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Synthesis, properties and photopolymerization of liquid crystalline dioxetanes

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The synthesis and photopolymerization of various liquid crystalline dioxetanes is described. The effects of the spacer length, structure of the mesogenic group and oxetane group on the liquid crystalline properties, polymerization behaviour and optical properties (birefringence) of the oriented and crosslinked network formed in photo-polymerization are discussed. Thermally stable films with birefringence values up to 0.13 can be formed from these materials. The dioxetanes show significantly lower polymerization shrinkage than do structurally related diacrylates.

1. Introduction

Liquid crystalline diacrylates have found significant use in the formation of oriented and crosslinked polymers [1, 2]. The optical properties of such film-forming polymer networks are very interesting with respect to application in liquid crystal display technologies or in the field of optical recording. For example, mixtures of nematic diacrylates and monoacrylates form birefringent tilted films whose tilt angle is stabilized after polymerization. Such films are used to improve the viewing angle of liquid crystal displays [3]. Mixtures of nematic and chiral acrylates form the cholesteric phase with its characteristic helical structure, which is capable of reflecting polarized light with wavelengths depending on the helical pitch. Films obtained from such materials find application as broadband reflective polarizers for improving the brightness of liquid crystal displays [4, 5] and as colour filters for reflective liquid crystal displays [6, 7]. In all these examples, thin films (3–15 μm) of monomers containing a photoinitiator are applied to a surface containing an orientation layer. After alignment and other optional processes, the film is photopolymerized to make it mechanically and thermally stable, with the properties of the mixture frozen into it [1, 2]. Other optical components such as polarization-sensitive lenses that find application in optical storage devices can also be obtained from with these materials [8]. The advantages of photopolymerization are that it can be performed at any temperature and conducted pattern-wise to obtain complex structures. The ability to use any desired temperature during the photopolymerization process is a particular advantage in view of the phase behaviour of liquid crystals, which makes the properties strongly temperature-dependent.

To date, research has focused on liquid crystalline diacrylates with structures such as **1** and **2** shown in table 1, but other polymerizable groups can also be used. Radical photopolymerization of thiolene molecules with structures **7** and **8** [9, 10] is one way of making the polymerization reaction less oxygen-sensitive, which may be of importance when thin films are polymerized. The disadvantages of such molecules are the formation of linear main chain liquid crystalline polymers and the fact that fairly complex chemical structures are required to obtain stable crosslinked materials [11]. Cationic vinyl polymerization and ring-opening polymerization are also less sensitive to oxygen than radical acrylate polymerization, which makes photopolymerization of liquid crystalline reactive molecules such as divinyl ethers like **3** and **4** and diepoxides like **5** and **6** an interesting option [12, 13]. An additional advantage of ring-opening polymerization of epoxides is that epoxides show less polymerization shrinkage than acrylates. Disadvantages of epoxides are their relatively slow rate of polymerization and the occurrence of side reactions. In the case of liquid crystalline diepoxides these effects were found to result in yellow scattering materials after polymerization [14].

Because of these disadvantages associated with epoxides we decided to investigate another form of cationic ring-opening polymerization, namely oxetane polymerization. In studies of the photopolymerization of dioxetanes a relatively fast, and clean polymerization

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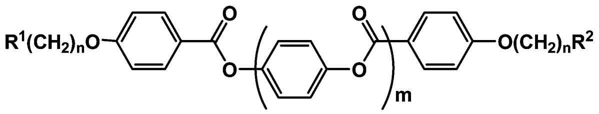
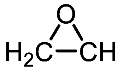
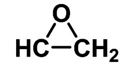
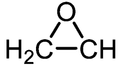
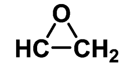
Table 1. Transition temperatures of various liquid crystalline polymerizable compounds.



Compound	*n*	*m*	*R*[1]	*R*[2]	Phase transitions/°C
1	6	0	$H_2C=CHCOO$	$OCOCH=CH_2$	(SmA 45 N 48 I) Cr 54 I
2	6	1	$H_2C=CHCOO$	$OCOCH=CH_2$	Cr 115 N 155 I
3	6	0	$H_2C=CHO$	$OCH=CH_2$	Cr 56 SmA 72 N 82 I
4	6	1	$H_2C=CHO$	$OCH=CH_2$	Cr 117 N 185 I
5	4	0			Cr 56 N 66 I
6	4	1			Cr 153 N 244 I
7	4	0	$HSCH_2CH_2$	$CH=CH_2$	Cr 43 N 80 I
8	4	1	$HSCH_2CH_2$	$CH=CH_2$	Cr 104 N 208 I

has been observed [15–17]. Oxetanes have moreover been found to show less polymerization shrinkage than the corresponding acrylates, which may be of advantage in the production of small optical components such as lenses for optical recording [8, 18].

Liquid crystalline side chain polyoxetanes have been described, implying that cationic oxetane polymerization can be effected in media containing mesogenic groups derived from aromatic esters [19–21]. We therefore decided to prepare liquid crystalline dioxetanes with structures similar to those presented in table 1. This paper describes the synthesis and properties of liquid crystalline dioxetanes. We also investigated the stability and optical properties of layers obtained after photopolymerization.

2. Experimental

2.1. *Materials*

The cationic photoinitiator Cyracure UVI 6990 was obtained from Ciba. Procedures described in the literature were used to prepare 4-{4-[(3-methyloxetan-3-yl)methoxy]butoxy}benzoic acid (**17b**), 4-{5-[(3-methyloxetan-3-yl)methoxy]pentyloxy}benzoic acid (**17c**) [22] and 3-toluenesulphonyloxymethyl-3-methyloxetane (**14**) [22]. The synthesis of **9a** is described in the next section. The synthesis of **9d** is similar to that of **9a**, and involves replacing 3-chloropropanol with 6-chlorohexanol. The syntheses of **10a–d** and **12a–d** were performed in similar ways. The synthesis of **12a** will be given as an example in the following section. Compounds **11b,c** and **13b,c** were prepared in a similar fashion to compounds **10b,c** and **12b,c**, respectively, except that 2-hydroxymethyl-2-methyloxetane was replaced with 2-hydroxymethyl-2-ethyloxetane as the starting compound. The synthesis of **11b** will be outlined as an example in the following section. All the other chemicals were obtained from Acros or Aldrich.

2.2. *Synthesis of 4-{3-[(3-methyloxetan-3-yl)-methoxy]propyloxy}phenyl 4-[3-(3-methyloxetan-3-yl]methoxy)propyloxybenzoate (**9a**) and 1,4-di{4-[3-((3-methyloxetan-3-yl)methoxy) propyloxy]benzoyloxy}-2-methylbenzene (**12a**)*

2.2.1. *1-Bromo-4-(3-hydroxypropyloxy)benzene (**15a**)*

42 ml of 3-chloropropanol were added to a solution of 86 g of bromophenol, 27 g of sodium methoxide and 15 g of sodium iodide in 300 ml of butanone. The resulting mixture was heated under reflux for 16 h. After cooling, the mixture was filtered and evaporated. The remaining oil was dissolved in 500 ml of diethyl ether and extracted twice with 125 ml of a 10% aqueous potassium hydroxide solution, and once using 125 ml of brine. 90 g of the product (78%) were obtained as an oil after drying over magnesium sulphate and evaporation of the diethyl ether.

2.2.2. *1-Bromo-4-{3-[(3-methyloxetan-3-yl)methoxy]-propyloxy}benzene(**16a**)*

24.7 g of 3-toluenesulphonyloxymethyl-3-methyloxetane (**14**) were added to a mixture of 9.8 g of milled potassium hydroxide, 20.2 g of compound **15a** and 28 ml of dimethylsulphoxide, stirred at 0°C. After the mixture had been stirred for 24 h at room temperature, 100 ml of diethyl ether and 80 ml of water were added. The organic layer obtained after separation was extracted twice with 80 ml of water and once with 40 ml of brine. 20.5 g of the product (74%) were obtained as an oil after evaporation, dissolution in 100 ml of dichloromethane, drying over magnesium sulphate and passage through a thin silica pad.

2.2.3. *4-{3-[(3-Methyloxetan-3-yl)methoxy]propyloxy}-benzoic acid (**17a**)*

36 ml of a 2.5 N *n*-butyllithium solution in hexane were added dropwise to a solution of 25 g of compound **16a** in 120 ml of tetrahydrofuran cooled to −70°C. The mixture was stirred for 1 h after which 14 g of solid dry ice was slowly added. 120 ml of diethyl ether and 100 ml of water were added after the mixture had reached room temperature. After separation, 36 ml of 2.5 N hydrochloric acid was added dropwise to the vigorously stirred aqueous layer. The precipitate was filtered off, washed with 150 ml of water and recrystallized from 200 ml of ethanol. 15.2 g of the product (67%) was obtained as a white powder, m.p. = 102°C.

2.2.4. *1-Benzyloxy-4-(3-hydroxypropyloxy)benzene (**18a**)*

41 ml of 3-chloropropanol were added to a solution of 50 g of 4-benzyloxyphenol, 13.5 g of sodium methoxide and 8 g of sodium iodide in 150 ml of butanone. The resulting mixture was heated under reflux for 16 h. The hot mixture was filtered and the crude product crystallized on cooling. 35 g of the product (55%) were obtained as needles with m.p. = 101°C after the solid had been washed with, successively, 150 ml of water and 100 ml of cold diethyl ether, and dried over silica in a desiccator.

2.2.5. *1-Benzyloxy-4-{3-[(3-methyloxetan-3-yl)methoxy]-propyloxy}benzene (**19a**)*

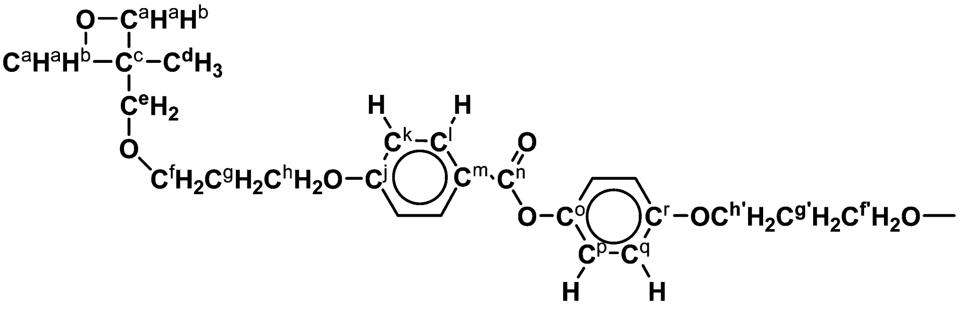
15.4 g of compound **14** were added to a mixture of 6.6 g of milled potassium hydroxide, 13 g of compound **18a** and 20 ml of dimethylsulphoxide, stirred at 0°C. After stirring for 24 h at room temperature, 80 ml of dichloromethane and 60 ml of water were added. The organic layer obtained after separation was evaporated. 10.2 g of the product (60%) was obtained as needles with m.p. = 88°C after crystallization from 80 ml of ethanol.

2.2.6. *4-{3-[(3-Methyloxetan-3-yl)methoxy]propyloxy}-phenol (**20a**)*

A mixture of 10.2 g of compound **19a**, 100 ml of ethanol, 50 ml of cyclohexene and 0.5 g of 5% Pd on carbon was heated under reflux for 16 h. After cooling, the mixture was filtered over celite and evaporated. 60 ml of diethyl ether and 60 ml of an aqueous 10% sodium hydroxide solution were added. After separation, 40 ml of dichloromethane and 80 ml of 2.4 N hydrochloric acid were added to the aqueous layer. The organic layer obtained after separation was dried over magnesium sulphate and evaporated. 6.4 g of the product (85%) was obtained as an oil.

2.2.7. *4-{3-[(3-Methyloxetan-3-yl)methoxy]propyloxy}-phenyl 4-{3-[(3-methyloxetan-3-yl)methoxy]-propyloxy}benzoate (**9a**)*

2.1 g of *N*,*N*′-dicyclohexylcarbodiimide (DCC) were added to a mixture of 2.5 g of compound **20a**, 2.8 g of compound **17a**, 0.12 g of 4-*N*,*N*-dimethylaminopyridine (DMAP) and 40 ml of dichloromethane stirred in an ice bath. After the mixture had been stirred for 16 h at room temperature, it was passed through a thin silica pad. 2.8 g of the product (55%) were obtained as a white powder with m.p. = 54°C after evaporation and recrystallization from ethanol. IR (KBr in cm^{-1}): 2939 + 2867 (CH alif.), 1724 (C=O), 1605 + 1512 (aromatic ring), 1253 (C–O–Ar), 1068 (C–O–C), 1168 (C–O of ester), 975 (oxetane). MS (MALDI): calculated for $C_{29}H_{38}O_8$ 514.26, found 514.31. ^1H NMR (δ in ppm, relative to TMS, J in Hz): 8.13 (d, 2H, $J = 8.6$, H^l), 7.10 (d, 2H, $J = 8.6$, H^p), 6.97 (d, 2H, $J = 8.6$, H^k), 6.92 (d, 2H, $J = 2.5$, H^q), 4.51 (d, 4H, $J = 5.6$, H^a), 4.35 (d, 4H, $J = 5.6$, H^b), 4.16 (t, 2H, $J = 6.2$, H^h), 4.07 (t, 2H, $J = 6.2$, $H^{h'}$), 3.67 (t, 2H, $J = 6.2$, H^f), 3.66 (t, 2H, $J = 6.2$, $H^{f'}$), 3.51 (s, 4H, H^e), 2.11, (q, 4H, $J = 6.2$, H^g), 2.07 (q, 4H, $J = 6.2$, H^g), 1.31 (s, 6H, H^d).



^{13}C NMR (δ in ppm, relative to TMS): 165.7 (C^{n}), 163.7 (C^{j}), 157.0 (C^{r}), 144.9 (C^{o}), 132.6 (C^{l}), 122.9 (C^{p}), 122.3 (C^{m}), 115.5 (C^{q}), 114.6 (C^{k}), 80.5 (C^{a}), 76.6 (C^{e}), 68.3 (C$^{f'}$), 68.0 (C^{f}), 65.6 (C^{h}), 65.5 (C$^{h'}$), 40.3 (C^{c}), 30.0 (C$^{g'}$), 29.8 (C^{g}), 21.8 (C^{d}).

2.2.8. *1,4-di-{4-[3-((3-methyloxetan-3-yl)methoxy) propyloxy]benzoyloxy}-2-methylbenzene (**12a**)*

2.1 g of DCC were added to a mixture of 0.62 g of methylhydroquinone, 2.8 g of compound **17a**, 0.12 g of DMAP and 40 ml of dichloromethane stirred in an ice bath. After the mixture had been stirred for 16 h at room temperature, it was passed through a thin silica pad. 2.2 g of the product (67%) were obtained as a white powder with m.p. = 100°C after evaporation and recrystallization from ethanol. IR (KBr in cm^{-1}): 2935 + 2867 (CH alif.), 1729 (C = O), 1605 + 1512 (aromatic ring), 1253 (C–O–Ar), 1068 (C–O–C), 1164 (C–O of ester), 975 (oxetane). MS (MALDI): calculated for $C_{37}H_{44}O_{10}$ 648.29, found 648.38. ^{1}H NMR (δ in ppm, relative to TMS, J in Hz): 8.17 (d, 2H, J = 8.6, Hl′), 8.14 (d, 2H, J = 8.6, Hl), 7.18 (d, 1H, J = 8.5, Hp′), 7.13 (d, 1H, J = 2.5, Hq), 7.08 (dd, 1H, $J1$ = 8,5, $J2$ = 2.5, Hp), 6.99 (d, 2H, J = 8.6, Hk′), 6.98 (d, 2H, J = 8.6, Hk), 4.52 (d, 4H, J = 5.7, Ha), 4.36 (d, 4H, J = 5.7, Hb), 4.17 (t, 4H, J = 6.0, Hh), 3.56 (t, 4H, J = 6.0, Hf), 3.51 (s, 4H, He), 2.24, (s, 3H, Hr), 2.12 (q, 4H, J = 6.0, Hg), 1.31 (s, 6H, Hd).

^{13}C NMR (δ in ppm, relative to TMS): 165.3 (C^{n}), 164.9 (C$^{n'}$), 163.8 (C^{j} and C$^{j'}$), 148.8 (C$^{o'}$), 147.4 (C^{o}), 132.7 (C^{l} and C$^{l'}$), 132.2 (C$^{q'}$), 124.5 (C^{q}), 123.3 (C$^{p'}$), 121.9 and 122.1 (C^{m} and C$^{m'}$), 120.4 (C^{p}), 114.5 (C^{k} and C$^{k'}$), 80.4 (C^{a}), 76.6 (C^{e}), 68.0 (C^{f}), 65.5 (C^{h}), 40.3 (C^{c}), 29.8 (C^{g}), 21.8 (C^{d}), 16.8 (C^{r}).

2.3. *Synthesis of 1,4-di{4-[4-((3-ethyloxetan-3-yl)methoxy)butyloxy]benzoyloxy}benzene (**11b**)*

2.3.1. *3-(4-Bromobutyloxymethyl)-3-ethyloxetane (**21b**)*

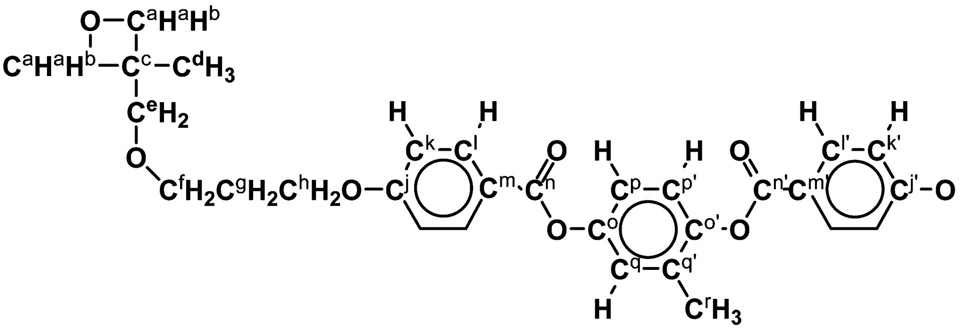
A mixture of a solution of 114 g of sodium hydroxide in 200 ml of water, 20 g of 3-(hydroxymethyl)-3-methyloxetane, 1 g of tetrabutyl ammonium bromide, 65 ml of 1,4-dibromobutane and 200 ml of hexane was stirred for 48 h at room temperature. After separation, the aqueous layer was extracted with 100 ml of hexane. The combined organic layers were extracted with 50 ml of brine and dried over magnesium sulphate. 26.9 g of the product (62%) was obtained as an oil after evaporation and fractionation (b.p. = 73°C at 0.5 mbar).

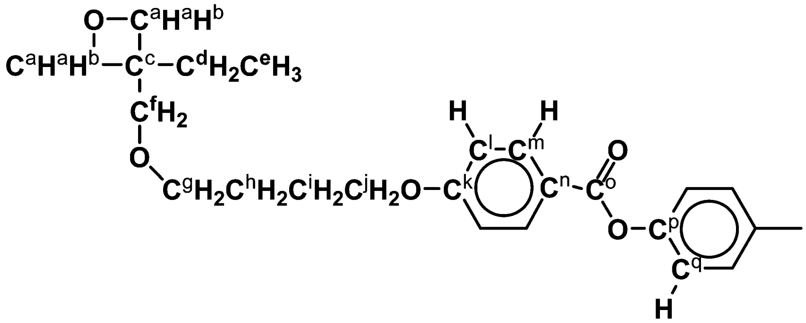
2.3.2. *4-{4-[(3-ethyloxetan-3-yl)methoxy]butyloxy}-benzoic acid (**22b**)*

A mixture of 9.0 g of compound **21b**, 5.8 g of 4-hydroxyethylbenzoate, 6.84 g of potassium carbonate and 40 ml of butanone was heated under reflux for 16 h. After cooling, the solution was filtered and evaporated. 50 ml of diethyl ether was added, and the mixture extracted with 40 ml of 10% aqueous sodium hydroxide and evaporated. The organic layer was separated and evaporated. A mixture of the remaining oil, 3.1 g of potassium hydroxide and 75 ml of water was heated under reflux for 4 h, during which time the mixture became a clear solution. After cooling, the solution was extracted with 70 ml of diethyl ether; 25 ml of 2.4 M hydrochloride solution was then added dropwise with vigorous stirring. A white powder precipitated, which was filtered off, washed with 70 ml of water and dried in the desiccator. 9.8 g of the product (85%) was obtained as a white powder with m.p. = 78°C.

2.3.3. *1,4-Di{4-[(3-ethyloxetan-3-yl)methoxy]butyloxy}-benzoyloxybenzene (**11b**)*

4.3 g of DCC were added to a mixture of 1.2 g of hydroquinone, 6.6 g of compound **22b**, 0.25 g of DMAP and 80 ml of dichloromethane stirred in an ice bath. After the mixture had been stirred for 16 h at room temperature, it was passed through a thin silica pad. 4.4 g of the product (60%) was obtained as a white powder with m.p. = 67°C after it had been evaporated and washed twice with 40 ml of ethanol. IR (KBr in cm^{-1}): 2932 + 2867 (CH alif.), 1729 (C = O), 1605 + 1512 (aromatic ring), 1258 (C–O–Ar), 1068 (C–O–C), 1162 (C–O of ester), 971 (oxetane). MS





(MALDI): calculated for $C_{40}H_{50}O_{10}$ 690.34, found 690.31. ^{1}H NMR (δ in ppm, relative to TMS, J in Hz): 8.15 (d, 4H, $J=8.7$, H^m), 7.26 (s, 4H, H^q), 6.97 (d, 4H, $J=8.7$, H^k), 4.46 (d, 4H, $J=5.7$, H_a), 4.39 (d, 4H, $J=5.7$, H^b), 4.09 (t, 4H, $J=6.0$, H^j), 3.55 (s, 4H, H^f), 3.50 (t, 4H, $J=6.0$, H^g), 1.93, (m, 4H, H^h), 1.80 (m, 4H, H^d), 1.75 (q, 4H, $J=7.5$, H^d), 0.89 (t, 6H, $J=7.5$, H^e).

^{13}C NMR (δ in ppm, relative to TMS): 165.2 (C^o), 163.9 (C^k), 148.8 (C^p), 132.7 (C^q), 123.0 (C^n), 121.9 (C^m), 114.7 (C^l), 78.9 (C^a), 73.9 (C^f), 71.5 (C^g), 68.4 (C^j), 48.8 (C^c), 27.2 (C^i), 26.5 (C^h), 8.6 (C^b).

2.4. *Characterization methods*

^{1}H NMR and ^{13}C NMR spectra were measured using a Brucker DPX 300 spectrometer in $CDCl_3$ with TMS as an internal standard. All intermediates and products exhibited NMR spectra that were in accordance with their structures. FTIR spectra were recorded on an ATI Mattson Genesis II spectrometer. Maldi-TOF mass spectra were recorded on a Voyager-De Pro machine using α-cyano-4-hydroxycinamic acid as matrix.

The thermodynamic parameters associated with the phase transitions were measured using a Perkin-Elmer DSC-7 instrument. For the photo DSC measurements, this spectrometer was equipped with a UV lamp (Philips PL10W) with a standard intensity of 7 mW cm^{-2} within a range of 340–410 nm. Samples were illuminated for approximately 25 min. The degree of conversion (C) was calculated from the following equation:

$$C=(A\times M)/(2\times H)\times 100\%$$

where A (kJ g^{-1}) is the integrated area of the measurement, M (g mol^{-1}) is the molecular mass of the polymerizable molecule and H is the heat of polymerization of the oxetane group, two of which were present in the molecule; $H=59$ kJ mol^{-1} [15].

The birefringence measurements were performed in glass cells with a gap of approximately 5 μm obtained from Linkam. The internal cell surfaces were coated with thin layers of polyimide, which had been rubbed to induce homogeneous uniaxial orientation of the LC material. The glass cells were filled by means of capillary suction. The thickness of the cell was measured via interference of an empty cell using an UV-Vis spectrometer. The thickness of the cell (d) was calculated according to:

$$d=\frac{0.5a\lambda_1\lambda_2}{\lambda_2-\lambda_1}$$

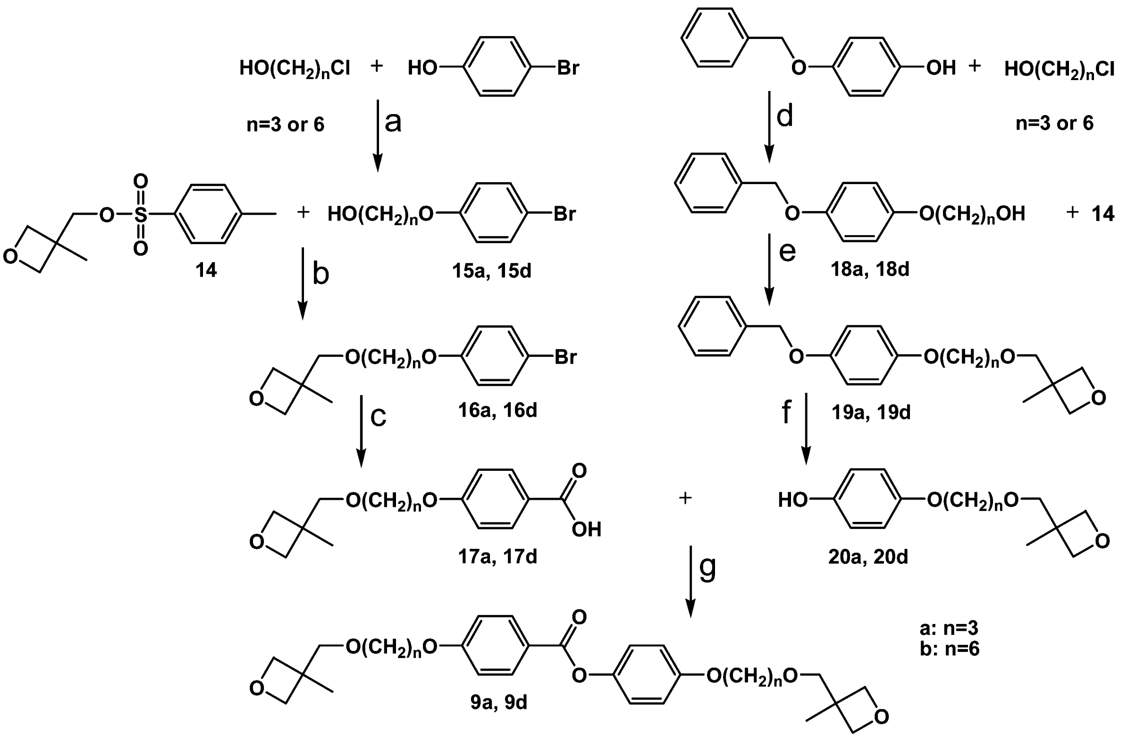
where λ_1 and λ_2 are wavelengths at maximum interference and a is the number of maxima between λ_1 and λ_2. The retardation (R) was measured as the average of the retardation values at 480, 546, 589 and 644 nm using a light microscope [23]. The sample was placed between crossed polarizers and the orientation axis of the cell was 45° relative to the polarizers. An optical compensator (Leitz Tilting Compensator 1942 K) was placed perpendicularly to the orientation axis of the cell. The birefringence (Δn) was obtained according to $\Delta n=R/d$. The temperature was controlled with the aid of a Mettler Toledo fp5 hot stage.

Densities were determined using conventional pycnometry with water as the filling liquid. No significant weight gain due to absorption of water was detected (<0.1%).

3. Results and discussion

3.1. *Synthesis*

The synthesis of liquid crystalline dioxetanes with the same mesogenic two-ring system as diacrylate **1**, divinyl ether **3**, diepoxide **5** and thiolene **7** was first conducted. The synthesis of compounds **9a** and **9d**, with $n=3$ and 6, respectively, is outlined in scheme 1. The etherification products **15a** and **15d** were transformed into oxetanes **16a** and **16d**, respectively, through alkylation of the alcoholic function with the tosylate of 3-hydroxymethyl-3-methyl oxetane (**14**), a known reagent. [22]. In order to introduce the acid function, we attempted to cause bromides **16a** and **16d** to react with magnesium so that reaction of the magnesium compound with CO_2 could be induced. Unfortunately, attempts to obtain the Grignard compound failed. Part of the oxetane ring opened during the reaction, leading



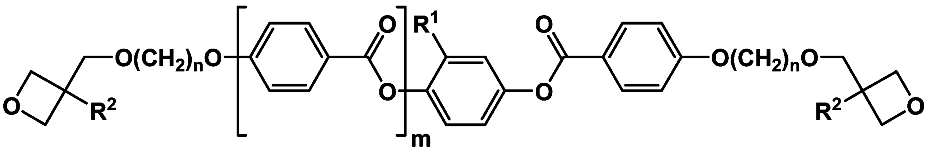
Scheme 1. Synthesis of compounds **9a** and **9d**. a: NaOMe, NaI in butanone. b: KOH in DMSO. c: BuLi in THF, CO_2, HCl in H_2O. d: NaOMe, NaI in butanone. e: Pd/C, cyclohexene in ethanol. f: DCC and DMAP in CH_2Cl_2.

to inactivation of the magnesium. Lithiation of **16a** and **16d** with the aid of butyl lithium proved more successful. Reaction of the lithiated products with CO_2 followed by acidification of the aqueous solution of the lithium carboxylates led to good yields of the acids **17a** and **17d** without destruction of the oxetane ring.

The hydroquinone derivatives **20a** and **20d** needed for esterification with **17a** and **17d**, respectively, were prepared in the same manner, by replacing 4-bromophenol with the protected hydroquinone, in this case 4-benzyloxyphenol. The deprotection reaction required to form **20a** and **20d** through hydrogenation of **19a** and **19d**, respectively, took place with no effect on the oxetane ring. We tried using hydroquinone protected as tetrahydropyranyl ether instead of 4-benzyloxyphenol; this compound has been successfully used in the formation of a wide range of liquid crystalline acrylates [2]. However, deprotection of this group by the weakly acidic pyridinium 4-toluenesulphonate resulted in partial destruction of the oxetane ring. The final compounds **9a** and **9d** were obtained after esterification under non-acidic conditions using DCC and DMAP. Compound **9a** was crystallized from ethanol. Compound **9d** was not crystalline at room temperature. It was difficult to purify: only at −20°C did a precipitate form from 2-propanol in a low yield. Table 2 shows the properties of these compounds. Compound **9a** melted at 38°C; no transition to a liquid crystalline phase was observed before crystallization at about 0°C. Compound **9d** was an oil with a clearing point from the nematic phase at 1°C. Comparison of the thermal data of the similar compounds containing other polymerizable groups in table 1 ($m=0$) with those of **9a** and **9d** shows that the oxetane groups have a negative influence on the liquid crystalline behaviour of such compounds. For this reason we decided to produce dioxetanes with a larger mesogenic group, such as those in table 1 with $m=1$. The liquid crystalline phases obtained with these mesogenic groups are broader than those of the smaller molecules ($m=0$). This we assumed would compensate for the effect of the oxetane groups.

Dioxetanes **10a** and **12a** were obtained through esterification of acid **17a** with hydroquinone and methylhydroquinone, respectively, following the same procedure as described for the formation of **9a**. Compounds **10b–d** and **12b–d** were produced in a similar fashion. The formation of derivates **15b** and **15c** is less straight forward due to cyclization of the bromoalcohols with $n=4$ and 5 during the etherification reaction. Acids **17b** and **17c** were therefore prepared according to procedures described in the

Table 2. Transition temperatures of the liquid crystalline dioxetanes synthesized in this study.



Compound	m	R^1	n	R^2	Phase transitions/°C
9a	0	H	3	CH_3	Cr 55 I
9d	0	H	6	CH_3	N 1 I
10a	1	H	3	CH_3	(N 104 I) Cr 138 I
10b	1	H	4	CH_3	Cr 94 N 116 I
10c	1	H	5	CH_3	(N 106 I) Cr 119 I
10d	1	H	6	CH_3	Cr 99 N 119 I
11b	1	H	4	C_2H_5	Cr 67 N 98 I
11c	1	H	5	C_2H_5	(N 90 I) Cr 120 I
12a	1	CH_3	3	CH_3	(N 23 I) Cr 100 I
12b	1	CH_3	4	CH_3	Cr 65 N 74 I
12c	1	CH_3	5	CH_3	(N 59 I) Cr 75 I
12d	1	CH_3	6	CH_3	Cr 36 N 74 I
13b	1	CH_3	4	C_2H_5	Cr 57 N 65 I
13c	1	CH_3	5	C_2H_5	Cr 54 I

literature using dibromides as a starting product instead of bromoalcohols [20].

The thermal properties of the three aromatic ring-type dioxetanes derived from methyloxetane are shown in table 2. Compounds **10a–d** with $R^1 = H$ had an odd–even effect on the isotropic transition. No such effect was observed in the case of liquid crystals derived from the same mesogenic group with linear aliphatic end groups. Liquid crystalline diacrylates derived from this mesogenic group with the same spacers ($n = 3$–6) also do not show this effect [2]. A reverse odd–even effect was observed with respect to the melting point. As a result of these two effects, the dioxetanes with odd spacers **10a** and **10c** ($n = 3$ or 5) were monotropic. A more pronounced odd–even effect on the isotropic transition was observed in the case of compounds **12a–d** with $R^1 = CH_3$. These compounds showed the same behaviour as compounds **10a–d**. An advantage of compounds **12b–d** over the corresponding compounds **10b–d** is their lower melting points. This implies less risk of unwanted thermal polymerization during alignment of the mixture following the melting of mixtures of the di-oxetanes with a photoinitiator. In experiments with divinylethers such as **4**, a high melting temperature was found to result in thermal polymerization of the mixture with cationic photoinitiators, while the methylated derivatives with lower melting points could be easily aligned [12]. Thermal polymerization of mixtures of the initiator with the thermotropic compounds **10b** and **10d** was indeed observed.

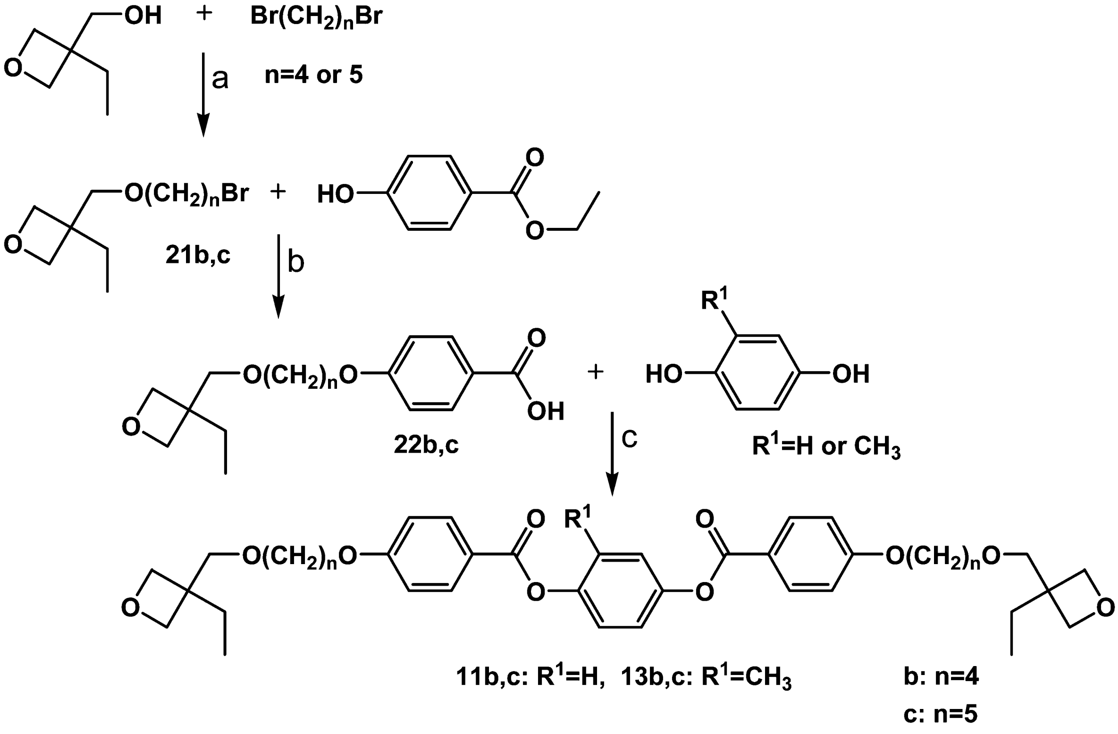
We assumed that compounds with mesogenic groups derived from hydroquinone ($R^1 = H$) such as **10b** would exhibit a higher optical anisotropy (e.g. birefringence) than those derived from methylhydroquinone ($R^1 = CH_3$) such as **12b**. This effect has been observed in the case of diacrylates and may be attributed to the lateral methyl group in the middle ring, which lowers the order of the liquid crystalline system. We also assumed that compounds derived from 2-ethyloxetane ($R^2 = C_2H_5$) would exhibit lower melting points than those derived from 1-methyloxetane ($R^2 = CH_3$). Thus, in order to obtain liquid crystalline dioxetanes with the same mesogenic group as **10b** and **10c** but with a lower melting point, we produced compounds **11b** and **11c** using 2-hydroxymethyl-2-ethyloxetane as a starting product instead of 2-hydroxymethyl-2-methyloxetane. The synthetic procedure employed is very similar to that of the synthesis of **10b** and **10c** and is outlined in scheme 2. In both cases this structural change led to a significant lowering of the clearing point, but only in the case of compound **11b** was the melting point lowered to such an extent that the material could be aligned without unwanted thermal polymerization after melting in the presence of a photoinitiator. We also produced the 2-ethyloxetane analogues **13b** and **13c** of compounds **12b** and **12c**, respectively. These compounds showed no advantages over the methyloxetane analogues. Comparison of the methyloxetane derivatives ($R^2 = CH_3$) and the ethyloxetane derivatives ($R^2 = C_2H_5$) shows that the derivatives with $n = 4$ had higher clearing points than the corresponding derivatives with $n = 5$. It appears, therefore, that these methyl or ethyl groups were not responsible for the odd–even effect. This means that in the liquid crystalline state these molecules are probably stretched as shown in figure 1, with the methyl or ethyl group in a lateral position and the oxetane ring forming part of the stretched chain. Because the oxetane ring is part of the stretched chain, the $n = 4$ compounds contain an odd membered chain (structure A) in the more favourable all-*trans*-conformation. As a result, these compounds have a higher clearing point than the compounds with $n = 5$ (structure B) containing the even membered chain.

Complete crystallization of the molten compounds **12b–d** took a long time, from several hours in the case of **12b** and **12c** to several days in the case of **12d**. The slow crystallization of **12d** was a disadvantage because it was also extremely difficult to purify this compound by means of crystallization. Because **12b**, derived from methyloxetane, is thermotropic and relatively easy to purify it is the preferred compound for investigating the polymerization behaviour and physical properties of networks formed from it. The thermotropic compound **11b** is also interesting because it is assumed to form networks with higher birefringence values due to the absence of the methyl group in the middle ring.

3.2. *Photopolymerization*

In order to study the photopolymerization of **12b–d** we mixed them with 2.5 wt% of the cationic initiator Cyracure 6990. This caused the clearing point of these mixtures to drop to approximately 3°C below that of pure compounds. Upon irradiation of the mixture containing **12b** at 60°C in a photo-DSC apparatus a sharp exotherm was observed that lasted about 1 min, as shown in figure 2. The calculated degree of conversion of the polymerization was almost 100%. This is much higher than that of the cationic photopolymerization of liquid crystalline diepoxides after 1 min under the same conditions [13, 14], suggesting much faster polymerization kinetics for dioxetanes.

The degree of conversion of oxetane groups as a function of temperature was measured using the heat of polymerization obtained with **12b** in the photo-DSC experiments at different temperatures; see figure 3. The polymerization below the melting point was performed after the sample had been heated to 80°C followed by cooling to the polymerization temperature. Figure 3 shows that almost 100% conversion was obtained in



Scheme 2. Synthesis of **11b**, **11c**, **13b** and **13c**. a: $(C_4H_9)_4N^+$ Br^-, NaOH in hexane-H_2O. b: K_2CO_3 in butanone, NaOH in H_2O and HCl in H_2O. b: DCC and DMAP in CH_2Cl_2.

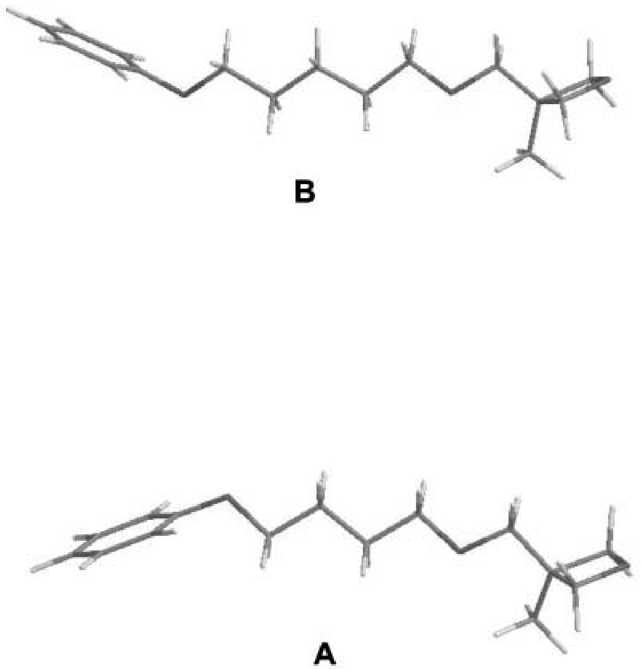


Figure 1. Structures of the compounds derived from a butyl spacer (A) and a pentyl spacer (B).

polymerization at temperatures above 60°C. The network formation immobilizes the system and this probably caused the lower degree of conversion at lower temperatures. Similar results were obtained with **12c**. With **12d**, the degree of conversion at temperatures below 60°C was considerably higher than with **12b**. The longer spacer of **12d** probably kept the oxetane groups more mobile during the formation of the network

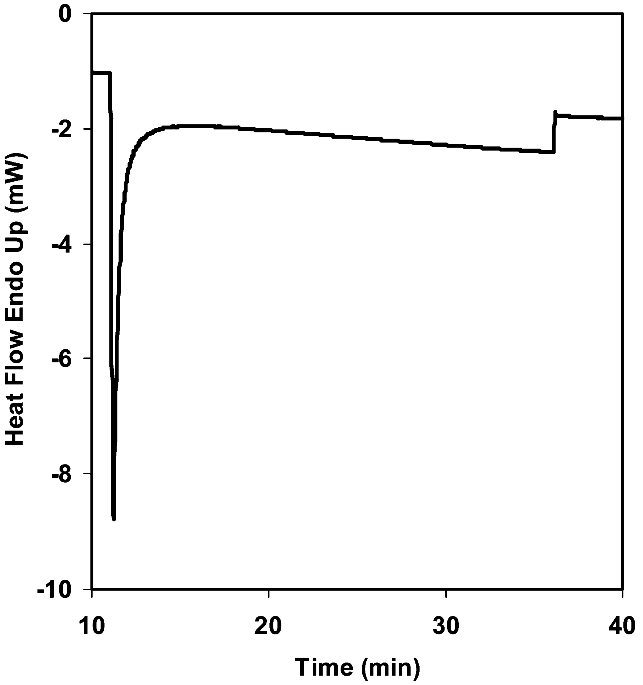


Figure 2. Photo-DSC curve of a mixture of dioxetane **12b** containing 2.5% Cyracure irradiated with a Philips PL10W UV source with an intensity of 7 mW cm^{-2} at 60°C.

In order to measure the volume shrinkage upon polymerization, we melted about 1 g of the polymerizable mixture obtained from **12b** and polymerized it at 60°C. Volume measurements in a pycnometer at the same temperature revealed polymerization shrinkage of 2%. This value is lower than the 6% polymerization shrinkage of diacrylates [2] with a structure similar to that of **12b**. Comparison of simple non-liquid crystalline diacrylates and dioxetanes revealed an almost threefold decrease in polymerization shrinkage. So the mesogenic oxetanes do indeed show lower polymerization shrinkage than the liquid crystalline acrylates.

3.3. *Optical properties*

A 5 μm cell with rubbed polyimide layers was filled with a mixture of monomer **12b** and the photoinitiator. Figure 4 shows the birefringence as a function of temperature measured in this cell. A curve typical of nematic compounds was observed, in which the birefringence reaches zero near the isotropic transition where the order is completely lost. Photopolymerization at 60°C led to an increase in birefringence of about 20%. Although polymerization shrinkage and the associated increase in density may account for part of the observed increase in refractive indices, which in turn will increase the birefringence, this substantial increase is probably ultimately attributable to the formation of the polymer network. Figure 4 shows that the polymerizations were performed in the temperature range

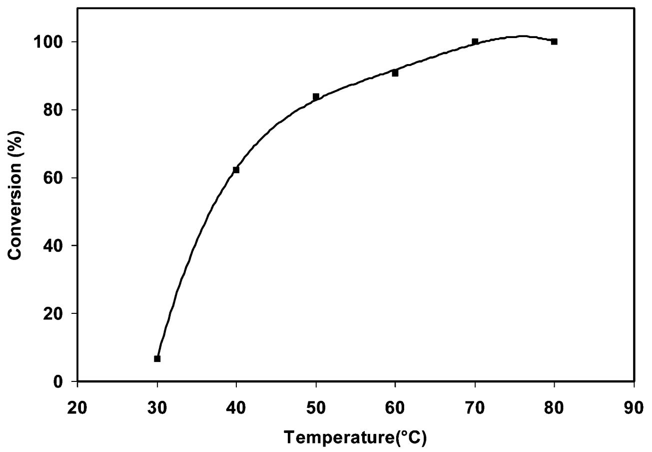


Figure 3. Dependence of the degree of conversion on the temperature of a mixture of **12b** containing 2.5% Cyracure irradiated with a Philips PL10W UV source with an intensity of 7 mW cm^{-2}.

near the isotropic transition where the birefringence curve has a relatively large slope. This means that the polymerization was performed in a relatively low ordered system. Upon polymerization, the growing polymer chain will increase the isotropic transition temperature resulting in an increase of the order at the polymerization temperature. This effect can be relatively high due to the steep slope of the birefringence curves of the monomers. Of course, this effect is only effective at the beginning of the polymerization; at later stages changes are no longer possible due to the formation of the crosslinks that immobilize the system completely. Figure 4 also shows that the birefringence after polymerization is temperature-independent. This demonstrates the thermal stability of the physical properties of the polymeric network, which is important for many applications of such materials. Polymerization at higher temperatures resulted in films with a lower birefringence. At lower temperatures multidomain formation was observed; this was probably due to the formation of small crystallites. The thermal stability after polymerization below 50°C was also found to be poorer; heating after polymerization and cooling led to irreversible birefringence values, probably due to thermal post-polymerization at higher temperatures leading to a less ordered network.

Figure 4 also shows the results of the birefringence measurement of the mixture of **12d** and the photoinitiator. The graph is similar to that for **12b**. After polymerization at 60°C, the increase in birefringence was lower than that observed in the case of **12b**. This means that the increase in order was also lower. In addition, the thermal stability of the network was lower; the figure shows a decrease in birefringence with increasing temperature. As this effect was found to be reversible, it is assumed not to be a consequence of the lower degree of conversion of **12d**, because at temperatures up to 150°C thermal decomposition of the initiator should tighten the network, leading to irreversibility in the birefringence values. This irreversibility was only observed when photopolymerization was performed at lower temperatures, as described above for compound **12b**. The combination of the longer spacer ($n=6$) and the relatively mobile polyether (polyoxetane) chain was probably responsible for the lower order after polymerization and the lower thermal stability of the network relative to that of the compound with the shorter spacer ($n=4$). Similar effects were observed by comparison of polymers obtained from liquid crystalline diacrylates with butyl and hexyl spacers. In that case, however, the differences in thermal stability of the birefringence values were smaller [24]. The higher mobility of the polyoxetane chain compared with that of the polyacrylate chain is probably responsible for the differences between these two classes of polymers. Thus a shorter spacer ($n=4$), such as that in compound **12b**, is to be preferred.

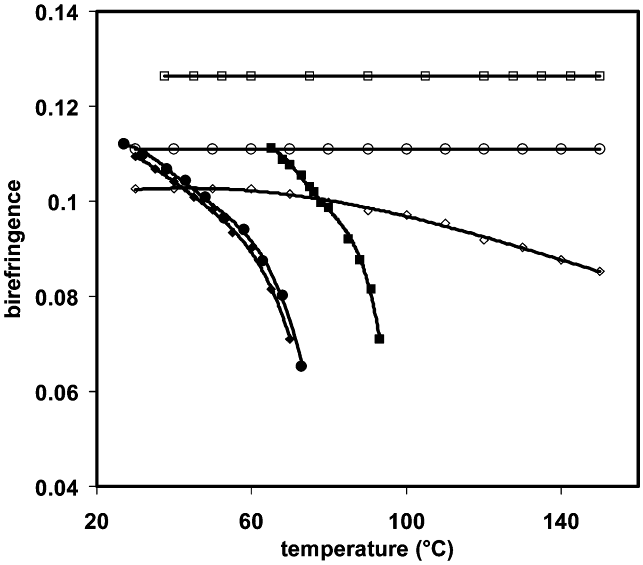


Figure 4. Dependence of the birefringence on the temperature of **11b** mixed with 2.5% Cyracure 6990 before (■) and after polymerization at 80°C (□); **12b** mixed with 2.5% Cyracure 6990 before (●) and after polymerization at 60°C (○); and **12d** mixed with 2.5% Cyracure 6990 before (◆) and after polymerization at 60°C (◇).

Compounds derived from the mesogenic group that lacks a methyl group in the central ring such as **10b** and **11b** are expected to give films with higher birefringence because with these materials better packing is expected due to the lack of the steric hindrance of the methyl group in compounds such as **12b**. Unfortunately it was not possible to fill cells with mixtures of **10b** and the photoinitiator due to thermal polymerization upon melting as mentioned in the previous section. We were however able to introduce mixtures of compound **11b** and the initiator into the cells because the melting point of these mixtures was more than 20°C lower. Figure 4 shows the birefringence of these mixtures before and after photopolymerization at 80°C. Indeed, a thermally stable network was formed with a birefringence value that was higher than that of the polymer formed from **12b**. Crosslinked films made from liquid crystalline diacrylates derived from the same mesogenic group as in **11b** were found to exhibit higher birefringence values than films made from liquid crystals derived from the mesogenic group as in **12b** having the same spacer length [25]. These oxetanes show the same behaviour. The fact that **11b** was derived from ethyloxetane, which is assumed to induce a lower order than molecules derived from methyloxetane, does not seem to play an important role.

4. Conclusion

Liquid crystalline dioxetanes are very suitable for producing ordered networks. They polymerize as fast as the commonly used liquid crystalline diacrylates and much faster than diepoxides. The main differences between dioxetanes and acrylates concern the polymerization mechanism (cationic ring-opening polymerization versus radical addition polymerization) and the polymerization shrinkage, which is lower in the case of dioxetanes. The latter property in particular makes these materials suitable for the production of micro-optical components. The relation between the chemical structure and the properties of the monomers and polymeric networks formed from them is rather critical; the odd–even effect makes use of only even spacers of interest, and spacers of four carbon atoms are preferable for use to obtain networks with very stable physical properties (birefringence).

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