1}H-NMR : 10,1 (s; H-C=O;1H), 8,7 (s;carbazole 5; 1H), 8,2 (d;carbazole 5; 2H), 8,0 (d; carbazole 4; 2H); 7,6-7,2 (m; carbazole 1,7,8; 3H), 6,3 (s; aromat.gallate;2H), 5,4 (s; N-CH_2 ; 2H), 3,9 (para -OCH_2 ;2H), 3,8 (t;ortho -OCH_2; 4H), 2,3-2,0 (m; CH_2CF_2 ; 6H), 1,9 -1,4 (m; CH_2 ; 12H)

N- (3,4,5-tris(n-dodecan-1-yloxy)benzyl)-3-carboxycarbazole

^{1}H-NMR : 10,1 (s; H-C=O;1H), 8,7 (s;carbazole 5; 1H), 8,2 (d;carbazole 5; 2H), 8,0 (d; carbazole 4; 2H); 7,6-7,2 (m; carbazole 1,7,8; 3H), 6,3 (s; aromat.gallate;2H), 5,4 (s; N-CH_2 ; 2H), 3,9 (para -OCH_2 ;2H), 3,8 (t;ortho -OCH_2; 4H), 1,9-1,2 (m; CH_2 ; 60H), 0,9 (t; CH_3 ; 9H)

6) N-(3,4,5-tris(4-perfluoro-octylbutyl-1-yloxy)benzyl)-3-hydroxymethylcarbazole (6a) and N- (3,4,5-tris(n-dodecane-1-yloxy)benzyl)-3-hydroxymethylcarbazole (6b)

To a suspension of N-(3,4,5-tris(4-perflouro-octylbutyl-(resp.n-dodecane)-1-yloxy)-benzyl)-3-carboxycarbazole in 2-propanol was added at 40°C dropwise a solution of $NaBH_4$ in 10% NaOH. Ten minutes after the addition was complete the reaction mixture was refluxed for 4h. The products were recrystallized from ethanol.

N-(3,4,5-tris(4-perfluoro-octylbutyl-1-yloxy)benzyl)-3-hydroxymethylcarbazole;
mp (by DSC) = 106-108°C

^{1}H-NMR : 8,1 (d; carbazole 4,5; 2H), 7,5-7,1 (m; carbazole 1,2,5,7,8; 6H), 6,3 (s; aromat. gallate; 2H), 5,4 (s; N-CH_2 ; 2H), 4,9 (s; CH_2OH; 2H), 3,9 (t; para -OCH_2 ;2H), 3,8 (t; ortho -OCH_2; 4H), 2,2-1,9 (m; CH_2CF_2 ; 6H), 1,9 -1,4 (m; CH_2 ; 12H)

^{13}C-NMR : 153,1 (gallate3), 141,1 and 140.4 (carbazole 9a and 8a), 137,1 (gallate4), 132,9 (carbazole 3), 132,0 (gallatel), 126,0 and 125,7 (carbazole 2 and 7), 124,2 and 123,4 (carbazole 4a and 4b), 121,5(carbazole 6), 119,5 (carbazole 4 and 5), 110,7 (carbazole 1 and 8), 104,8 (gallate2), 72,5 (-OCH_2 para), 68,3 (-OCH_2 ortho), 65,4 (CH_2OH), 30,6 (t;$\underline{CH_2}CF_2$; J=22,6Hz), 30,3(-$OCH_2\underline{CH_2}$ para), 29,6(-$OCH_2\underline{CH_2}$ ortho), 17,0 (-$OCH_2CH_2\underline{CH_2}$)

Elemental analysis: calcd (for $C_{56}H_{38}F_{51}NO_4$): C 38,26%, H 2,18%, N 0,8%
found : C 37,57%, H 2,04%, N 0,95%

N- (3,4,5-tris(n-dodecane -1-yloxy)benzyl)-3-hydroxymethylcarbazole;
mp (by DSC) = 79-81°C

^{1}H-NMR : 8,1 (d; carbazole 4,5; 2H), 7,5-7,1 (m; carbazole 1,2,5,7,8; 6H), 6,3 (s; aromat. gallate; 2H), 5,4 (s; N-CH_2 ; 2H), 4,9 (s; CH_2OH; 2H), 3,9 (t; para -OCH_2 ;2H), 3,8 (t; ortho -OCH_2; 4H), 1,9-1,2 (m; CH_2 ; 60H), 0,9 (t; CH_3 ; 9H)

^{13}C-NMR :153,1 (gallate 3), 140,8 and 140.1 (carbazole 9a and 8a), 137,2 (gallate4), 132,0 and 131,7 (carbazole 3 and gallate 1), 125,5 and 125,2 (carbazole 2 and 7), 122,7 (carbazole 4a and 4b), 120,0 (carbazole 6), 119,0 (carbazole 4 and 5), 108,7 (carbazole 1 and 8), 104,6 (gallate 2), 73,1 (-OCH_2 para), 68,7 (-OCH_2 ortho), 65,4 (CH_2OH), 46,6 (NCH_2), 32,7-22,4 (CH_2), 13,8 (CH_3)

Elemental analysis: calcd (for $C_{56}H_{89}NO_4$) : C 80,04%, H 10,67%, N 1,67%
found : C 78,52%, H 10,30%, N 1,52

D. Polymerizations

1g N-(3,4,5-tris(n-dodecane-1-yloxy)benzyl)-3-hydroxymethylcarbazole was dissolved in a mixture of 15g THF and 6g trifluoracetic anhydride. After 15 min 0,5g $ZnCl_2$ were added. The reaction mixture was stirred for 5d at 70 °C and then poured into 300 ml of ethanol. The product was filtered and dissolved in heptane. The heptane solution was filtered over basic Al_2O_3. Yield: 0,8g

The polymerizations of N-(3,4,5-tris(4-perfluoro-octylbutyl-1-yloxy)benzyl)-3-hydroxymethylcarbazole and of the 1:1 mixture of both monomers were carried out under the same conditions.

Characterization of the polymers

Elemental analysis

Poly-6a: calcd (for $C_{56}H_{38}F_{51}NO_3$): C 38,62%, H 2,20%, N 0,8%
found : C 38,52%, H 2,14%, N 0,85%

Poly-6b: calcd (for $C_{56}H_{87}NO_3$) : C 81,70%, H 10,77%, N 1,70%
found : C 81,49%, H 10,85%, N 1,66%
Copoly 1:1 6a / 6b calcd (for $C_{112}H_{125}F_{51}N_2O_6$): C 52,46%, H 4,91%, N 1,09%
found : C 52,20%, H 4,85%, N 0,99%

GPC analysis yielded for Poly-6b Mn=5000 and U=0.4, respective Mn=8000 and U=0,3 for the 1:1 Copoly 6a / 6b. These values correspond to a degree of polymerization of 6 for both polymer and copolymer. Since the Poly 6a is soluble only in fluorinated solvents or solvent mixtures the molecular weight could not be determined.

In all published papers (2),(3),(4),(5) it is mentioned that the ^{1}H-NMR spectra of the poly(carbazolylmethylene)s are very broad and poorly resolved. The carbazole protons and the NCH_2 resonances are slightly shifted to higher field. We observed for the poly-6b and the copolymer that the signal of the CH_2OH group at 4,7 ppm disappeared completly. Instead the bridging CH_2 group appears as a very broad signal from 4,4 to 4,0 ppm. All other signals appear at the same positions as in the monomers. The 1:1 composition of the obtained copolymer was proved by the ratio of the integrals of the CH_3 and of the carbazol protons and by elemental analysis, respectively.

In ^{13}C-NMR spectrum the signal of the CH_2OH peak at 66,7 ppm disappears. Instead a new signal for the bridging methlene group at 41,6 ppm is observed and the six aromatic C resonances of the carbazole nucleus are splitted. According to (5) the splitting is attributed to sequence and end group effects in short polymer chains. Additional the explanation of weak shielding effects by adjacent carbazole groups may be assumed (2). The other ^{13}C-NMR chemical shifts remain nearly unchanged as compared to the monomers.

Thermal characterization of monomeric analogous and polymers

Figure 1 shows the termal transition temperatures observed by DSC of N-(3,4,5-tris(4-perfluoro-octylbutyl-1-yloxy)benzyl)carbazole (4a) and of N-(3,4,5-tris(n-dodecane-1-yloxy)benzyl)carbazole (4b) together with those of the studied polymers. Both 4a and 4b show crystalline melting (T_m) on heating and crystallization (T_c) on cooling. An amorphous solid results if in poly-6b the 4b units are connected by methylene bridges. The poly-6a on the contrary, shows beside the Tg a low enthalpy transition both on heating at 130,6 °C and on cooling at 103 °C. The transitions appear even during the first heating and cooling scans and do not depend on the thermal history of the sample. The enthalpy of this first order transition is of 0,34 kcal/mol repeating unit. The poly-6b and the 1:1 copolymer show only a glass transition. The fact that the Tg of the 1:1 copolymer is higher (around 50°C) than of the two homopolymers (situated around 20°C) suggests that the glass temperatures may be related to the aliphatic and/or flourocarbon tails. In the the copolymer the aliphatic and fluorocarbon tails tend to segregate releasing the the rotational mobility characteristic of Tg only at higher temperature.

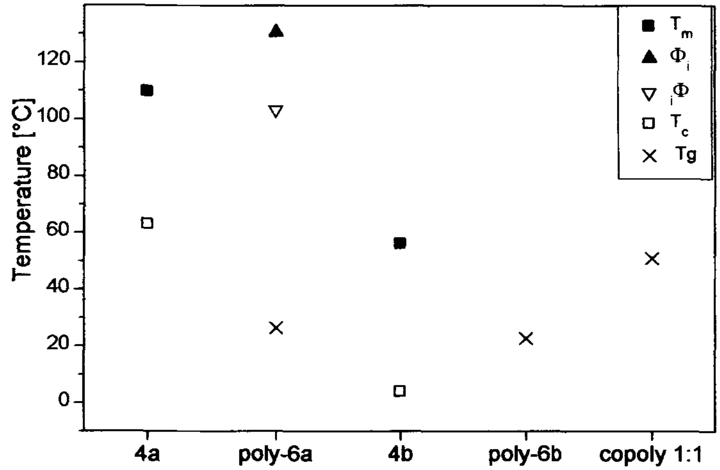


Fig.1 Thermal transitions of 4a / 4b and polymers

X-ray

Table 1 lists the d-spacings obtained from powder diffraction spectra of the poly-6a at room temperature. Beneath two strong reflections at 34,7 Å and 5,2 Å are observed two weaker reflections at 17,6Å and 13,1 Å, respectively, and one very weak at 11,6 Å. This is a strong evidence for a hexagonal columnar mesophase (12)(7). A detailed discussion of the structure will be presented later.(11)

Tabl. 1

	d_{100}	$d_{110}^{\cdot}$ $(d_{100}\cdot\frac{1}{\sqrt{3}})$	$d_{200}^{\cdot}$ $(d_{100}\cdot\frac{1}{\sqrt{4}})$	$d_{210}^{\cdot}$ $(d_{100}\cdot\frac{1}{\sqrt{7}})$	$d_{300}^{\cdot}$ $(d_{100}\cdot\frac{1}{\sqrt{9}})$	
Poly-6b	34,7 Å	17,6 Å	–	13,1 Å	11,6Å	5,2 Å

Conclusions

The syntheses of soluble poly(3,5-carbazolylmethylene)s were realized. The polymerization proceeds without any crosslinking. Elemental analysis, ^{13}C-NMR and ^{1}H-NMR data confirm the proposed structure and are in accord with literature data for other poly(3,5-carbazolylmethylene)s (2), (3), (5). The poly-6a shows by DSC a liquid crystalline phase which undergoes isotropization at 130°C. Preliminary X-ray results offer strong evidence for a columnar hexagonal phase (12). It is well known that poly-(3,5-carbazolylmethylene)s form reversible one electron redox systems (5). A study concerning the presence of a mesophase on the redox behaviour is in progress. Furthermore we will report in a following paper, that it is possible to induce mesomorphic behaviour in the amorphous copolymer by selective complexation of fluorinated or nonfluorinated sequences of the copolymer with an electron-acceptor based on 3,5 dinitrobenzoic acid.

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