ELSEVIER

Journal of Fluorine Chemistry 74 (1995) 185–189

JOURNAL OF FLUORINE CHEMISTRY

Synthesis of liquid-crystalline poly(meth)acrylates with 4-trifluoromethoxy-azobenzene mesogenic side-groups

Dietrich Prescher [a,*], Thomas Thiele [b], Ralf Ruhmann [b], Günter Schulz [b]

[a] *Institut für Festkörperphysik, Universität Potsdam, Rudower Chaussee 5, Haus 12.5, D-12484 Berlin-Adlershof, Germany*
[b] *Institut für Angewandte Chemie Berlin-Adlershof eV, Rudower Chaussee 5, Haus 12.5, D-12484 Berlin-Adlershof, Germany*

Received 3 November 1994; accepted 11 May 1995

Abstract

Side-group liquid-crystalline polymers with fluorine-containing mesogens were synthesized and characterized. 4-Trifluoromethoxy-aniline was diazotized and coupled with phenol to give 4-hydroxy-4′-trifluoromethoxy-azobenzene. Alkylation of this compound with α,ω-dibromoalkanes, followed by reaction with the potassium salts of acrylic or methacrylic acid, yielded the monomers. Their radical polymerization gave the corresponding polyacrylates or polymethacrylates, respectively.

The polymers were characterized by size exclusion chromatography (SEC) and by differential scanning calorimetry (DSC).

Keywords: Liquid crystal polymer; 4-Trifluoromethoxy-azobenzene; Polyacrylates; Polymethacrylates

1. Introduction

Side-group liquid-crystalline polymers (SGLCP) with photochromic groups are of interest for applications in the field of non-linear optics, optical information storage and processing, and electro-optical displays [1–2]. Moreover, it was found by studies on low-molar-mass liquid crystals that materials containing fluorine combine several advantageous properties such as favourable mesophase behaviour, low viscosity, high stability and polarity [3–4].

Only a limited number of fluorine-containing SGLCPs have been reported [5–9]. Therefore we have started to study the influence of fluorine on the mesophase behaviour of such compounds [10].

In the present work, the synthesis of polyacrylates and polymethacrylates with 4-trifluoromethoxy-azobenzene mesogens is described.

2. Experimental details

2.1. General techniques

^{1}H NMR spectra were run on a Bruker WP 200 SY (200 MHz) spectrometer. ^{13}C broad-band decoupled NMR spectra were recorded on a Varian Gemini 300 (75 MHz) spectrometer. Internal hexamethyldisilazane (HMDS) was used as the respective reference, and the solvent used was always $CDCl_3$.

Infrared (IR) spectra were recorded on a Zeiss Specord 75 IR spectrometer using KBr discs.

Melting points are uncorrected.

Elemental analyses (for F) were carried out according to a standard method.

Size exclusion chromatography (Knauer HPLC-pump 64; column, 2 Knauer PL Mixed Gel, 10 μm, linear; injection volume, 100 μl; flow, 1 ml min^{-1}; internal standard, toluene; Knauer detectors, UV and RI) of the polymers was performed in tetrahydrofurane (THF Lichrosolvc, Merck) with calibration by polystyrene standards.

The thermal behaviour of the polymers was investigated by a DSC 7 differential scanning calorimeter (Perkin–Elmer). The scanning rate of the heating runs was 20 K min^{-1}. The maximum in DSC enthalpic peaks was taken as the phase transition temperature.

2.2. Synthesis

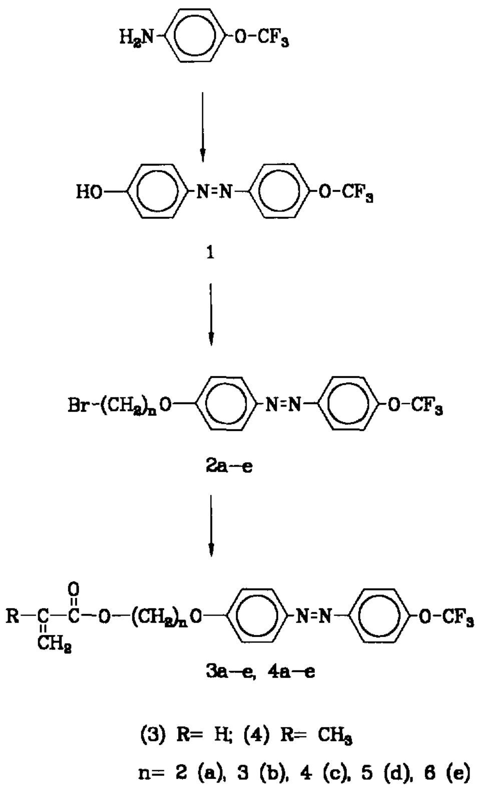
*4-Hydroxy-4′-trifluoromethoxy-azobenzene (**1**)*

13.5 g (75 mmol) 4-trifluoromethoxy-aniline (Aldrich) were dissolved under heating in a mixture of 21 ml concentrated sulphuric acid and 21 ml water, and after cooling diazotized by dropping a solution of 7 g $NaNO_2$ in 40 ml water at 0–5 °C to the acid mixture. Then the coupling was carried

---

* Corresponding author.

SSDI 0022-1139(95)03291-6



Scheme 1.

out by slowly adding the diazotization solution to a solution of 7.5 g phenol, 3 g NaOH and 47 g Na_2CO_3 in 270 ml water at 0–5 °C. The yellow–orange coloured precipitate of **1** was filtered off, dried and recrystallized from *n*-hexane (14.8 g, 70%). M.P. 116.5–117.5 °C. Anal. Found: F, 20.19%. $C_{13}H_9F_3N_2O_2$ (282.2). Calc.: F, 20.20%. IR: 3400 vs (OH); 1305 vs (C–OH); 1240–1085 s (CF_3) cm^{-1}. ^1H NMR: δ 6.88 (2H, m, J = 8.8 Hz); 7.27 (2H, m, J = 8.8 Hz); 7.43 (4H, 2m, J = 8.8 Hz) ppm. ^{13}C NMR: δ 115.9 (C–Ar); 120.4 (q, CF_3, ^1J(C–F) = 256 Hz); 121.3 (C–Ar); 124.0 (C–Ar); 125.2 (C–Ar); 147.0 (C–Ar); 150.5 (C–Ar); 150.8 (C–Ar); 158.5 (C–Ar) ppm.

4-(ω-Bromo-alkoxy)-4′-trifluoromethoxy-azobenzenes (2a–2e)

A mixture of 0.4 mol of the corresponding α,ω-dibromoalkane, 0.2 mol of dry potassium carbonate, 0.04 mol of 4-hydroxy-4′-trifluoromethoxy-azobenzene and a trace of potassium iodide in 250 ml of dry acetone was stirred vigorously and refluxed for 16 h. After cooling, the precipitated salt was filtered off and the filtrate was evaporated. The crude product was purified by recrystallization from *n*-hexane.

2a: Yield: 84%. M.P. 103–103.5 °C. Anal. Found: F, 13.85%. $C_{15}H_{12}BrF_3N_2O_2$ (389.17). Calc.: F, 14.65%. IR: 2905 w, 2850 w (CH_2); 640 w (C–Br) cm^{-1}. ^1H NMR: δ 3.61 (2H, t, J = 6.2 Hz); 4.31 (2H, t, J = 6.2 Hz); 6.96 (2H, m, J = 9 Hz); 7.27 (2H, m, J = 9 Hz); 7.85 (4H, 2m, J = 9 Hz) ppm. ^{13}C NMR: δ 28.7 (CH_2Br); 68.0 (CH_2O); 114.9 (C–Ar); 120.4 (q, CF_3, ^1J(C–F) = 256 Hz); 121.3 (C–Ar); 124.0 (C–Ar); 125.0 (C–Ar); 147.2 (C–Ar); 150.5 (C–Ar); 150.8 (C–Ar); 160.7 (C–Ar) ppm.

2b: Yield: 76%. M.P. 81–82 °C. Anal. Found: F, 13.91%. $C_{16}H_{14}BrF_3N_2O_2$ (403.20). Calc.: F, 14.14%. IR: 2935 w, 2925 w, 2850 w (CH_2); 635 w (C–Br) cm^{-1}. ^1H NMR: δ 2.29 (2H, m); 3.55 (2H, t, J = 6.4 Hz); 4.12 (2H, t, J = 5.8 Hz); 6.95 (2H, m, J = 9 Hz); 7.26 (2H, m, J = 9 Hz); 7.84 (4H, 2m, J = 9 Hz) ppm.

2c: Yield: 77%. M.P. 74–75 °C. Anal. Found: F, 13.54%. $C_{17}H_{16}BrF_3N_2O_2$ (417.23). Calc.: F, 13.66%. IR: 2940 w, 2865 w (CH_2); 640 w (C–Br) cm^{-1}. ^1H NMR: δ 1.93–2.10 (4H, m); 3.44 (2H, t, J = 6.3 Hz); 4.02 (2H, t, J = 5.8 Hz); 6.93 (2H, m, J = 9 Hz); 7.27 (2H, m, J = 9 Hz); 7.85 (4H, 2m, J = 9 Hz) ppm.

2d: Yield: 50%. M.P. 73–73.5 °C. Anal. Found: F, 13.64%. $C_{18}H_{18}BrF_3N_2O_2$ (431.25). Calc.: F, 13.22%. IR: 2935 m, 2925 w, 2855 w (CH_2); 650 m (C–Br) cm^{-1}. ^1H NMR: δ 1.54–1.65 (2H, m); 1.80 (2H, m); 1.90 (2H, m); 3.40 (2H, t, J = 6.7 Hz); 4.00 (2H, t, J = 6.3 Hz); 6.94 (2H, m, J = 9 Hz); 7.27 (2H, m, J = 9 Hz); 7.85 (4H, 2m, J = 9 Hz) ppm.

2e: Yield: 79%. M.P. 71.5–73 °C. Anal. Found: F, 12.73%. $C_{19}H_{20}BrF_3N_2O_2$ (445.28). Calc.: F, 12.80%. IR: 2930 m, 2850 w (CH_2); 640 w (C–Br) cm^{-1}. ^1H NMR: δ 1.40–1.50 (4H, m); 1.70–1.90 (4H, m); 3.36 (2H, t, J = 6.78 Hz); 3.98 (2H, t, J = 6.3 Hz); 6.94 (2H, m, J = 9 Hz); 7.26 (2H, m, J = 9 Hz); 7.84 (4H, 2m, J = 9 Hz) ppm. ^{13}C NMR: δ 25.2; 27.9; 29.0; 32.6; 33.7 (C-spacer); 68.1 (CH_2O); 114.7 (C–Ar); 120.4 (q, CF_3, ^1J(C–F) = 256 Hz); 121.3 (C–Ar); 124.0 (C–Ar); 125.9 (C–Ar); 146.7 (C–Ar); 150.3 (C–Ar); 150.9 (C–Ar); 161.9 (C–Ar) ppm.

4-(ω-Acryloxy-alkoxy)-4′-trifluoromethoxy-azobenzenes (3a–3e)

A mixture of 20 mmol of the corresponding **2** and 40 mmol of potassium acrylate in 150 ml dried DMF was stirred vigorously at 60 °C for 8 h. The cooled reaction mixture was diluted with water. Then the precipitate was isolated and dried. The crude product was purified by column chromatography on silica gel, using dichloromethane as eluent, and by recrystallization from *n*-hexane.

3a: Yield: 41%. M.P. 84–86 °C. Anal. Found: F, 14.51%. $C_{18}H_{15}F_3N_2O_4$ (380.32). Calc.: F, 14.99%. IR: 1715 s (C=O) cm^{-1}. ^1H NMR: δ 4.23 (2H, t, J = 4.7 Hz); 4.49 (2H, t, J = 4.7 Hz); 5.80 (1H, dd, J = 10.3 + 1.5 Hz); 6.15 (1H, dd, J = 17.2 + 10.3 Hz); 6.40 (1H, dd, J = 17.2 + 1.5 Hz); 6.97 (2H, m, J = 9 Hz); 7.26 (2H, m, J = 8.4 Hz); 7.85 (4H, 2m, J = 9 Hz) ppm.

3b: Yield: 72%. M.P. 67–68 °C. Anal. Found: F, 13.97%. $C_{19}H_{17}F_3N_2O_4$ (394.34). Calc.: F, 14.45%. IR: 1715 s (C=O) cm^{-1}. ^1H NMR: δ 2.15 (2H, quint., J = 6.2 Hz); 4.10 (2H, t, J = 6.2 Hz); 4.33 (2H, t, J = 6.2 Hz); 5.78 (1H, dd, J = 10.4 + 1.5 Hz); 6.08 (1H, dd, J = 17.4 + 10.4 Hz); 6.36 (1H, dd, J = 17.4 + 1.5 Hz); 6.95 (2H, m, J = 9 Hz); 7.27 (2H, m, J = 9 Hz); 7.85 (4H, 2m, J = 9 Hz) ppm.

3c: Yield: 36%. M.P. 63–64 °C. Anal. Found: F, 13.62%. $C_{20}H_{19}F_3N_2O_4$ (408.37). Calc.: F, 13.96%. IR: 1705 s

(C=O) cm^{-1}. ^{1}H NMR: δ 1.75–2.00 (4H, m); 4.03 (2H, t, J=5.5 Hz); 4.20 (2H, t, J=5.9 Hz); 5.77 (1H, dd, J=10.3+1.5 Hz); 6.06 (1H, dd, J=17.3+10.3 Hz); 6.36 (1H, dd, J=17.3+1.5 Hz); 6.94 (2H, m, J=8.9 Hz); 7.28 (2H, m, J=8.6 Hz); 7.85 (4H, 2m, J=8.9 Hz) ppm.

3d: Yield: 61%. M.P. 72–73 °C. Anal. Found: F, 12.69%. $C_{21}H_{21}F_3N_2O_4$ (422.40). Calc.: F, 13.49%. IR: 1715 vs (C=O) cm^{-1}. ^{1}H NMR: δ 1.53 (2H, m); 1.71 (2H, m); 1.81 (2H, m); 4.00 (2H, t, J=6.3 Hz); 4.14 (2H, t, J=6.5 Hz); 5.76 (1H, dd, J=10.3+1.5 Hz); 6.06 (1H, dd, J=17.3+10.3 Hz); 6.35 (1H, dd, J=17.3+1.5 Hz); 6.94 (2H, m, J=9 Hz); 7.27 (2H, m, J=8.1 Hz); 7.85 (4H, 2m, J=9 Hz) ppm.

3e: Yield: 35%. M.P. 70.5–71.5 °C. Anal. Found: F, 13.01%. $C_{22}H_{23}F_3N_2O_4$ (436.42). Calc.: F, 13.06%. IR: 1720 vs (C=O) cm^{-1}. ^{1}H NMR: δ 1.45–1.55 (4H, m); 1.66 (2H, m); 1.77 (2H, m); 3.98 (2H, t, J=6.3 Hz); 4.12 (2H, t, J=6.5 Hz); 5.74 (1H, dd, J=10.5+1.5 Hz); 6.05 (1H, dd, J=17.3+10.3 Hz); 6.34 (1H, dd, J=17.3+1.5 Hz); 6.93 (2H, m, J=9 Hz); 7.26 (2H, m, J=8.4 Hz); 7.84 (4H, 2m, J=9 Hz) ppm. ^{13}C NMR: δ 25.7; 25.7; 28.5; 29.0 (C-spacer); 64.4 (CH_2OCO); 68.1 (CH_2OAr); 114.7 (C–Ar); 120.4 (q, CF_3, ^1J(C–F)=256 Hz); 121.3 (C–Ar); 124.0 (C–Ar); 124.9 (C–Ar); 128.6 ($CH{=}CH_2$); 130.5 ($CH{=}CH_2$); 146.7 (C–Ar); 150.3 (C–Ar); 151.9 (C–Ar); 161.9 (C–Ar); 166.3 (C=O) ppm.

4-(ω-Methacryloxy-alkoxy)-4′-trifluoromethoxy-azobenzenes (4a–4e)

A mixture of 37.5 mmol of the corresponding **2** and 75 mmol potassium methacrylate in 100 ml dried DMF was stirred vigorously and heated for 4 to 10 h at 60 °C. The cooled reaction mixture was diluted with water. Then the precipitate was filtered and dried. The crude product was purified by column chromatography on silica gel, using dichloromethane as eluent, and by recrystallisation from *n*-hexane.

4a: Yield: 68%. M.P. 90–92 °C. Anal. Found: F, 14.56%. $C_{19}H_{17}F_3N_2O_4$ (394.35). Calc.: F, 14.45%. IR: 1705 s (C=O) cm^{-1}. ^{1}H NMR: δ 1.90 (3H, s, broad); 4.25 (2H, t, J=4.8 Hz); 4.48 (2H, t, J=4.8 Hz); 5.54 (1H, s, broad); 6.10 (1H, s, broad); 7.68 (2H, m, J=9 Hz); 7.27 (2H, m, J=9 Hz); 7.85 (4H, 2m, J=9 Hz) ppm.

4b: Yield: 71%. M.P. 78–80 °C. Anal. Found: F, 13.99%. $C_{20}H_{19}F_3N_2O_4$ (408.32). Calc.: F, 13.96%. IR: 1700 vs (C=O) cm^{-1}. ^{1}H NMR: δ 1.89 (3H, s, broad); 2.15 (2H, quint., J=6.2 Hz); 4.10 (2H, t, J=6.2 Hz); 4.31 (2H, t, J=6.2 Hz); 5.51 (1H, s, broad); 6.05 (1H, s, broad); 6.94 (2H, m, J=8.9 Hz); 7.27 (2H, m, J=8.7 Hz); 7.85 (4H, 2m, J=8.9 Hz) ppm.

4c: Yield: 78%. M.P. 66–66.5 °C. Anal. Found: F, 13.44%. $C_{21}H_{21}F_3N_2O_4$ (422.40) Calcd.: F, 13.49%. IR: 1710 vs (C=O) cm^{-1}. ^{1}H NMR: δ 1.83–1.90 (4H, m); 1.89 (3H, s, broad); 4.03 (2H, t, J=5.8 Hz); 4.19 (2H, t, J=6 Hz); 5.50 (1H, m); 6.05 (1H, s, broad); 6.94 (2H, m, J=9 Hz); 7.27 (2H, m, J=9 Hz); 7.85 (4H, 2m, J=9 Hz) ppm.

4d: Yield: 54%. M.P. 66–70 °C. Anal. Found: F, 12.47%. $C_{22}H_{23}F_3N_2O_4$ (436.43). Calc.: F, 13.06%. IR: 1705 vs (C=O) cm^{-1}. ^{1}H NMR: δ 1.49–1.59 (2H, m); 1.72 (2H, m); 1.82 (2H, m); 1.89 (3H; s, broad); 4.00 (2H, t, J=6.3 Hz); 4.13 (2H, t, J=6.5 Hz); 5.50 (1H, s, broad); 6.04 (1H, s, broad); 6.94 (2H, m, J=9 Hz); 7.27 (2H, m, J=8.1 Hz); 7.84 (4H, 2m, J=8.4 Hz) ppm.

4e: Yield: 78%. M.P. 82–83 °C. Anal. Found: F, 12.48%. $C_{23}H_{25}F_3N_2O_4$ (450.46). Calc.: F, 12.65%. IR: 1705 vs (C=O) cm^{-1}. ^{1}H NMR: δ 1.36–1.54 (4H, m); 1.67 (2H, m); 1.78 (2H, m); 1.88 (3H, s, broad); 3.99 (2H, t, J=6.4 Hz); 4.11 (2H, t, J=6.6 Hz); 5.49 (1H, s, broad); 6.04 (1H, s, broad); 6.93 (2H, m, J=9 Hz); 7.27 (2H, m, J=8.1 Hz); 7.84 (4H, m, J=9 Hz) ppm. ^{13}C NMR: δ 18.3 (CH_3); 25.7; 25.8; 28.5; 29.0 (C-spacer); 64.6 ($\underline{C}H_2OCO$); 68.1 ($\underline{C}H_2OAr$); 114.7 (C–Ar); 120.4 (q, CF_3, ^1J(C–F)=256 Hz); 121.3 (C–Ar); 123.9 (C–Ar); 124.9 (C–Ar); 125.2 ($C{=}\underline{C}H_2$); 136.5 ($\underline{C}{=}CH_2$); 146.7 (C–Ar); 150.3 (C–Ar); 151.0 (C–Ar); 161.9 (C–Ar); 167.5 (C=O) ppm.

2.3. Polymerization

About 2 g of the monomer was dissolved in 20 ml of DMF, and 2 mol.% (based on the monomer) of AIBN was added. The monomer solution was degassed by passing nitrogen for 30 min and polymerized at 70 °C for 24 h. The polymers obtained were precipitated in ethanol and purified by reprecipitations from dichloromethane/ethanol. The purified polymers were dried under reduced pressure at 40 °C for 48 h. For yields and properties of the prepared polymers see Table 1.

Poly[4-(6-acryloxy-hexoxy)-4′-trifluoromethoxy-azobenzene]

^{13}C NMR: δ 25.7; 25.7; 28.5; 29.1 (C-spacer); 35.6 (CO–CH–$\underline{C}H_2$); 41.5 (CO–$\underline{C}$H–CH_2); 64.6 ($\underline{C}H_2$–O–CO); 68.1 (O–$\underline{C}H_2$); 114.6 (C–Ar); 120.4 (q, CF_3, ^1J(C–F)=256 Hz); 121.2 (C–Ar); 123.9 (C–Ar); 124.9 (C–Ar); 146.6 (C–Ar); 150.3 (C–Ar); 150.8 (C–Ar); 161.8 (C–Ar); 174.9 (C=O) ppm.

Poly[4-(6-methacryloxy-hexoxy)-4′-trifluoromethoxy-azobenzene]

^{13}C NMR: δ 18.5 (CH_3); 25.7; 25.8; 28.1; 29.1 (C-spacer); 35.3 (CO–C–$\underline{C}H_2$); 44.8 (CO–$\underline{C}$–CH_2); 64.8 ($\underline{C}H_2$–O–CO); 68.0 (O–$\underline{C}H_2$); 114.5 (C–Ar); 120.4 (q, CF_3, ^1J(C–F)=256 Hz); 121.2 (C–Ar); 123.9 (C–Ar); 124.9 (C–Ar); 146.6 (C–Ar); 150.3 (C–Ar); 150.7 (C–Ar); 161.7 (C–Ar); 174.4 (C=O) ppm.

3. Results and discussion

3.1. Synthesis

The monomeric acrylates **3a–3e** and methacrylates **4a–4e** were synthesized corresponding to Scheme 1.

Table 1
Yields and properties of the polyacrylates from **3a**–**3e** and the polymethacrylates from **4a**–**4e**

Polymer from	*n*	Yield (%)	% F Calc.	% F Found	M_n (10^3 g mol^{-1})	M_w (10^3 g mol^{-1})	M_w/M_n [a]	Phase behaviour [b] (°C)
3a	2	24	14.99	14.52	5.2	6.6	1.3	g 61 LC 112 i
3b	3	60	14.45	13.39	4.9	6.1	1.2	g 55 (66) LC 76 LC 97 i
3c	4	18	13.96	13.45	5.9	7.0	1.3	g 53 LC 64 LC 98 LC 110 i
3d	5	70	13.49	12.81	3.7	4.8	1.4	g 46 (64) LC 68 LC 79 i
3e	6	21	13.06	12.90	5.7	7.0	1.2	g 47 LC 68 LC 101 LC 106 i
4a	2	33	14.45	14.40	20	59	2.9	g 73 LC 144 i
4b	3	75	13.96	14.04	23	53	2.3	g 75 LC 122 i
4c	4	58	13.49	13.44	29	72	2.5	g 67 LC 96 LC 114 i
4d	5	74	13.06	13.04	17	39	2.4	g 66 LC 120...125 LC 132 i
4e	6	60	12.65	12.63	30	72	2.4	g 58 LC 90 LC 109 i

[a] Ratio of weight-average to number-average molecular weight.
[b] g, glassy; LC, liquid-crystalline; i, isotropic.

Diazotization of 4-trifluoromethoxy-aniline by sodium nitrite in aqueous sulphuric acid at 0–5 °C, followed by coupling with phenol at the same temperature, give the expected substituted azobenzene **1** (70%). The O-alkylation of **1** in dried acetone under reflux and in the presence of potassium carbonate needs a high excess of α,ω-dibromoalkanes to get a convenient yield of **2** (50–84%). Progress and success of the reaction can be controlled by thin-layer chromatography on silica gel with dichloromethane as solvent.

The reaction of **2** with the potassium salt of acrylic acid and methacrylic acid in *N*,*N*-dimethylformamide (DMF) at 60 °C leads to the corresponding monomers; the acrylates **3a**–**3e** (35–72%) and the methacrylates **4a**–**4e** (54–78%), respectively.

The polymerization of the monomers was carried out with 2,2′-azoisobutyronitrile (AIBN) as initiator at 70 °C and in DMF as solvent to give polymers in acceptable yield for the polymethacrylates (33% only at **4a**, generally 58–75%), but less for the polyacrylates (18–70%). Additional attempts at polymerization of the acrylates in benzene did not give products with higher yield.

Samples of the polymers were characterized by size exclusion chromatography (SEC). Whereas the polymethacrylates have number-average molecular weights M_n from about 17 000 to 30 000 and M_w/M_n ratios from 2.3 to 2.9 (Table 1), the polyacrylates prepared gave values for M_n from about 4900 to 6700 and unusually low M_w/M_n ratios from 1.2 to 1.4. The molar mass is here obviously too low. The tenfold greater amount of the initiator AIBN led to a higher yield, but did not lower the value of M_n! The narrow distribution of the polyacrylates is linked with their low molar masses, and was probably caused by fractionation during the purification of the products.

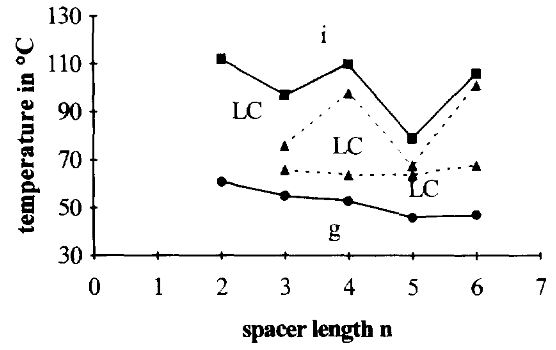


Fig. 1. Phase behaviour of polyacrylates depending on the spacer length: g, glassy; LC, liquid-crystalline; i, isotropic.

The degrees of polymerization reached allow one to neglect the dependence of the phase transition temperatures on the molecular weight only in the case of the polymethacrylates. Nevertheless, a comparison of the polyacrylates with each another is permitted. Thus, it is possible to recognize the general orientation for the slope of the phase transition temperatures within the polyacrylates.

All synthesized intermediate and final products are *trans* azobenzene isomers. The transformation of these thermodynamically stable isomers into the *cis* isomers is only possible by irradiation with UV light.

3.2. Liquid-crystalline behaviour

The phase transition temperatures recorded by DSC are given in Table 1 in detail. The glass transition temperatures of the polymethacrylates from **4a**–**4e** decrease slightly with increasing spacer length. This behaviour is well documented for side-group liquid-crystalline polymers [1]. But in comparison to the non-fluorinated analogues, the glass transition temperatures are strongly reduced. For instance, polymer from **4a** has the glass transition at a temperature of 73 °C, while the glass transition of the corresponding non-fluorinated polymer is described at 100 °C [11]. The clearing temperatures decrease too with increasing spacer length.

The phase transition temperatures of the polyacrylates from **3a**–**3e** are summarized additionally in a phase diagram (Fig. 1), showing these temperatures depending on the spacer length *n*. The tendency of reduced glass transition and clearing temperatures with increasing spacer length is well demonstrated for the polyacrylates too.

Furthermore, the phase diagram shows much more phase transitions than for the analogous non-fluorinated compounds. These non-fluorinated polyacrylates, reported in the literature [11] without any information about their molar mass, certainly possess a higher molar mass than the polyacrylates from **3a–3e**. Therefore a direct comparison of the absolute values of the phase transition temperatures of both types of polymers is not possible. However, the increased number of phase transitions points to the enhanced formation of smectic phases in the fluorine-containing polymers. This is in agreement with the behaviour of low-molar-mass liquid crystals substituted by fluorine compared with their non-fluorinated analogues [3].

A more detailed study of the phase behaviour of this interesting new group of liquid-crystalline polymers was presented recently [12].

Acknowledgement

Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

[1] C.B. McArdle, *Side Chain Liquid Crystal Polymers*, Blackie, Glasgow, 1989.

[2] S. Xie, A. Natansohn and P. Rochon, *Chem. Mater.*, *5* (1993) 403.

[3] E.P. Janulis, D.W. Osten, M.D. Radcliff, J.C. Novack, M. Tristani-Kendra, K.A. Epstein, M. Keyes, G.C. Johnson, P.M. Savu and T.D. Spawn, *SPIE*, *1665* (1992) 146.

[4] E. Bartmann, *Ber. Bunsengesell. Phys. Chem.*, *97* (1993) 1349.

[5] V. Percec, D. Tomazos and A.E. Feiring, *Polymer*, *32* (1991) 1897.

[6] G.S. Attard, J.S. Dave and A. Wallington, *Makromol. Chem.*, *192* (1991) 1495.

[7] T. Kitazume, T. Ohnogi and K. Ito, *J. Am. Chem. Soc.*, *112* (1990) 6608.

[8] P. LeBarny, G. Ravaux, J.C. Dubois, J.P. Parnaix, R. Njeumo, C. Legrand and A.M. Levelut, *Proc. SPIE. — Int. Soc. Opt. Eng. (USA)*, *682* (1987) 56.

[9] C. Legrand, C. Bunel, A. le Borgne, N. Lacondre, N. Spassky and J.-P. Vairan, *Makromol. Chem.*, *191* (1990) 2971.

[10] D. Prescher, R. Ruhmann and D. Wolff, *14th Int. Symp. on Fluorine Chemistry*, Yokohama, 31 July–5 August 1994.

[11] A. Möller, U. Czajka, V. Bergmann, J. Lindau, M. Arnold and F. Kuschel, *Z. Chem.*, *27* (1987) 218.

[12] R. Ruhmann, T. Thiele, D. Prescher and D. Wolff, *Macromol. Rapid Commun.*, *16* (1995) 161.