

Thermal Stability of an Azo Dye-Containing Liquid Crystalline Side Group Polymer

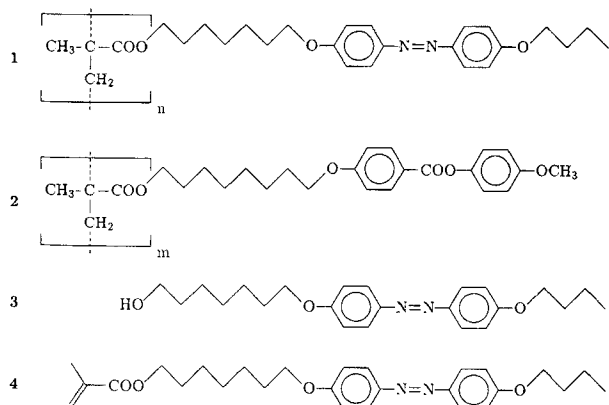
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On the basis of the spacer concept [1], a wide variety of polymeric side group liquid crystals has been synthesized and investigated during the last few years [2–4].

Recently we investigated the influence of lateral substituents on the phase behaviour of liquid crystalline side group polymethacrylates (i.e. SGPMAs) containing azo-dyes [5]. During our experiments on the application of these materials for optical devices thermal degradation at moderate temperatures occurred. Since this behaviour can be observed for i.e. SGPMAs with and without azo-dyes we were surprised to find no literature dealing with this effect. On the other hand the thermal degradation of polyalkylmethacrylates, which occurs almost exclusively by depolymerization, has been intensively studied [6, 7].



Formula 1 Examples of liquid crystalline polymethacrylates for which thermal degradation at moderate temperatures has been observed (**1** and **2**, with n and m indicating the degree of polymerization) and the decomposition products of **1** (**3** and **4**)

In the following the degradation of poly-2-methylpropenyl- ω -[4-(4-butoxyphenazo)-phenoxy]-heptylester **1** (formula 1) will be discussed. The thermal degradation of **2** at moderate temperatures has been investigated by Runke [8] by comparing diagrams of gel permeation chromatography (GPC) measurements of polymer samples after different thermal treatments.

Experimental

The synthesis of **1** as well as the investigation of its phase behaviour has been described in a different paper [9].

The thermogravimetry (TG) was performed on a Seteram B70 thermobalance in a nitrogen or oxygen gas flow (3 l/h). For each experiment approximately 40 mg of the polymer were heated in a magnesium oxide pan with a rate of 2.43 K/min. The molecular weight distribution and the weight-average molecular weight of the polymers were determined by GPC, whereas their phase behaviour was investigated by differential scanning calorimetry (DSC), polarizing microscopy and X-ray diffraction. The experimental procedures and the instrumentation are described elsewhere [10].

Each annealing experiment was carried out with approximately 5 mg of the polymer in a 50 μ l aluminium pan BO14-3017 from Perkin-Elmer. It was placed in a 7 ml test tube which was sealed with a silicone plug and inserted into a Haake N3B thermostat filled with Baysilon M100. Additionally 1 g of the polymer was held at 150 $^{\circ}$ C for two months in air in a Heraeus T 6060 oven. It was dissolved in 8 ml THF and poured into 200 ml methanol. After filtration and evaporation of the solvents under reduced pressure, the different compounds of the solid residue were separated with preparative layer chromatography (PLC) using precoated PLC plates (silica gel 60 F-254 from Merck) as stationary and a mixture of ethyl acetate/*n*-hexane (1/3) as mobile phase.

The distillation of the volatile products of polymer degradation was done in a conventional sublimation apparatus within a distance of approximately 2,8 cm at 0,7 Pa. It was heated with a Bunsen burner which was controlled with a gas relay combined with a contact thermometer. The deposit of the products took place on the surface of a water-cooled cylinder [11].

UV/VIS spectra were recorded on a UVIKON 860 (Kontron) spectrometer, mass spectra on a MAT 711 (Varian) spectrometer (direct inlet), ^1H NMR spectra on a WM 400 (Bruker) spectrometer and ^{13}C NMR on a AC 200 (Bruker) spectrometer.

ω -[4-(4-Butoxyphenazo)-phenoxy]-heptanol (**3**)

UV/VIS (THF): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/(\text{l mol}^{-1} \text{cm}^{-1})$) = 359 (19000), 440 (800). – ^1H NMR (CDCl_3 , 400 MHz): δ/ppm = 7,86

(ddd, 4H, $J=9, 2, 2$ Hz), 6,99 (ddd, 4H, $J=9, 2, 2$ Hz), 4,04 (t, 4H, $J=7$ Hz), 3,68 (t, 2H, $J=7$ Hz), 1,82 (tt, 4H, $J=7, 7$ Hz), 1,24–1,67 (m, 10H), 0,99 (t, 3H, $J=7$ Hz). – ^{13}C NMR (CDCl_3 , 50,1 MHz): $\delta/\text{ppm} = 161,1, 161,0, 146,9, 124,3, 114,6, 68,0, 62,2, 31,3, 29,2, 28,9, 28,5, 26,9, 26,0, 19,2, 13,9$. – MS (70 eV): m/z 384 (M^+ , 15%), 270 ($\text{M}^+ - \text{C}_7\text{H}_{14}\text{O}$), 165 ($\text{C}_{10}\text{H}_{15}\text{NO}$), 149 (100%, $\text{C}_6\text{H}_7\text{NO}$), 73 ($\text{C}_4\text{H}_9\text{O}$), 57 (C_4H_9).

2-Methylpropenacid- ω -[4-(4-butoxyphenazo)-phenoxy]-heptylester(4)

UV/VIS (THF): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/(\text{l mol}^{-1} \text{cm}^{-1}) = 358 (22000), 435 (600)$. – ^1H NMR (CDCl_3 , 400 MHz): $\delta/\text{ppm} = 7,86$ (ddd, 4H, $J=9, 2, 2$ Hz), 6,99 (ddd, 4H, $J=9, 2, 2$ Hz), 4,04 (t, 4H, $J=7$ Hz), 3,68 (t, 2H, $J=7$ Hz), 1,82 (tt, 4H, $J=7, 7$ Hz), 1,24–1,67 (m, 10H), 0,99 (t, 3H, $J=7$ Hz). – ^{13}C NMR (CDCl_3 , 50,1 MHz): $\delta/\text{ppm} = 167,5, 161,1, 161,0, 146,9, 136,5, 125,1, 124,2, 114,6, 68,0, 67,9, 64,7, 31,2, 29,1, 29,0, 28,5, 26,9, 25,9, 19,2, 18,3, 13,8$. – MS (70 eV): m/z 453 ($\text{M}^+ + 1$), 452 (M^+ , 43%), 366 ($\text{M}^+ + 1 - \text{C}_4\text{H}_5\text{O}$), 366 ($\text{M}^+ - \text{C}_4\text{H}_6\text{O}_2$), 270 ($\text{M}^+ - \text{C}_{11}\text{H}_{18}\text{O}_2$), 177 ($\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}$), 149 (100%, $\text{C}_{10}\text{H}_{13}\text{O}$), 109 ($\text{C}_6\text{H}_7\text{NO}$), 73 ($\text{C}_4\text{H}_9\text{O}$), 69 ($\text{C}_4\text{H}_5\text{O}$), 57 (C_4H_9).

Results and Discussion

The TG curves for samples of **1** obtained in a nitrogen or oxygen atmosphere are given in Fig. 1. They show two steps of weight loss beginning at approximately 320 and 350 °C, respectively.

Nevertheless, degradation of **1** can be observed at much lower temperatures. Polymer samples which were annealed for at least one day in air at 110 °C or higher temperatures possess a molecular weight distribution deviating significantly from the initial one. An additional peak at the elution volume of approximately 29.3 ml ($M_w \cong 500$ g/mol) broadening to higher molecular weights were detected. As a result M_w increases for the example given in Fig. 2 from 98 000 g/mol to 2 260 000 g/mol during 7 days of annealing at 170 °C. A thermal treatment of two weeks and more under the same

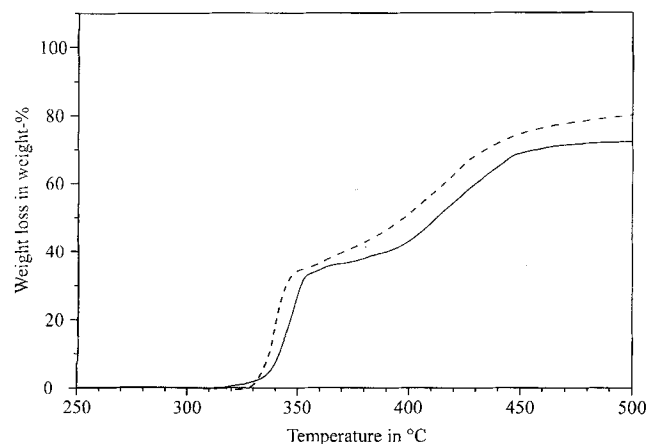


Fig. 1 TG curves for samples of **1** degrading in nitrogen (continuous line) and oxygen (dashed line) obtained with a heating rate of 2.43 K/min

conditions lead to samples that are only partially soluble in THF at room temperature. The change of M_w and solubility can be attributed to cross linking reactions. These observations are in good agreement with those made by Runke [8] after the thermal treatment of **2**.

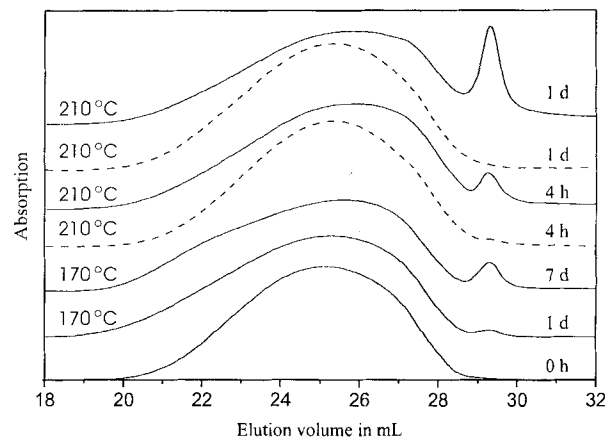


Fig. 2 Elution curves corresponding to GPC runs of **1** after different times of annealing at 170 °C and 210 °C in air (continuous line) and at 210 °C under reduced pressure (0.7 Pa; dashed line)

In order to gain information about the developed low-molecular weight products, we tried to separate them from a polymer sample degraded for 60 days at 150 °C in air. One of the various products ω -[4-(4-butoxyphenazo)-phenoxy]-heptanol **3** was isolated using PLC. It remains unknown whether this substance originates from polymer degradation or consecutive reactions.

A method to suppress consecutive reactions of the arised low-molecular weight substances is to remove them from the sample directly after their formation. If this is done at 210 °C and 0.7 Pa, the volatile products are removed from the sample to a large extent (Fig. 2) and consist of monomer **4**. After one day, 6.07 weight-% of **4** are obtained related to the weight of the virgin sample. The molecular weight distribution of the residue shows only minor changes compared to those observed for the polymers degraded in air. Assuming the degradation processes in air and *in vacuo* are the same this indicates that the presence of the monomer promotes the cross linking process. In consequence of the high boiling temperature of **4** (approximately 170 °C at 0.7 Pa) no experiments could be made to verify whether depolymerization is also the main degradation process under standard pressure. As up to now only the degradation products of **1** have been determined, general conclusions concerning the mechanism and influence of the side group on the thermal degradation of lc SGPMAs can not be drawn.

One effect of the thermal degradation on **1** is the change of its phase behaviour. For the virgin sample, the phase sequence (glass (G) \rightarrow monolayer smectic C phase (S_{C1}) \rightarrow monolayer smectic A phase (S_{A1}) \rightarrow nematic phase (N) \rightarrow isotropic phase (I)) can be determined (Fig. 3). After a month of annealing at 170 °C, the sample exhibits only one liquid crystalline phase (S_{C1}) and is to a large extent insoluble in tetrahydrofuran.

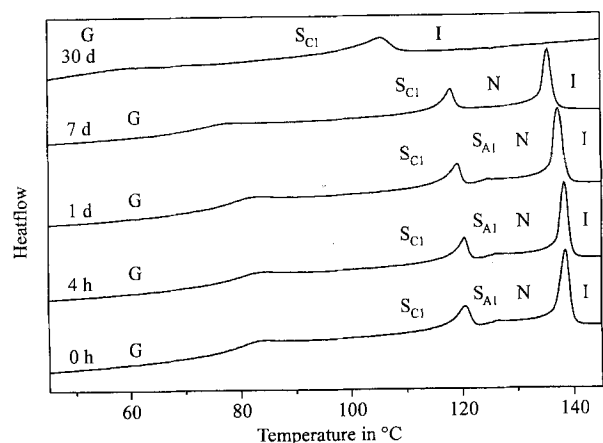


Fig. 3 DSC traces for samples of **1** after different times of annealing at 170 °C in air (second heating, rate 10 K/min)

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