Liquid Crystalline Thermosets Based on Branched Bismethacrylates

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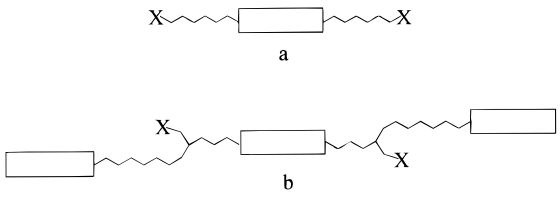
ABSTRACT: Synthesis and characterization of a novel type of liquid crystalline thermoset (LCT) based on branched liquid crystalline (LC) bismethacrylate monomers are described. The characteristic structural feature of these branched LC bismethacrylates is the combination of three rigid units, namely a central biphenyl unit, prepared by reaction of 4,4′-dihydroxybiphenyl with glycidyl methacrylate and pendant cyanobiphenyl mesogens, linked to the bismethacrylate via a spacer unit by esterification of the hydroxyl groups. The spacer between pendant mesogens and the central unit was varied. Both branched bismethacrylates with C5 and C11 spacers exhibited the formation of a nematic phase in the temperature range between 10 and 70 °C. LC properties were characterized by differential scanning calorimetry, polarizing microscopy, and wide angle X-ray diffraction. LC phases were stable for prolonged periods at ambient temperature. Nonmesogenic model compounds with a central biphenyl segment and C2 as well as C11 side chains that did not form LC phases were also prepared. The LC monomers were oriented by shearing as well as deposition on unidirectionally rubbed polyimide layers and were photo-cross-linked at ambient temperature to ordered thermosets in the LC state. Polarized FT-IR spectroscopy was employed to study the dichroism of the absorption bands in oriented samples of the cross-linked thermosets, which indicated an orientation of the lateral and the central biphenyl units in the drawing direction. Order parameters for cooriented dye were determined before and after cross-linking (0.54 and 0.48, respectively), using polarized UV/vis spectroscopy. Low polymerization shrinkage (2.5%), as well as high moduli, was obtained for the novel LC thermosets.

Introduction

Recently, there has been increasing interest in liquid crystalline (LC) polymer networks,[1,2] such as liquid crystalline elastomers (LCE) and rigid thermosets (LCT). LCEs have been studied intensely with respect to the preparation of highly ordered monodomain LC materials with peculiar optical properties.[3] Thermosets with liquid crystalline order were first described in 1973.[4] The current research interest in LCTs has been stimulated by the work of Broer et al. since 1989.[5,6] Strictly speaking, cured LC thermosets constitute no LC polymers since such materials exhibit no mesomorphic phase behavior. The LC phase can be considered to be "frozen-in", i.e. permanently fixed by the cross-linking process. Alignment of the LC monomers can be achieved by deposition on oriented surfaces and by exposure to mechanical, electric, or magnetic fields prior to cross-linking, resulting in densely cross-linked, oriented polymer networks. This allows fabrication of thin films with highly anisotropic optical, thermal, and mechanical properties.[1,6] Furthermore, low shrinkage[1,7,8] upon curing in comparison with common thermosets has been reported.

Various synthetic pathways for the preparation of LCTs have been described in the literature. Polyaddition of bisepoxides with amines,[9−13] sulfanilamides,[14,15] carbonic acids,[16] or anhydrides[12] has been employed as well as thermal polymerization of mesogenic monomers.[4,17−19] Photopolymerization of mesogenic monomers[5,6,20−25] or prepolymers[26] represents a particularly elegant route to LCTs. This strategy allows variation of the polymerization temperature within the different mesophases of the LC monomers. Thus, a particular type of mesomorphic order and orientation can be fixed permanently.

Scheme 1



The photo-cross-linkable monomer systems described to date are based on acrylates,[5−8] vinyl ethers,[20,21] epoxides,[22,23] or methacrylates[24,25] as reactive functional groups. A drawback of these systems is the formation of LC phases at elevated temperatures, resulting in complicated experimental conditions as well as restricted practical usefulness. In order to circumvent these problems, Broer et al. prepared bisepoxides[22] that exhibit decreased melting points and form a metastable nematic phase at ambient temperature for certain periods. Hoyle et al. applied an alternative strategy by using a mixture of various methacrylates to depress the melting point and obtained a smectic mesophase that was relatively stable at room temperature after cooling.[24]

The common structural principle for LCT monomers is based on mesogens bearing two cross-linkable functionalities, as illustrated in Scheme 1a. The polymerizable moieties (X) and the mesogenic unit are arranged in a linear fashion in this type of monomer. In the current paper, we wish to report a new class of LCT monomers based on bismethacrylates with a branched structure that form LC phases at ambient temperature.

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The general structure of the compounds, which consist of three coupled rigid units, is shown in Scheme 1b. The molecules consist of a rigid, linear bismethacrylate central unit, linked with mesogenic groups via alkyl spacers. The branched structure was expected to impede crystallization, yet not disable mesophase formation. Low molar mass glassy LCs have been known for many years and were reviewed recently by Bunning and Kreuzer.[27] This class of materials combines the low melt viscosity of conventional low molar mass LCs with the glass-forming ability of conventional polymeric structures. Low glass transitions for branched LC structures were also described by Percec and co-workers for the case of hyperbranched and dendritic LC polymers[28,29] and were found for carbosilane dendrimers with lateral mesogens developed in our laboratory.[30] In analogy to these approaches, suppression of crystallization by a slightly branched topology should lead to LCT monomers that form LC phases at ambient temperature.

Experimental Section

Synthesis. 4,4′-Bis((2-hydroxy-3-(methacryloxy)propyl)oxy)biphenyl (B). A mixture of 60 g (0.422 mol) of glycidyl methacrylate, 0.4 g of 2,6-di-*tert*-butyl-4-methylphenol (BHT) stabilizer, 39.3 g (0.21 mol) of 4,4'-dihydroxybiphenyl, and 250 mL of 1-methoxy-2-propanol was heated under nitrogen until a clear solution was formed. Subsequently, 0.3 g of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added. The reaction mixture was stirred for 15 h at 115 °C. After cooling to ambient temperature, the solution was concentrated, 250 mL of petroleum ether was added, and the mixture was cooled to 0 °C. The precipitate was filtered, washed with petroleum ether, and dried. Subsequently, the solid was refluxed with 100 mL of methanol and filtered after cooling. This procedure was repeated after addition of 0.2 g of BHT. The remaining residue was dried in vacuo. Subsequently, the crude product was refluxed with 200 mL of dichloromethane after addition of 0.1 g of BHT. The insoluble fraction was filtered, refluxed with 100 mL dichloromethane, and filtered again. The last two filtrates were unified and heated to boiling after addition of 200 mL of additional dichloromethane. The solution was filtered warm over 40 g of silica and rinsed three times with 250 mL of dichloromethane. Subsequently, the solvent was evaporated and the remaining solid slurried with 50 mL of methanol, filtered, washed with a small portion of methanol, and dried in vacuo to yield 12.7 g (13%) of **B**. 300 MHz ^{1}H-NMR (DMSO-d_6): δ = 1.9 (s, 6 H, CH_3), 4.05 (t, 4 H, Biph-O-CH_2), 4.1−4.3 (m, 6 H, −CH(OH)CH_2O$_2$C−), 5.45 (d, 2H, OH), 5.7 (s, 2H, *trans*-HC═C(CO$_2$)), 6.15 (s, 2H, *cis*-HC═C(CO$_2$)), 7.05 (d, 4 H, aromatic), 7.6 (d, 4 H, aromatic) 75 MHz ^{13}C-NMR (DMSO-d_6): δ = 17.8 (*C*H$_3$), 65.5 (−*C*H$_2$O$_2$C−), 66.6 (−*C*H(OH)−), 69.0 (Biph-O-*C*H$_2$), 114.4, 127.1, 132.3, 157.4 (aromatic), 125.8 (H$_2$*C*═), 135.6 (═*C*(CO$_2$)−), 166.3 (−*C*O$_2$−).

Ethyl 5-Bromovalerate (5E). A solution of 50 g (0.239 mol) of 5-bromovaleric acid in 45 mL of ethanol and 20 mL of toluene was refluxed with 7 drops of H_2SO_4 for 2 h, during which time 35 mL of solvent was collected in a Dean−Stark trap. The reaction mixture was cooled to ambient temperature, dissolved in 120 mL of ether/hexane (1:1), and washed twice with 50 mL of water, twice with 50 mL of saturated $NaHCO_3$, and once again with 25 mL of water. The organic phase was dried with Na_2SO_4, filtered over a short alumina column (act. II/III, ether), and evaporated to yield 44.9 g (90%) of **5E**.

Ethyl 11-Bromoundecanoate (11E). A solution of 200 g (0.754 mol) of 11-bromoundecanoic acid in 150 mL of ethanol and 70 mL of toluene was refluxed with 0.5 mL of H_2SO_4 for 2 h, during which time 110 mL of solvent was collected in a Dean−Stark trap. The remaining solution was concentrated and, after addition of 300 mL of ether/petroleum ether (1:1), washed twice with 150 mL of water, twice with 150 mL of saturated $NaHCO_3$, and once again with 100 mL of water. The organic phase was dried with Na_2SO_4, filtered over a short alumina column (act. II/III, ether), and evaporated to yield 187.13 g (85%) of **11E**. 300 MHz ^{1}H-NMR ($CDCl_3$): δ = 1.2 (t, 3 H, CH_3), 1.2−1.7 (m, 14 H, −(CH_2)$_7$CH$_2$CO$_2$−), 1.85 (m, 2 H, BrCH$_2$CH_2), 2.25 (t, 2H, −CH_2CO$_2$−), 3.4 ppm (t, 2H, BrCH_2), 4.1 (q, 2H, CH_2CH$_3$). 75 MHz ^{13}C-NMR ($CDCl_3$): δ = 14.3 (*C*H$_3$), 24.8−34.3 (10 C, Br(*C*H$_2$)$_{10}$), 60.1 (*C*H$_2$CH$_3$), 173.6 (−*C*O$_2$−).

Ethyl 5-((4′-Cyano(1,1′-biphenyl)-4-yl)oxy)valerate (M5E). K_2CO_3 (30.58 g, 0.221 mol) was added to a solution of 36 g (0.184 mol) of 4-cyano-4′-hydroxybiphenyl in 750 mL of ethyl methyl ketone, and the mixture was refluxed for 1.5 h. Subsequently, 44 g (0.210 mol) of ethyl 5-bromovalerate was added and the mixture refluxed for another 16.5 h. After cooling, the solid was filtered, the turbid filtrate filtered once more, and the solvent evaporated. The crude product was dissolved in 480 mL of ether/ethyl methyl ketone (3:1) under reflux and cooled to 0 °C after addition of 750 mL of petroleum ether. The precipitate was filtered, washed with 200 mL of ether/petroleum ether (1:1), and dried at 50 °C in vacuo to yield 50.15 g (84%) of **M5E**. 300 MHz ^{1}H-NMR ($CDCl_3$): δ = 1.25 (t, 3 H, CH_3), 1.9 (m, 4 H, −OCH$_2$(CH_2)$_2$−), 2.4 (t, 2 H, −CH_2-CO$_2$−), 4.05 (t, 2H, ArOCH_2), 4.15 (q, 2H, CH_2CH$_3$), 7.0−7.7 (8 H, aromatic). 75 MHz ^{13}C-NMR ($CDCl_3$): δ = 14.3 (*C*H$_3$), 21.6−33.9 (3 C, −OCH$_2$(*C*H$_2$)$_3$−), 60.4 (CO$_2$*C*H$_2$CH$_3$), 67.5 (ArOCH_2), 110.0−159.6 (12 C, aromatic), 119.1 (CN), 173.4 (−*C*O$_2$−).

Ethyl 11-((4′-Cyano(1,1′-biphenyl)-4-yl)oxy)undecanoate (M11E). K_2CO_3 (20.39 g, 0.148 mol) was added to a solution of 24 g (0.123 mol) of 4-cyano-4′-hydroxybiphenyl in 700 mL of ethyl methyl ketone and the mixture was refluxed for 1.5 h. Subsequently 41 g (0.140 mol) of ethyl 11-bromoundecanoate was added and the mixture refluxed another 16.5 h. After cooling, the solid was removed, the turbid filtrate filtered once again, and the solvent evaporated. The crude product was dissolved in 200 mL of ether/ethyl methyl ketone (3:1) at boiling and cooled to 0 °C after addition of 750 mL of petroleum ether. The precipitate was filtered and washed with 200 mL of ether/petroleum ether (1:1) and dried at 50 °C in vacuo to yield 40.36 g (81%) of **M11E**. 300 MHz ^{1}H-NMR ($CDCl_3$): δ = 1.25 (t, 3 H, CH_3), 1.25−1.7 (m, 14 H, ArOCH$_2$CH$_2$(CH_2)$_7$), 1.8 (m, 2 H, ArOCH$_2$CH_2), 2.3 (t, 2 H, −CH_2CO$_2$−), 4.0 (t, 2H, ArOCH_2), 4.1 (q, 2H, CH_2CH$_3$), 7.0−7.7 ppm (8 H, aromatic). 75 MHz ^{13}C-NMR ($CDCl_3$): δ = 14.3 (*C*H$_3$), 24.7−29.5 (8 C, −OCH$_2$(*C*H$_2$)$_8$−), 34.4 (−*C*H$_2$CO$_2$−), 60.2 (CO$_2$*C*H$_2$CH$_3$), 68.1 (ArO*C*H$_2$), 110.0−159.8 (12 C, aromatic), 119.1 (CN), 173.9 (−*C*O$_2$−).

5-((4′-Cyano(1,1′-biphenyl)-4-yl)oxy)valeric Acid (M5A). **M5E** (50 g, 0.155 mol) was dissolved in 975 mL of ethanol/ethyl methyl ketone (12:1) while the mixture was warmed to 75 °C. Subsequently, a solution of 10 g (0.178 mol) of KOH in 100 mL of water was added and the mixture was stirred for 2 h at 75 °C. After cooling, the solution was stirred for 24 h at ambient temperature. Subsequently, the pH was adjusted to pH ∼2 with 1 N HCl and the reaction mixture stirred overnight. After addition of 750 mL water, the precipitate was filtered, washed with water, and dried. The crude product was refluxed with 200 mL of ethyl acetate and the hot solution was filtered. The product was precipitated from the filtrate with petroleum ether, dried, and recrystallized from toluene to yield 30.50 g (67%) of **M5A**. 300 MHz ^{1}H-NMR (DMSO-d_6): δ = 1.7 (m, 4 H, −OCH$_2$(CH_2)$_2$−), 2.4 (t, 2 H, −CH_2CO$_2$), 4.0 (t, 2H, ArOCH_2), 7.0−7.85 (8 H, aromatic). 75 MHz ^{13}C-NMR (DMSO-d_6): δ = 22.1−34.2 (3 C, −OCH$_2$(*C*H$_2$)$_3$−), 68.1 (ArO*C*H$_2$-), 110.0−160.2 (12 C, aromatic), 119.9 (CN), 175.3 (*C*O$_2$H).

11-((4′-Cyano(1,1′-biphenyl)-4-yl)oxy)undecanoic Acid (M11A). **M11E** (40 g, 0.098 mol) was dissolved in 800 mL of ethanol/ethyl methyl ketone (3:1) during warming. Subsequently, a solution of 6.5 g (0.116 mol) of KOH in 75 mL of water was added and the mixture stirred for 30 min at 75 °C. After cooling, the reaction mixture was stirred for 24 h at ambient temperature, and afterwards it was adjusted to pH ∼2 with 1 N HCl and stirred overnight. After addition of 400 mL of water, the precipitate was filtered off, washed with water, and dried. The crude product was refluxed with 150 mL of dioxane and the hot solution filtered. The product was precipitated from the filtrate with petroleum ether, dried,

recrystallized from toluene, and dried at 50 °C in vacuo to yield 23.15 g (62%) of **M11A**. 300 MHz ^{1}H-NMR (DMSO-d_6): δ = 1.25−1.55 (m, 14 H, ArOCH$_2$CH$_2$(C*H*$_2$)$_7$−), 1.7 (m, 2 H, ArOCH$_2$C*H*$_2$), 2.2 (t, 2 H, −C*H*$_2$CO$_2$−), 4.0 (t, 2H, ArOC*H*$_2$), 7.0−7.85 (8 H, aromatic). 75 MHz ^{13}C-NMR (DMSO-d_6): δ = 25.4−29.8 (8 C, −OCH$_2$(*C*H$_2$)$_8$−), 34.5 (−*C*H$_2$CO$_2$−), 68.4 (ArO*C*H$_2$), 110.0−160.2 (12 C, aromatic), 119.9 (CN), 175.4 (*C*O$_2$H).

Monomer BM5. B (4.71 g, 10 mmol) and 0.25 g of 4-(dimethylamino)pyridine (DMAP) was added to a solution of 6.50 g (22 mmol) of **M5A** dissolved in 85 mL of dichloromethane/DMF (9:8). 1,3-Dicyclohexylcarbodiimide (DCC) (5.0 g, 24.2 mmol) was slowly added and the mixture stirred at ambient temperature for 24 h. Subsequently, the precipitate was filtered off and the solvent evaporated after addition of 0.1 g of BHT. The residue was taken up in 100 mL of dichloromethane, filtered after cooling to 0 °C, and washed twice with 50 mL of 1 N HCl, 1 N NaHCO$_3$, and water, respectively. The organic phase was dried with Na$_2$SO$_4$ and evaporated. The crude product was dissolved in 30 mL of dichloromethane, the remaining solid was filtered off, and the filtrate concentrated. The product was purified by column chromatography (silica, dichloromethane) to yield 5.51 g (54%) of **BM5**. 300 MHz ^{1}H-NMR (CDCl$_3$): δ = 1.85 (m, 8 H, ArOCH$_2$(C*H*$_2$)$_2$), 1.95 (s, 6 H, C*H*$_3$), 2.45 (t, 4 H, −C*H*$_2$CO$_2$−), 4.0 (t, 4H, ArOC*H*$_2$(CH$_2$)$_3$), 4.15 (d, 4 H, BiphOC*H*$_2$CH(O$_2$C)), 4.45 (m, 4 H, −CH(O$_2$C)C*H*$_2$O$_2$C−), 5.5 (m, 2 H, −CH$_2$C*H*(O$_2$C)CH$_2$−), 5.6 (s, 2H, *trans*-*H*C=C(CO$_2$)), 6.1 (s, 2H, *cis*-*H*C=C(CO$_2$)), 6.95−7.7 (24 H, aromatic). 75 MHz ^{13}C-NMR (CDCl$_3$): δ = 18.3 (2 C, *C*H$_3$), 21.6−33.8 (6 C, −OCH$_2$(*C*H$_2$)$_3$−), 62.8 (2 C, −CH(O$_2$C)*C*H$_2$O$_2$C−), 66.3 (2 C, BiphO*C*H$_2$CH(O$_2$C)), 67.4 (2 C, ArO*C*H$_2$(CH$_2$)$_3$), 69.7 (2 C, −CH$_2$*C*H(O$_2$C)CH$_2$−), 110.0−159.5 (36 C, aromatic), 119.1 (2 C, CN), 126.3 (2 C, H$_2$*C*=), 135.8 (2 C, =*C*(CO$_2$)−), 166.9 (2 C, =C(*C*O$_2$)−), 175.3 (2 C, −(CH$_2$)$_4$*C*O$_2$−).

Monomer BM11. B (6.59 g, 14 mmol) and 0.32 g of DMAP were added to a solution of 11.39 g (30 mmol) of **M11A** in 160 mL of dichloromethane/DMF (5:3). 1,3-Dicyclohexylcarbodiimide (6.60 g, 32 mmol) was slowly added and the mixture stirred at room temperature for 27 h. Subsequently, the precipitate was removed and the solvent evaporated after addition of 0.15 g of BHT. The residue was dissolved in 200 mL of dichloromethane, filtered after cooling to 0 °C, and after addition of 50 mL of dichloromethane, washed twice with 150 mL of 1 N HCl, 150 mL of 1 N NaHCO$_3$, and 75 mL of water. The organic phase was dried with Na$_2$SO$_4$ and evaporated. The crude product was dissolved in 50 mL of dichloromethane and filtered. The product was purified by column chromatography (silica, dichloromethane) to yield 6.90 g (41%) of **BM11**. 300 MHz ^{1}H-NMR (CDCl$_3$): δ = 1.25−1.65 (m, 28 H, ArOCH$_2$CH$_2$-(C*H*$_2$)$_7$), 1.8 (m, 4 H, ArOCH$_2$C*H*$_2$), 1.95 (s, 6 H, C*H*$_3$), 2.35 (t, 4 H, −C*H*$_2$CO$_2$−), 4.0 (t, 4H, ArOC*H*$_2$(CH$_2$)$_9$), 4.15 (d, 4 H, BiphOC*H*$_2$CH(O$_2$C)), 4.45 (m, 4 H, −CH(O$_2$C)C*H*$_2$O$_2$C−), 5.5 (m, 2 H, −CH$_2$C*H*(O$_2$C)CH$_2$−), 5.6 (s, 2H, *trans*-*H*C=C(CO$_2$)), 6.1 (s, 2H, *cis*-*H*C=C(CO$_2$)), 6.95−7.7 (24 H, aromatic). 75 MHz ^{13}C-NMR (CDCl$_3$): δ = 18.3 (2 C, *C*H$_3$), 24.9−34.3 (18 C, −OCH$_2$(*C*H$_2$)$_9$−), 62.9 (2 C, −CH(O$_2$C−)*C*H$_2$O$_2$C−), 66.3 (2 C, BiphO*C*H$_2$CH(O$_2$C)), 68.1 (2 C, ArO*C*H$_2$(CH$_2$)$_9$), 69.4 (2 C, −CH$_2$*C*H(O$_2$C)CH$_2$−), 110.0−159.8 (36 C, aromatic), 119.1 (2 C, CN), 126.2 (2 C, H$_2$*C*=), 135.8 (2 C, =*C*(CO$_2$)−), 166.9 (2 C, =C(*C*O$_2$)−), 173.4 (2 C, −(CH$_2$)$_4$*C*O$_2$−).

The nonmesogenic monomers **BE** and **BU** were prepared in analogy to the monomers **BM5** and **BM11** using acetic acid in DMF for the preparation of **BE** and undecanoic acid and DMF/CH$_2$Cl$_2$ (5:8) for **BU**. NMR data are given below.

BE: 300 MHz ^{1}H-NMR (CDCl$_3$): δ = 1.95 (s, 6 H, HC=C-(CO$_2$)C*H*$_3$), 2.35 (t, 6 H, O$_2$CC*H*$_3$), 4.2 ppm (d, 4 H, BiphOC*H*$_2$-CH(O$_2$C)), 4.45 (m, 4 H, BiphCH$_2$CH(O$_2$C)C*H*$_2$), 5.45 (m, 2 H, BiphOCH$_2$C*H*(O$_2$C)CH$_2$), 5.6 (s, 2H, *trans*-*H*C=C(CO$_2$)−), 6.1 (s, 2H, *cis*-*H*C=C(CO$_2$)−), 6.95, 7.45 (8 H, aromatic). 75 MHz ^{13}C-NMR (CDCl$_3$): δ = 18.3 (2 C, HC=C(CO$_2$)*C*H$_3$), 21.0 (2 C, O$_2$C*C*H$_3$), 62.8 (2 C, −CH(O$_2$C)*C*H$_2$O$_2$C−), 66.3 (2 C, BiphO*C*H$_2$-CH(O$_2$C)), 69.7 (2 C, −CH$_2$*C*H(O$_2$C)CH$_2$−), 114.9, 127.8, 134.0, 157.5 (12 C, aromatic), 126.2 (2 C, H$_2$*C*=), 135.8 (2 C, =*C*(CO$_2$)-), 166.9 (2 C, =C(*C*O$_2$)−), 170.3 (2 C, H$_3$C*C*O$_2$). **BU**: 300 MHz ^{1}H-NMR (CDCl$_3$): δ = 0.85 (t, 6 H, (CH$_2$)$_9$C*H*$_3$), 1.25 (m, 28 H, (CH$_2$)$_2$(C*H*$_2$)$_7$CH$_3$), 1.6 (m, 4 H, CH$_2$C*H*$_2$(CH$_2$)$_7$CH$_3$), 1.95 (s, 6 H, HC=C(CO$_2$)C*H*$_3$), 2.35 (t, 4 H, −C*H*$_2$CO$_2$−), 4.15 (d, 4 H, BiphOC*H*$_2$CH(O$_2$C)), 4.45 (m, 4 H, BiphCH$_2$CH(O$_2$C)C*H*$_2$), 5.5 (m, 2 H, BiphOCH$_2$C*H*(O$_2$C)CH$_2$), 5.6 (s, 2H, *trans*-*H*C=C-(CO$_2$)), 6.1 (s, 2H, *cis*-*H*C=C(CO$_2$)), 6.95, 7.45 (8 H, aromatic). 75 MHz ^{13}C-NMR (CDCl$_3$): δ = 14.1 (2 C, (CH$_2$)$_9$*C*H$_3$), 18.3 (2 C, HC=C(CO$_2$)*C*H$_3$), 22.7−34.3 (18 C, (*C*H$_2$)$_9$CH$_3$), 62.9 (2 C, −CH(O$_2$C)*C*H$_2$O$_2$C), 66.3 (2 C, BiphO*C*H$_2$CH(O$_2$C)), 69.4 (2 C, −CH$_2$*C*H(O$_2$C)CH$_2$−), 114.9, 127.8, 134.0, 157.5 (12 C, aromatic), 126.2 (2 C, H$_2$*C*=), 135.8 (2 C, =*C*(CO$_2$)−), 166.9 (2 C, =C(*C*O$_2$)−), 173.1 (2 C, −(CH$_2$)$_9$*C*O$_2$−).

Physical Measurements and Polymerization Procedures. Solution 300 MHz ^{1}H-NMR and 75 MHz ^{13}C-NMR spectra were recorded on a Bruker ARX-300 spectrometer in CDCl$_3$ and DMSO-d_6. A Perkin-Elmer 7 Series thermal analysis system was used to monitor thermal transitions. The instrument was calibrated with high-purity samples of indium and cyclohexane. The optical microscope used was a Leitz Ortholux II Pol-BK equipped with a Mettler FP82 hotstage. Wide-angle X-ray diffraction (WAXD) exposures were taken using Cu Kα radiation and Kiessig geometry. The scattered radiation was detected by an image plate system detector. FT-IR experiments were performed using a Bruker IFS 88 spectrometer with MIR-DTGS detector. Polarized FT-IR measurements were carried out with a gold grid wire polarizer (KRS-5). A Perkin-Elmer Lambda 2 UV/vis spectrophotometer and polarizer sheets were used for polarized UV/vis spectroscopy.

The volume shrinkage measurements were performed using the flotation method. For this purpose the monomer was encapsulated into a small polyethylene sheet and the density determined before and after photopolymerization. A Rheometrics solids analyzer RSA II was employed for dynamic mechanical analysis (DMA) at 1 Hz with a heating rate of 5 K/min using dual cantilever geometry.

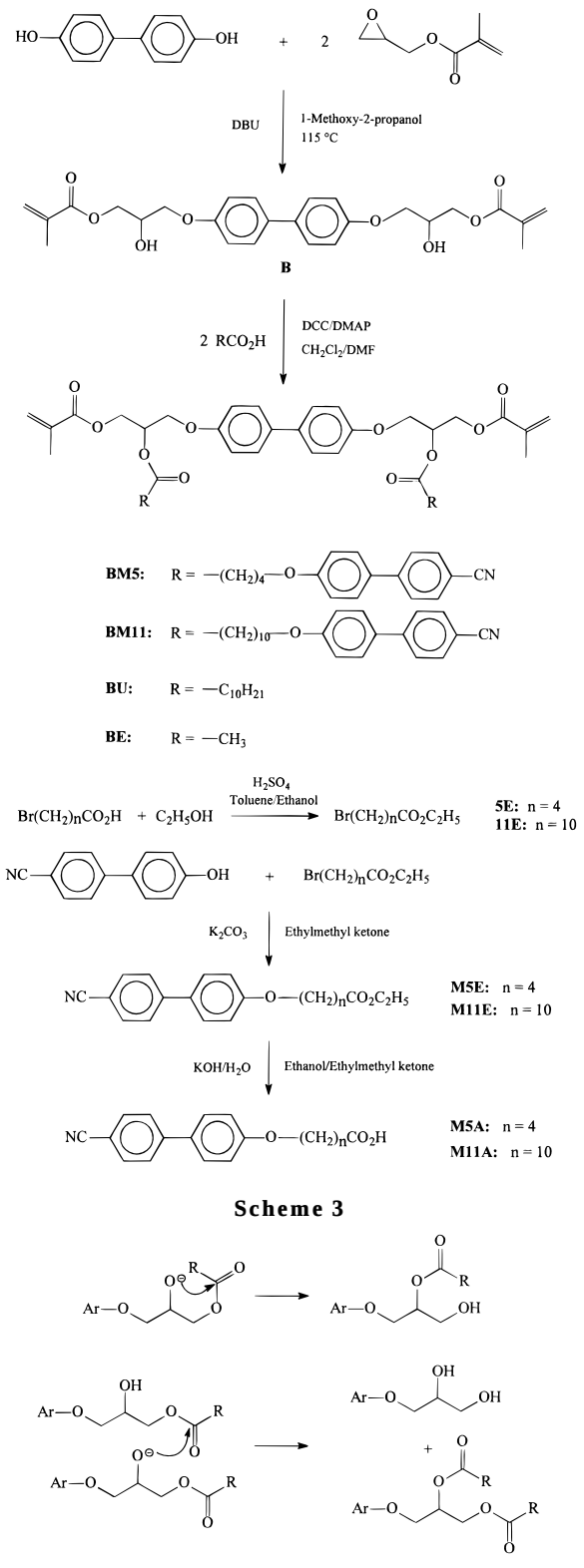
Polymerization mixtures were prepared by mixing 99 wt % of the monomer (**BM5** or **BM11**) and 1 wt % of 1,1-dimethoxy-1-phenylacetophenone at 75 or 65 °C, respectively, and subsequent degassing at the same temperature. A Dentsply De Trey Triad 2000 lamp (270 W), which produces light in a spectral range from 320 to 520 nm, served as the UV source for photopolymerization. Samples for WAXD were polymerized in an Ar atmosphere. Cross-linked oriented films for polarized FT-IR spectroscopy were prepared by warming up **BM5** within the nematic phase and drawing between the edges of two microscopic cover glasses during cooling until a transparent film was generated. Subsequently the film was irradiated for 12 min in an ambient atmosphere.

Results and Discussion

A. Synthesis. A general synthetic scheme for the preparation of the branched monomers is shown in Scheme 2, which also shows the structures of the compounds designated **B**, **BE**, **BU**, **BM5**, and **BM11** in the following text.

The synthetic route chosen is based on the preparation of a bismethacrylate with a central rigid biphenyl segment in the first step, which is subsequently employed for all further modification reactions with mesogenic as well as linear *n*-alkyl side chains via esterification of the hydroxyl groups. The 4,4′-bis((2-hydroxy-3-(methacryloxy)propyl)oxy)biphenyl **B** was prepared in one reaction step from 4,4′-dihydroxybiphenyl and glycidyl methacrylate. A number of purification steps were necessary to isolate **B** without side products. However, a rigorous purification procedure is crucial in view of the LC behavior of the final bismethacrylate monomers, which can be expected to be strongly influenced by impurities. The eventual yield of **B** after the base-catalyzed reaction is determined by a competition between the conversion of phenolic hydroxyl groups and transesterification of the methacrylate. The transesterification occurs both intra- and intermolecularly. In order to suppress these side reactions as much as possible, we have carried out a detailed NMR study

Scheme 2



Scheme 3

that showed that transesterifications constitute the main side reactions that lead to lowered yields of **B** (Scheme 3).

*Intra*molecular transesterification can hardly be suppressed since the alkoxide ion and the ester group are always in spatial vicinity. Use of an alcohol with a structure similar to the product as solvent for the reaction leads to a reduction of the extent of transesterification reactions between the product molecules. In an inert solvent, the rate of *inter*molecular transesterification reactions increases with reaction time due to the increasing concentration of already converted groups. Other potential side reactions, such as the reaction of alkoxide ions with epoxide rings or an attack at the higher substituted carbon atom of the epoxide rings, may also play a role, but they were not observed. Compound **B** structurally resembles the commercially widely used 2,2-bis((4-(2-hydroxy-3-(methacryloxy)propyl)oxy)phenyl)propane (Bis-GMA). **B** only differs in the linkage of the phenyl rings. We have compared **B** with commercial Bis-GMA (Röhm Co.) with respect to purity. Whereas commercial Bis-GMA was always observed to contain different isomers (mainly due to exchange of hydroxyl and methacrylate groups within 15−20% of the hydroxy−methacryl−oxypropyl groups), we were able to obtain bismethacrylate **B** without any impurities detectable by NMR (Figure 1a). Interestingly, **B** has not been described as a pure compound yet.

The LC bismethacrylates **BM5** and **BM11** were obtained by attachment of two cyanobiphenyl groups via flexible C5 and C11 spacers, respectively, to **B**. The mesogens were coupled with the spacer units via a three-step synthesis starting from the respective ω-bromo acids and 4-cyano-4′-hydroxybiphenyl. Details are given in the Experimental Section. The resulting mesogen-substituted acids were attached to the hydroxyl groups of **B** using DCC as dehydrating agent in a mixture of DMF and CH_2Cl_2. ^{1}H- and ^{13}C-NMR spectra of the branched LC bismethacrylate **BM5** are shown in Figure 1b.

Besides, for comparison two aliphatic acids have also been attached to the basic molecular scaffold **B** in order to obtain nonmesogenic model compounds (designated **BE** and **BU**) for the branched bismethacrylates. **BU** bears long flexible C11 side chains that are structurally analogous to the alkyl spacers of the mesogenic monomers.

B. Liquid Crystalline Properties. Phase transitions, i.e. transformations to LC phases and isotropization of all bismethacrylate monomers as well as the respective acid precursors prepared, are summarized in Table 1. Clearly, substitution of **B** with pendant mesogens is a prerequisite for the formation of LC phases. The bismethacrylate **B** was obtained as a crystalline material at ambient temperature and autopolymerization set in at 145 °C concurrent with melting. In contrast to **B**, the aforementioned Bis-GMA is a viscous liquid under ambient conditions. This illustrates the effect of the bent structure of Bis-GMA due to the central isopropyl moiety that impedes crystallization.

The influence of the hydroxyl groups of **B** and the resulting hydrogen bonds on the melting point becomes obvious when comparing **B** with the structurally analogous 4,4′-bis((3-(methacryloxy)propyl)oxy)biphenyl described by Litt et al.,[8] which exhibits a melting point of 84 °C in comparison to 145 °C for **B**.

BE and **BU** were prepared as model compounds without mesogenic units in order to evaluate the effect of the branched structure on crystallization and mesophase formation. Esterification of **B** with acetic acid leads to a relatively small decrease of the melting point (Table 1). In contrast, esterification with undecanoic acid leads to a drastic decrease of the melting point, which demonstrates the influence of the long, flexible alkyl chains. In addition, the polarity of the molecule is reduced in comparison with **BE** and **B**. Another consequence of a branched structure is a strong crystallization delay for **BU** and **BE**. Upon cooling, both **BE** and **BU** could be supercooled and exhibited metastable isotropic phases at ambient temperature. **BE** crystallization occurred within a few minutes, whereas several

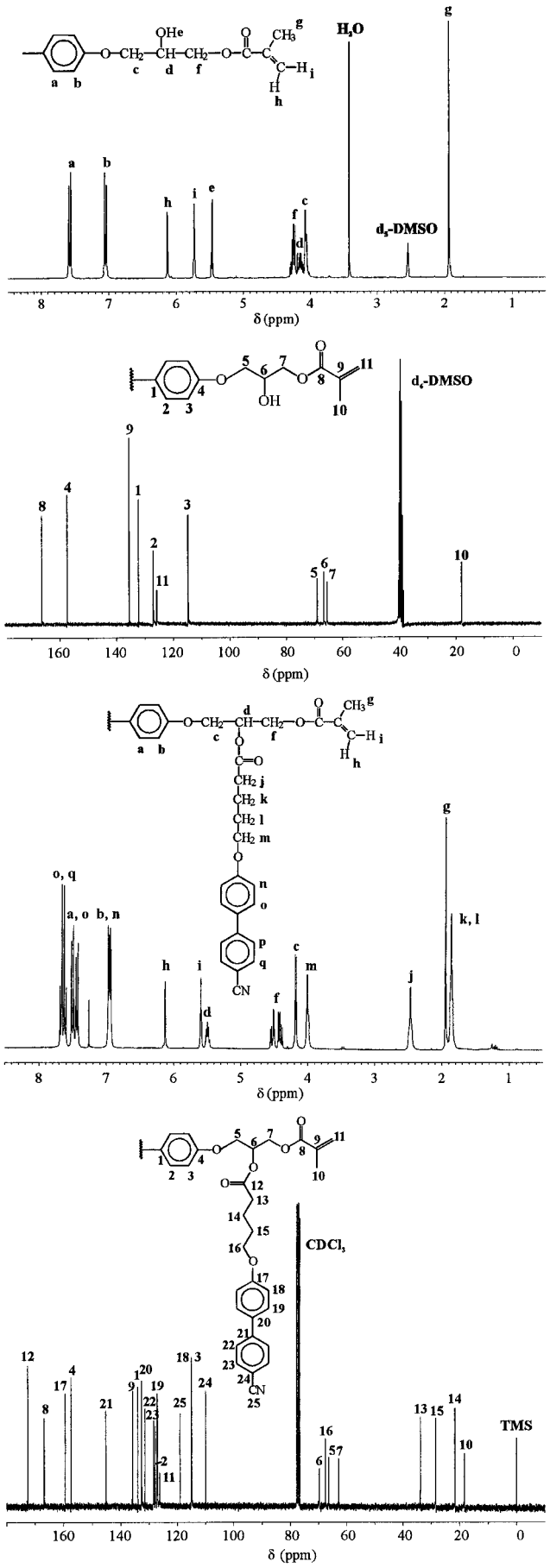


Figure 1. (a) ^{1}H-NMR spectrum and ^{13}C-NMR spectrum of **B.** (b) ^{1}H-NMR spectrum and ^{13}C-NMR spectrum of **BM5**.

hours were required for **BU**. The linear bismethacrylate prepared by Litt et al.[8] did not show such behavior.

Table 1. Phase Transitions of the Compounds Prepared

compd	phase transition[a] (°C) heating	cooling
B	k 145 (i)[b]	*b*
BE	k 110 i	*c*
BU	k 56 i	*c*
BM5	g 18 n 67.5 i	i 66 n 15.5 g
BM11	g 6 n 59.5 i	i 57 n 3 g
M5E	k 98 i	i 87 k
M11E	k 89 i	i 75 k
M5A	k 136 i	i 133 n 66 k
M11A	k 96 s 117 i	i 115 s 97 lc 79 k

[a] k = crystalline, g = glassy ("frozen-in" LC phase; mesoglass), i = isotropic, n = nematic, s = smectic phase, not characterized in detail, lc = liquid crystalline phase, not characterized in detail. [b] Autopolymerization starts at 145 °C concurrent with melting. [c] Can be supercooled to ambient temperature.

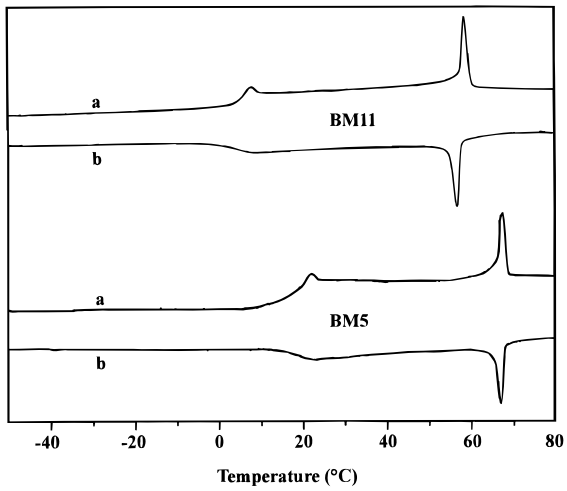


Figure 2. DSC thermograms of **BM5**: (a) heating and (b) cooling runs.

The mesogenic acids **M5A** and **M11A** (Scheme 2) used for modification of **B** exhibit mesomorphic behavior. **M5A** is monotropic nematic, whereas **M11A** is enantiotropically liquid crystalline (an exact characterization of the mesophases has not been carried out yet). However, it is worthwhile to mention that in contrast to the acids, the ethyl esters (**M5E**, **M11E**) exhibit no mesophases. Presumably, the great difference between the phase behavior of the mesogenic acids and their ethyl esters despite the similar structure is due to dimer formation by the acids.

As shown in Figure 2, the branched monomers **BM5** and **BM11** exhibit glass transitions at 18 and 6 °C, respectively. This behavior is observed in many cases for LCPs, but it is unusual for LC monomers of relatively low molecular weight. This fact confirms that structural principles of low molar mass glassy LCs[27] are also valid for the polymerizable LCs presented in this paper. Polarizing microscopy evidenced that the endothermic transitions observed at higher temperatures for both monomers are due to isotropization. Thus, **BM5** exhibits an LC phase between 18 °C and the clearing temperature of 67.5 °C. Below 18 °C, **BM5** is in a "frozen" mesomorphic state ("mesoglass"). On cooling, the same phase transitions as found in heating scans can be observed with only slight thermal hysteresis (Table 1). **BM11** resembles **BM5** in its thermal behavior, with a glass transition of 6 °C and a clearing point of 59.5 °C on heating.

Polarizing microscopy, as well as WAXD, was employed to characterize the LC phases of **BM5** and **BM11**. Figure 3 shows the texture of **BM5**, which can be

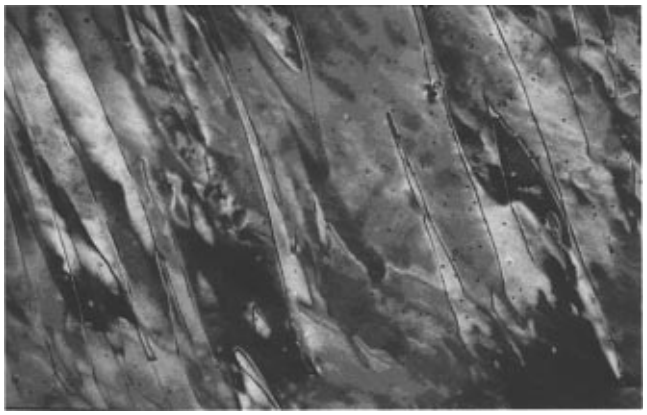


Figure 3. Texture of the LC phase of **BM5** at ambient temperature.

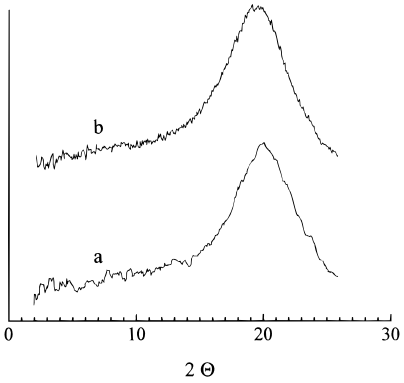


Figure 4. WAXD traces at ambient temperature: (a) monomer **BM5** and (b) polymer **PBM5.**

described as marbled. Nematic order was confirmed by WAXD experiments for both monomers. Powder diffractograms of both monomers showed a broad reflection at 4.4 Å, which is typical for the lateral distances of the mesogens in nematic phases. No other reflections could be discerned. As an example, Figure 4a gives the WAXD trace of **BM5** at ambient temperature. Similar data have been obtained for **BM11**.

Thus, the combination of both methods unequivocally evidences the nematic order of **BM5** and **BM11** in the LC phase.

In summary, **BM5** and **BM11** represent unusual LC bismethacrylate monomers that display nematic phases at ambient temperature. **BM5** could not be obtained in the crystalline state at ambient temperature, whereas for **BM11** in some samples crystallization was observed after several days. **BM11** crystals melted at 59 °C, forming an isotropic liquid. Thus, the melting temperature was nearly identical with the clearing point of the liquid crystalline samples. This indicates the metastable character of the mesophases and shows that they are only observed because crystallization is hindered; i.e. the branched structure impedes crystallization and possibly also the formation of higher ordered smectic phases. The observation of nematic phases at ambient temperature in combination with the low clearing temperatures also indicates that the three rigid biphenyl units are motionally decoupled within the molecule by the flexible alkyl chains, in complete analogy to the spacer concept generally employed in LC polymers.

Compared with the analogous 4,4′-bis(((4′-cyano(1,1′-biphenyl)-4-yl)oxy)alkoxy)biphenyl series described recently by Luckhurst,[31] one may describe these monomers as LC trimers with reactive methacrylate side groups.

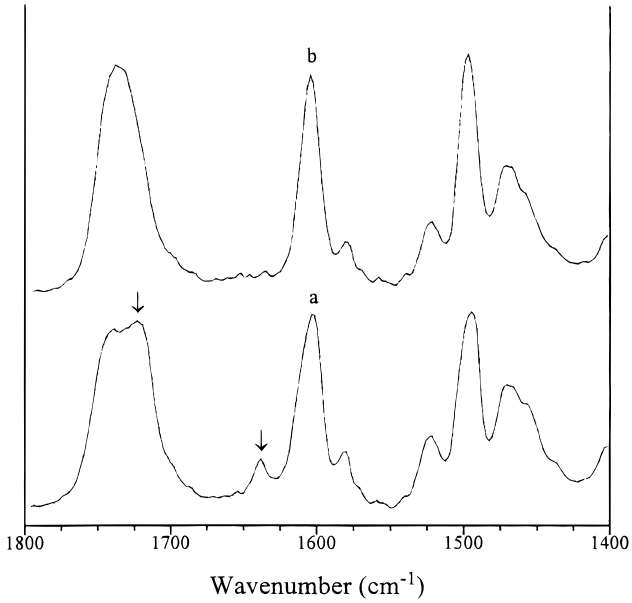


Figure 5. FT-IR spectra of **BM11** before (a) and after (b) prolonged irradiation (16 min).

C. Photopolymerization of the LC Monomers. Since the first description of photopolymerization of LC monomers by Broer and co-workers,[32] a number of reports have appeared on this subject. An initiator widely used for radical photopolymerization is 1,1-dimethoxy-1-acetophenone (DMAP). Photoinitiation by this initiator system is based on a highly reactive methyl radical, formed by fragmentation. For the photopolymerization of **BM5** and **BM11** 1 wt % DMAP was added.

No variation of the textures was observed for both **BM5** and **BM11** between crossed polarizers after cross-linking of the thermosets. In order to compare the structure before and after cross-linking, the thermosets were studied by WAXD. Figure 4b shows the WAXD trace of the thermoset obtained after polymerization at ambient temperature of **BM5** (**PBM5**). Clearly, the diffraction pattern remained unchanged after cross-linking. This is interpreted in terms of "freezing in" the nematic structure of the monomers by photoinduced cross-linking. However, for **BM5** as well as **BM11**, a slight decrease of the lateral mesogen−mesogen distance in the range of 2% is noticed.

It has been suggested that polymerization of LCTs may lead to considerably higher conversion than attainable for isotropic monomers. The conversion of the methacrylate double bonds during the curing procedure was followed by FT-IR spectroscopy by monitoring the disappearance of the C═C stretching vibration at 1637 cm^{-1} (Figure 5). Although polymerization was carried out at ambient temperature, an influence of the temperature on the polymerization cannot be completely excluded, due to the heat of reaction or warming of the sample by the radiation source. From the FT-IR spectra, we were able to derive that in the case of **BM11** after 1 min approximately 35% of the methacrylate groups remained unreacted. The ultimate conversion after prolonged periods of irradiation was on the order of 80%. Although this value is rather high, it is difficult to judge whether higher order within the mesophase in fact led to an advantageous arrangement of the polymerizable groups that would result in higher conversions in a "quasi-topochemical" reaction. Since such high conversion may appear unexpected for a bulky and sterically hindered monomer like **BM11**, we show FT-IR spectra before and after 16 min irradiation in Figure

5. Besides a decrease of the intensity of the C═C stretching vibration, a decrease of the C═O stretching band of the unsaturated ester at 1722 cm^{-1} is observed.

The branched LC monomers **BM5** and **BM11** may be considered both as a small segment of a main chain LCP or as part of a combined main and side chain LC polymer.[33] The preparation of oriented films was important with respect to the assessment of the structure of the thermosets obtained after cross-linking. First experiments on uniaxial orientation of the monomers showed that the compounds could easily be oriented by deposition on unidirectionally rubbed polyimide-coated glass surfaces or by shearing. For studies with polarized FT-IR spectroscopy **BM5** was oriented by a flow orientation process and polymerized in the oriented state. This was achieved by drawing a film out of the liquid crystalline melt. **BM5** shows a T_g close to ambient temperature; thus, the compound is particularly suitable for this orientation procedure, due to its relatively high viscosity at this temperature. The monomer was warmed up within the nematic phase in order to reduce the viscosity, and during cooling, a transparent film was generated by drawing between the edges of two microscopic cover glasses. Polymerization was carried out in an ambient atmosphere. Using this procedure, only low conversions could be obtained, due to inhibition by oxygen. Nevertheless, the mesogens were permanently fixed, which could be demonstrated by heating the resulting films up to 225 °C between crossed polarizers without disappearance of the birefringence. In analogy to the procedure described by Hoyle et al.,[24] polarized FT-IR spectroscopy was employed to study the orientation of the cross-linked films, using the isolated stretching band of the C≡N bond at 2227 cm^{-1}. The oriented film was fixed on a silicon wafer for the dichroism measurements. Figure 6 shows the polarized infrared spectra with the polarization of the infrared beam parallel (∥) and perpendicular (⊥) to the drawing direction.

The dichroism of the isolated C≡N stretching vibration at 2227 cm^{-1} evidences that the transition moments of the C≡N bonds of the cyanobiphenyl units are oriented in the drawing direction. Some other bands also display dichroism, notably the alkyl C−H stretching bands at 2867 and 2958 cm^{-1}. In contrast to the nitrile groups, for these bands higher absorbance intensity is observed for perpendicularly polarized light. Since the transition moments of the C−H bonds of the alkyl chain are oriented perpendicularly to C−C bonds, we conclude that the alkyl spacers are predominantly oriented in the drawing direction. Analogous dichroism found for the out-of-plane vibration of the phenyl hydrogens at 815 cm^{-1} confirms the orientation. The order obtained after shearing of the sample does not represent a limiting value, due to structural perturbations and necking unavoidable in this orientation procedure. As a consequence of the high concentration of cyano groups within the thermoset, for polarization parallel to the drawing direction the absorbance at 2227 cm^{-1} was too intense to determine the precise order parameter from the IR dichroism. However, similar dichroism was found for the vibration of the para-substituted benzene rings[34,35,20] of the two types of biphenyl units at 1581 cm^{-1} (involving quadrant stretching)[34] for which the transition moment should also be in the long axis of the rigid units. In spite of the difficulties related to the high intensity of the cyano band, all dichroic bands strongly indicate orientation of the cyanobiphenyl groups as well as the central biphenyl group in drawing direction with similar order. This is interesting since the central biphenyl

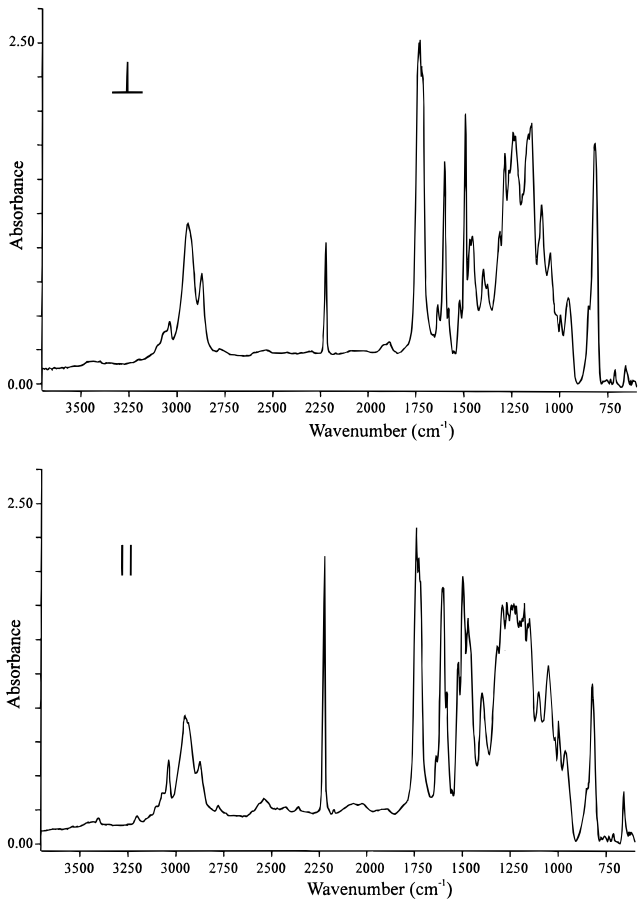


Figure 6. Polarized FT-IR spectra of **BM5** after mechanical orientation and cross-linking (∥ = parallel, ⊥ = perpendicular to drawing direction).

group did not behave as a mesogenic unit if there were no lateral cyanobiphenyl mesogens (**BE**, **BU**). However, without the central biphenyl group as mesogenic group, the formation of a nematic phase can hardly be explained and a smectic structure would be preferred to get efficient interaction between the cyanobiphenyl groups.

The order parameter was estimated using polarized UV/vis spectroscopy. For that purpose a mixture of **BM5** with 1 wt % 1,1-dimethoxy-1-phenylacetophenone and 1 wt % 4-(N,N-dihexylamino)-4′-nitrostilbene (DHANS, from Merck Co.) was prepared by dissolving the components in dichloromethane and subsequent evaporation of the solvent. The mixture was placed between two object slides coated with a unidirectionally rubbed polyimide layer, kept at 50 °C for 30 min and then cooled to ambient temperature. The film thickness was about 6 μm. No phase separation was observed on the length scale of the light microscope. Polarized UV/vis spectra taken of the same sample before and after polymerization are shown in Figure 7. The optical order parameter of the stilbene dye, $P_{2,dye}$, was calculated using eq 1. R represents the dichroic ratio of the absorbance parallel and perpendicular to the direction defined by the rubbing direction of the polyimide film (eq 2).

$$P_{2,dye} = (R - 1)/(R + 2) \quad (1)$$

$$R = A_{\parallel}/A_{\perp} \quad (2)$$

Equation 1 can be used if the transition moment and the main molecular axis are parallel.[36] Data calculated by Hanemann allow the assumption that the main

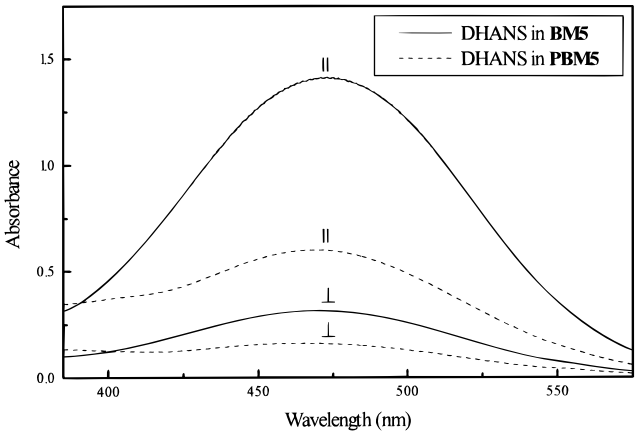


Figure 7. Polarized UV/vis spectra of **BM5** and **PBM5** parallel (||) and perpendicular (⊥) to rubbing direction of the polyimide film.

transition of DHANS in the visible range is parallel to the long axis of the molecule.[36] For the calculation of the order parameter, the dichroism of the absorption band at 470 nm was examined. The order parameter of the dye in the uncross-linked matrix was determined to be 0.54. After cross-linking of the monomer **BM5**, DHANS showed a P_2 value of 0.48 in the matrix. Since the order parameter of guest molecules in LC phases is generally smaller than that of the host molecules,[37] the P_2 values of 0.54 for the dye in the monomer **BM5** and 0.48 in the thermoset **PBM5** represent minimum values for the real order parameter of the LC matrix. The values indicate a loss of the order during the cross-linking procedure. Similar behavior was observed by Broer et al. for photopolymerization of LC diacrylates at low temperatures.[6]

The lower absorbance values observed in the cross-linked state (Figure 7) are due to isomerization of a fraction of DHANS from trans- to cis-configuration. The cis-isomer shows only weak to no absorbance in the examined area. However, higher absorbance of DHANS within the thermoset at lower wavelengths compared to the un-cross-linked state is caused by absorbance of the cis-isomer. At the wavelength used for calculation of order parameters, very weak absorbance of the cis-isomer was of no significance for the results. The absorbance measured for the dye in the cross-linked matrix leads to the conclusion that about 43% remained unisomerized after 12 min of irradiation. An influence of isomerization from cis- to trans-configuration on the resulting $P_{2,\mathrm{dye}}$ values can be excluded, since this isomerization could not be observed for irradiation of DHANS in dichloromethane solution, where complete conversion to the cis-form was possible, using the same radiation source. Besides, no isomerization was detectable, which could be possibly caused by irradiation of **BM5** in the UV/vis spectrometer.

Polarized FT-IR spectra shown in Figure 6 indicate that the branched LC monomers can be considered as LC telechelics with methacrylate side groups. Nevertheless, structurally the novel monomers differ from common LCTs, since the cyanobiphenyl mesogens are not included between the branching points of the network. With regard to the fact that **BM5** exhibits a nematic phase, the structure model shown in Figure 8 can be deduced for a cross-linked sample.

The bands of the unreacted methacrylate groups are also detected in the spectra (Figure 6, C=O stretching band at 1722 cm^{-1} and C=C stretching band at 1637 cm^{-1}). For these bands no dichroism is observed. Thus,

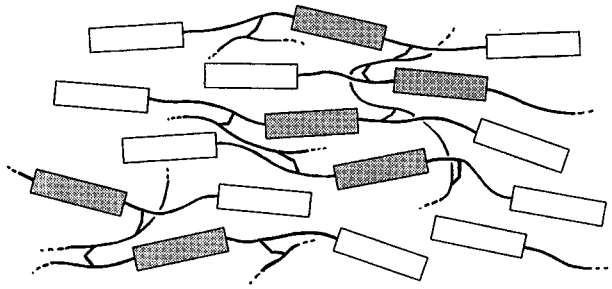


Figure 8. Structural model of cross-linked LCT **PBM5** (rigid central unit is shadowed).

the methacrylate groups obviously do not exhibit long-range orientational order. This lack of ordering contradicts the idea of a "quasi-topochemical" reaction within the nematic domains. However, on the basis of the experiments carried out, no conclusions can be drawn concerning the spatial vicinity of the methacrylate groups in the thermoset resins, which should play an important role for high conversions during cross-linking.

The thermosets obtained after cross-linking of **BM5** displayed good mechanical properties and showed a small volume change upon polymerization. The cross-linked LC thermoset possessed a T_g of 70 °C. The storage moduli measured by DMA are in the range of 2 GPa at ambient temperature; the volume reduction during polymerization was 2.5%. This low polymerization shrinkage is in agreement with the observation that neither the LC textures nor the WAXD patterns change noticeably during cross-linking.

At present, further studies on epitaxially oriented thin films of the materials as well as orientation of the monomers in electromagnetic fields are in progress. Furthermore, precise characterization of the mechanical properties of the networks with respect to cross-linking conditions is under way.

The mechanical properties in combination with the polymerizability at ambient temperature render the materials interesting for use in a number of areas, such as dental restoration, where Bis-GMA plays an important role. Furthermore, the novel monomers are intriguing with respect to their optical properties; e.g., coorientation of dyes with particular nonlinear optical (NLO) properties opens interesting perspectives.

Conclusion

A structurally novel type of LC monomer for LC thermosets has been prepared that is based on branched bismethacrylates, consisting of three coupled biphenyl units. The branched monomers exhibit nematic LC phases that are stable for prolonged periods of time at ambient temperature. The monomers could be oriented and cross-linked to anisotropic polymer networks with excellent mechanical properties.

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