Synthesis and Polymerization of Liquid Crystalline Donor−Acceptor Monomers

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ABSTRACT: The synthesis and polymerization of the following liquid crystalline monomers (containing both a vinyl ether group (electron donor) and a maleimide group (electron acceptor) within the same molecule) are described: 4-[(4-maleimidobenzoyl)oxy]phenyl 4-[[4-(vinyloxy)butyl]oxy]benzoate (**1**), 4-[[11-[(4-maleimidobenzoyl)oxy]undecyl]oxy]phenyl 4-[[4-(vinyloxy)butyl]oxy]benzoate (**2**), and 4-[[6-[(4-maleimidobenzoyl)oxy]hexyl]oxy]phenyl 4-[[4-(vinyloxy)butyl]oxy]benzoate (**3**). In the absence of photoinitiators, direct photolysis of a mixture of monomers **2** and **3**, oriented in the nematic phase, led to initiation of polymerization and the formation of an ordered nematic LC polymer network. The use of a nonliquid crystalline model substance, *N*-[4-[[[4-(vinyloxy)butyl]oxy]carbonyl]phenyl]maleimide (**4**), showed that irradiation with a high-power microwave lamp, without the presence of photoinitiators, resulted in fast and efficient polymerization.

Introduction

The preparation of oriented liquid crystalline polymers using *in-situ* photopolymerization has been known for some years now. This technique involves orientation of LC monomers and the subsequent polymerization to produce oriented polymer materials with a liquid crystalline molecular organization. The use of photoinitiation allows the temperature to be extensively varied. Polymerization of monofunctional monomers yields linear side-chain liquid crystalline polymers. This procedure has been used for the cationic polymerization of vinyl ethers and the free radical polymerization of acrylates.[1,2]

Polymerization of bifunctional monomers results in LC polymer network structures. A large number of anisotropic LC network polymers have been prepared by photoinitiated polymerization of oriented diacrylates, divinyl ethers, and diepoxides.[3−7] Cross-linked materials have also been prepared by spontaneous thermal polymerization of liquid crystalline bis(maleimide) and bis(acetylene) monomers.[8,9]

Electron donor−acceptor (EDA) complexes have shown to be of interest for polymer chemists, and Hall et al.[10] have reported on a large number of monomers that can form such complexes. In solution, mixtures of electron-rich and electron-poor monomers undergo free radical copolymerizations.[11] Certain highly reactive mixtures will polymerize spontaneously upon heating. For selective combinations of electron donor and electron acceptor monomers, photoinduced free radical polymerizations in the absence of photoinitiators have been performed, both in solution and in the bulk.[12,13] Jönsson et al.[13] have nicely reviewed those in the literature suggested possibilities for the formation of an excited state EDA complex followed by decay reactions, some resulting in polymerization.

This paper presents the initiator-free polymerization of liquid crystalline monomers containing both a vinyl ether group (donor) and a maleimide group (acceptor) within the same molecule. The importance of using an efficient radiation source will also be discussed, on the basis of the results from polymerization of a nonliquid crystalline model compound using different irradiation sources.

Experimental Section

Materials. 4-(Tolylsulfonyl)butyl vinyl ether was synthesized as reported previously[6] and *N*-[4-(chlorocarbonyl)phenyl]-maleimide was prepared according to a literature procedure.[14] 4-Hydroxybutyl vinyl ether was kindly provided by Nisso Maruzen Chemical Co., and 4-hydroxyphenyl 4-hydroxybenzoate (**5**) was a gift from Miles. All other reagents and solvents were purchased from Aldrich and Merck and used as obtained. The monomers were synthesized according to the route outlined in Scheme 1, and further details are given below.

4-Hydroxyphenyl 4-Sodiooxybenzoate (6). A solution of 4-hydroxyphenyl 4-hydroxybenzoate (**5**, 2.46 g, 10.74 mmol) was added dropwise to a suspension of sodium hydride (0.32 g, 10.74 mmol) in THF. The mixture was allowed to react for 10 h and then filtered and washed with THF to recover crystals of **6** (2.57 g, 95%). ^{1}H-NMR (DMSO-d_6, δ, ppm): 6.32−6.34 (2 H, aromatic, 3-H and 5-H, d), 6.71−6.74 (2 H, aromatic, 3′-H and 5′-H, d), 6.84−6.86 (2 H, aromatic, 2′-H and 6′-H, d), 7.63−7.65 (2 H, aromatic, 2-H and 6-H, d). ^{13}C-NMR (DMSO-d_6, δ, ppm): 109.5 (1 C, 1-C), 115.5 (2 C, 3′-C and 5′-C), 118.0 (2 C, 3-C and 5-C), 122.5 (2 C, 2′-C and 6′-C), 132.0 (2 C, 2-C and 6-C), 142.4 (1 C, 1′-C), 156.4 (1 C, 4′-C), 165.5 (1 C, C=O), 174.3 (1 C, 4-C).

4-Hydroxyphenyl 4-[[4-(Vinyloxy)butyl]oxy]benzoate (7). A mixture of 4-(tolylsulfonyl)butyl vinyl ether (2.89 g, 10.7 mmol) and **6** (2.57 g, 10.2 mmol) was reacted in DMF for 12 h at 70 °C. The solvent was removed by distillation and the residue extracted several times with methylene chloride and water. The organic phase was separated, dried with $MgSO_4$, and evaporated. The remaining solid was purified by column chromatography (silica gel) using a gradient of hexane/ethyl acetate. Recrystallization from a mixture of hexane/ethyl acetate produced white crystals of **7** (1.75 g, 53%). ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.88−1.95 (4 H, $-(CH_2)_2-$, m), 3.75−3.80 (2 H, $-CH_2-O-CH=CH_2$, t), 3.99−4.03 (1 H, $CH_2=CH-O-$ *trans*, d), 4.06−4.11 (2 H, $-CH_2-OPh$, t), 4.17−4.23 (1 H, $CH_2=CH-O-$ *cis*, d), 5.62 (1 H, $-OH$, s), 6.45−6.51 (1 H, $CH_2=CH-O-$, q), 6.80−6.83 (2 H, aromatic, 3′-H and 5′-H, d), 6.95−7.04 (4 H, aromatic, 2′-H, 6′-H, 3-H, and 5-H, m), 8.11−8.15 (2 H, aromatic, 2-H and 6-H, d).

4-[(6-Hydroxyhexyl)oxy]phenyl 4-[[4-(Vinyloxy)butyl]-oxy]benzoate (8). A mixture of **7** (3.56 g, 10.97 mmol), 6-bromohexanol (1.99 g, 10.99 mmol), and K_2CO_3 (4.55 g, 32.92 mmol) was allowed to react at 60 °C in acetone for 36 h. After cooling to room temperature, the mixture was filtered and the solvent evaporated. The resulting solid was extracted several

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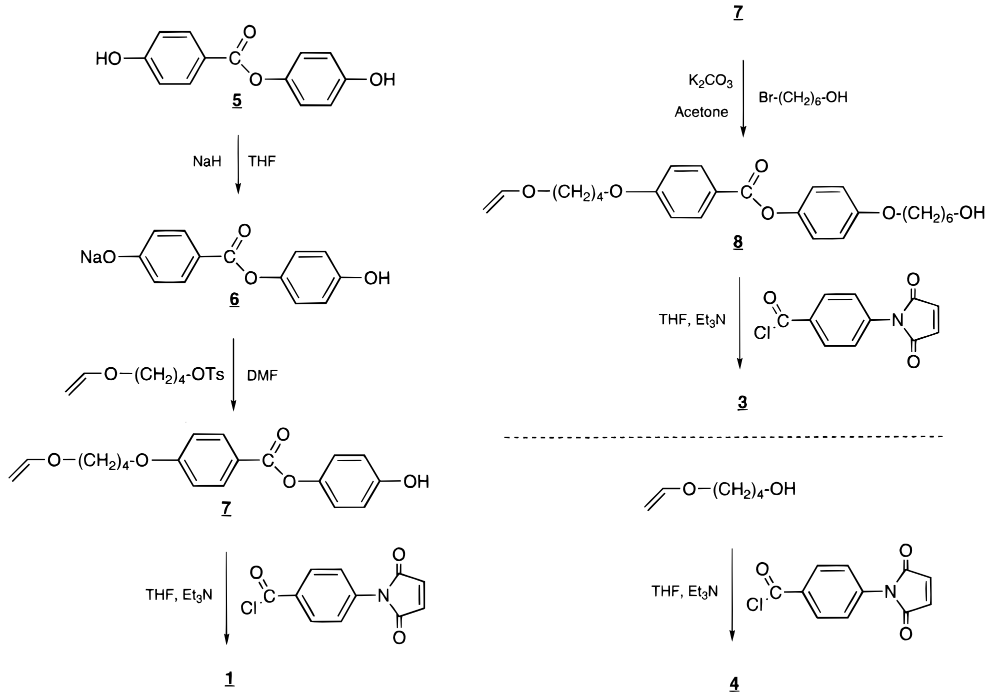
Scheme 1. Synthesis of Monomers



times with methylene chloride and water. The organic phase was separated, dried with $MgSO_4$, and evaporated. The crude product was purified by column chromatography (silica gel) using a gradient of hexane/ethyl acetate. Recrystallization from a mixture of hexane/ethyl acetate produced white crystals of **8** (3.20 g, 69%). ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.44−1.96 (12 H, $-(CH_2)_2-$ and $-(CH_2)_4-$, m), 3.65−3.68 (2 H, $-CH_2-OH$, t), 3.75−3.78 (2 H, $-CH_2-O-CH{=}CH_2$, t), 3.95−4.10 (5 H, 4 from $-CH_2-OPh$ and 1 H from $CH_2{=}CH-O-$ *trans*, m), 4.18−4.22 (1 H, $CH_2{=}CH-O-$, *cis*, d), 6.46−6.51 (1 H, $CH_2{=}CH-O-$, q), 6.90−6.97 (4 H, aromatic, 3-H, 5-H, 3′-H, and 5′-H, two doublets), 7.08−7.11 (2 H, aromatic, 2′-H and 6′-H, d), 8.12−8.14 (2 H, aromatic, 2-H and 6-H, d).

4-[[6-[(4-Maleimidobenzoyl)oxy]hexyl]oxy]phenyl 4-[[4-(Vinyloxy)butyl]oxy]benzoate (3). *N*-[4-(Chlorocarbonyl)phenyl]maleimide (1.0 g, 4.24 mmol) was dissolved in THF, and the solution was added dropwise to a solution of **8** (1.64 g, 3.86 mmol) and Et_3N (1.17 g, 11.56 mmol) in THF at 0 °C. After 1 h, the reaction mixture was stirred at room temperature for an additional 4 h. The solvent was evaporated and the residue extracted with methylene chloride and NH_4Cl(aq). The organic phase was washed with water and dried with $MgSO_4$. The crude product was purified by column chromatography (silica gel) using a gradient of hexane/methylene chloride/ethyl acetate. Recrystallization from a mixture of hexane/ethyl acetate produced white crystals of **3** (1.30 g, 54%). ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.54−1.94 (12 H, $-(CH_2)_2-$ and $-(CH_2)_4-$, m), 3.75−3.78 (2 H, $-CH_2-O-CH{=}CH_2$, t), 3.95−4.10 (5 H, 4 from $-CH_2-OPh$ and 1 H from $CH_2{=}CH-O-$ *trans*, two triplets and a doublet), 4.18−4.22 (1 H, $CH_2{=}CH-O-$ *cis*, d), 4.34−4.37 (2 H, $-CH_2-OOC-Ph$, t), 6.46−6.49 (1 H, $CH_2{=}CH-O-$, q), 6.87 (2 H, $-OC-HC{=}CH-CO-$, s), 6.90−6.97 (4 H, aromatic, 3-H, 5-H, 3′-H, and 5′-H, two doublets), 7.08−7.11 (2 H, aromatic, 2′-H and 6′-H, d), 7.48−7.50 (2 H, aromatic, *ortho* from −N, d), 8.11−8.15 (4 H, aromatic, 2-H, 6-H, and 2 *meta* from −N, m).

4-[[11-(4-Maleimidobenzoyl)oxy)undecyl]oxy]phenyl 4-[[4-(Vinyloxy)butyl]oxy]benzoate (2). This monomer was synthesized using the procedures described above, utilizing 11-bromoundecanol instead of 6-bromohexanol. ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.54−1.94 (12 H, $-(CH_2)_2-$ and $-(CH_2)_4-$, m), 3.75−3.78 (2 H, $-CH_2-O-CH{=}CH_2$, t), 3.95−4.10 (5 H, 4 from $-CH_2-OPh$ and 1 H from $CH_2{=}CH-O-$ *trans*, two triplets and a doublet), 4.18−4.22 (1 H, $CH_2{=}CH-O-$ *cis*, d), 4.34−4.37 (2 H, $-CH_2-OOC-Ph$, t), 6.46−6.49 (1 H, $CH_2{=}CH-O-$, q), 6.87 (2 protons, $-OC-HC{=}CH-CO-$, s), 6.90−6.97 (4 H, aromatic, 3-H, 5-H, 3′-H, and 5′-H, two doublets), 7.07−7.10 (2 H, aromatic, 2′-H and 6′-H, d), 7.48−7.50 (2 H, aromatic, *ortho* from −N, d), 8.11−8.15 (4 H, aromatic, 2-H, 6-H, and 2 *meta* from −N, m).

4-[(4-Maleimidobenzoyl)oxy]phenyl 4-[[4-(Vinyloxy)butyl]oxy]benzoate (1). This monomer was synthesized by reacting *N*-[4-(chlorocarbonyl)phenyl]maleimide and **7**, using the esterification procedure described above. ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.88−1.95 (4 H, $-(CH_2)_2-$, m), 3.75−3.80 (2 H, $-CH_2-O-CH{=}CH_2$, t), 4.00−4.03 (1 H, $CH_2{=}CH-O-$ *trans*, d), 4.07−4.11 (2 H, $-CH_2-OPh$, t), 4.17−4.23 (1 H, $CH_2{=}CH-O-$ *cis*, d), 5.62 (1 H, $-OH$, s), 6.45−6.51 (1 H, $CH_2{=}CH-O-$, q), 6.89 (2 H, $-OC-HC{=}CH-CO-$, s), 6.95−6.98 (2 H, aromatic, 3-H and 5-H, d), 7.27 (4 H, aromatic, 2′-H, 3′-H, 5′-H, and 6′-H, s), 7.57−7.60 (2 H, aromatic, *ortho* from −N, d), 8.13−8.17 (2 H, aromatic, 2-H and 6-H, d), 8.29−8.33 (2 H, aromatic, *meta* from −N, d).

***N*-[4-[[[4-(Vinyloxy)butyl]oxy]carbonyl]phenyl]maleimide (4).** *N*-[4-(Chlorocarbonyl)phenyl]maleimide and 4-hydroxybutyl vinyl ether were esterified using the above described procedure. ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.80−1.90 (4 H, $-(CH_2)_2-$, m), 3.73−3.76 (2 H, $-CH_2-O-CH{=}CH_2$, t), 3.99−4.01 (1 H, $CH_2{=}CH-O-$ *trans*, d), 4.16−4.19 (1 H, $CH_2{=}CH-O-$ *cis*, d), 4.35−4.38 (2 H, $-CH_2-OOC-Ph$, t), 6.46−6.50 (1 H, $CH_2{=}CH-O-$, q), 6.88 (2 H, $-OC-HC{=}CH-CO-$, s), 7.48−7.50 (2 H, aromatic, *ortho* from −N, d), 8.12−8.14 (2 H, aromatic, *meta* from −N, d).

Methods. The irradiation sources used in this study were a xenon−mercury lamp from ORIEL (model 8180), giving 5 mW/cm^2, and a high-power microwave irradiator from Fusion UV Curing System (model F 600), giving 720 mW/cm^2 with the H-bulb and 2160 mW/cm^2 with the D-bulb, in the wavelength band between 320 and 390 nm measured with a UVI map from EIT. When polymerizations were performed with the high-power lamp, the samples were run on a belt at a speed of 10 m/min under the lamp in order to avoid extensive heating. The samples were irradiated for 100 ms during a single run.

Photoinduced polymerizations were performed between glass slides, and the obtained films (10 μm) were pealed off from the slides prior to the infrared measurements, which were performed on a Perkin-Elmer 1760X FTIR. To be able to obtain spectra of samples with low degrees of conversion, the polymerizations were performed between KBr disks. Generally, the polymerizations were initiated by direct photolysis, without the presence of photoinitiators, but in some cases a

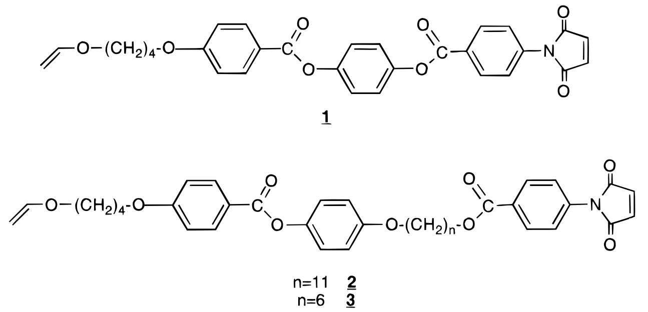


Figure 1. Structure of liquid crystalline donor−acceptor monomers.

Table 1. Thermal Transitions of Monomers and Monomer Mixtures Obtained from First Heating and Cooling Scans

monomer	heating	cooling
1	k152n−[a]	−[a]
2	k112i	i75n71k
3	k93i	i29n15s$_X$−5g
2/**3** (50/50)	k88k102i	i69n51k
2/**3** (30/70)	k88k95i	i47n−10g

[a] − indicates no transition observed.

free radical photoinitiator (Lucirin LR 8728, from BASF was used. The degree of conversion was assessed by monitoring the maleimide C−H bending[15,16] at 830 cm^{-1} and the vinyl ether C−H bending[15] at 960 cm^{-1}, with the aromatic C−H bending[16] at 770 cm^{-1} as an internal reference.

Thermally initiated polymerizations were performed in the DSC apparatus (Perkin-Elmer DSC 7) and the degree of conversion was estimated from monitoring the peak from the maleimide C−H bending[16] at 1073 cm^{-1} with the aromatic C=C stretch[16] at 1600 cm^{-1} as an internal reference, using a Perkin-Elmer 1760 FT-Raman.

Hot-stage polarized light microscopy (Leitz Ortholux POL BKII equipped with a Mettler Hot Stage FP 82) was used for morphological and thermal characterizations. Small-angle X-ray scattering (SAXS) patterns were recorded by a Statton camera, using Ni-filtered Cu Kα radiation from a Philips PW 1830 generator. ^{1}H-NMR and ^{13}C-NMR were performed on a Bruker 250 MHz. UV spectra were taken on a Perkin-Elmer 8415A diode array spectrophotometer using THF as solvent. The UV spectra of **4** as a thin film were obtained using a quartz disk, onto which the substance was spin coated.

Results and Discussion

The liquid crystalline donor−acceptor monomers synthesized in this study contain both a vinyl ether group (electron donor) and a phenylmaleimide group (electron acceptor) as polymerizable units within the same molecule. The mesogenic unit consists of a phenyl benzoate group, substituted in the *para* positions. Figure 1 shows the structure of the three monomers, different only in the length of the spacer group between the mesogenic unit and the phenylmaleimide group. As can be seen in Table 1, the length of the spacer group clearly affected the transition temperatures.

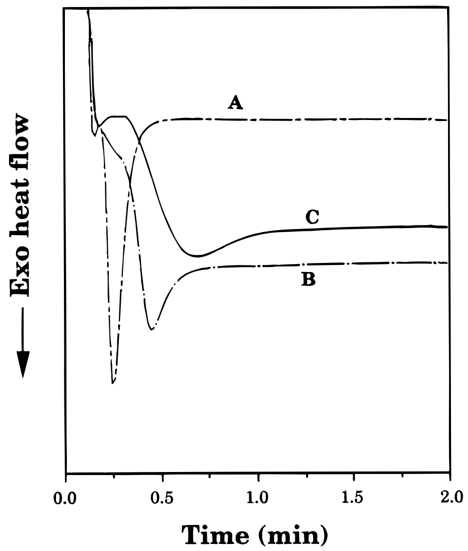


Figure 2. Thermograms showing polymerizations of **1** at 160 °C: (A) pure **1**, (B) **1** with 0.5 mol % hydroquinone, and (C) **1** with 1.0 mol % hydroquinone.

Spontaneous Thermal Polymerization. Monomer **1**, with a high degree of rigidity (Figure 1), entered a nematic phase at 155 °C and immediately polymerized spontaneously, indicating limitations for the preparation of oriented LC network films. However, by the use of low concentrations of hydroquinone acting as an inhibitor, this monomer melted into the nematic phase, allowed film formation and surface induced orientation and then subsequently polymerized into an oriented network with a nematic molecular organization. As can be seen from the calorimetric data presented in Figure 2, when polymerizations were performed at 160 °C in the DSC apparatus, a concentration of 0.5 mol % hydroquinone delayed the polymerization. The addition of 1.0 mol % led to further inhibition of polymerization. The degree of conversion was assessed by FT-Raman spectroscopy, by monitoring the maleimide vinyl group, and a difference in conversion between poly(**1**) formed with and without an inhibition period could be observed. The conversions were around 70% for pure poly(**1**), and around 60 and 50%, respectively, for the polymers formed with 0.5 and 1.0 mol % hydroquinone present.

Photopolymerization. Monomer **2**, with 11 methylene units in the spacer between the mesogenic unit and the phenylmaleimide group, melted from a crystalline phase at 112 °C into the isotropic phase. On cooling, a narrow monotropic nematic phase between 75 and 71 °C was observed prior to crystallization. Monomer **3**, having six methylene units in the spacer, melted at 93 °C from a crystalline phase into the isotropic state. On cooling it exhibited a monotropic nematic phase between 29 and 15 °C before entering a smectic phase. At −5 °C a glass transition was observed. During a second heating, the glass transition was observed again at −5 °C followed by several consecutive crystallization and melting processes when the mobility within the system increased. The high polarity, the relatively high molar mass (624 g/mol) together with the high degree of supercooling had an increasing effect on the viscosity of the system. The rather high viscosity reduced the ability of the monomer to be aligned using conventional surface techniques.

Blends of liquid crystalline compounds exhibit sometimes mesophases, stable within temperature ranges wider than that of the pure compounds; therefore mixtures of **2** and **3** were also investigated. The mixture **2**/**3** (30/70) entered a monotropic nematic mesophase at 47 °C on cooling, and it appeared to have considerably lower viscosity than the nematic phase of **3**, indicating possibilities for the use of surface-induced monomer orientation. On further cooling, a glass transition was observed at −10 °C. The 50/50 mixture exhibited a narrow nematic phase between 69 and 51 °C before crystallizing.

In order to investigate the curing efficiency of this vinyl ether−phenylmaleimide system, a model sub-

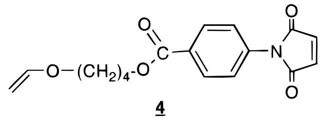


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Figure 3. Structure of donor−acceptor model substance.

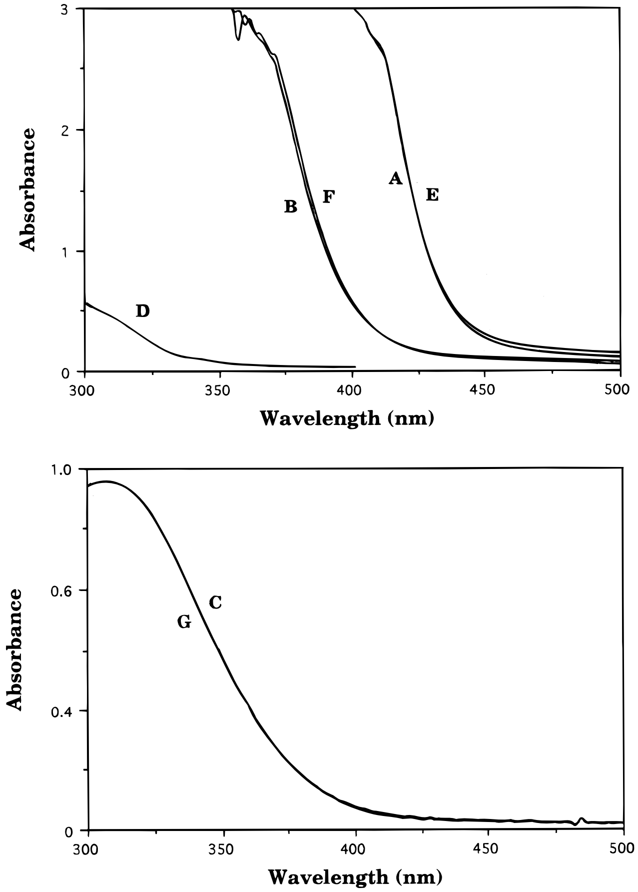

Figure 4. UV spectra of (4-carboxyphenyl)maleimide [(A) 0.5 M, (B) 0.05 M, and (C) 0.0025 M], 4-hydroxybutyl vinyl ether [(D) 0.5 M], and the mixture of the two [(E) 0.5 M, (F) 0.05 M, and (G) 0.0025 M of each].

stance **4** was synthesized (Figure 3). This monomer was liquid at room temperature. Refrigeration for a few days induced crystallization, and upon heating, these crystals melted at 42 °C. First of all, investigations on the presence of a ground-state electron donor−acceptor (EDA) complex were performed. The UV spectra for various concentrations (0.5, 0.05, and 0.0025 M) of the vinyl ether part and the phenylmaleimide part of the molecule as well as their mixtures were measured. As can be seen in Figure 4, no evidence of a ground state EDA complex could be observed. The absorption of such a complex, if present, was completely masked by the absorption of the phenylmaleimide part of the molecule.

Polymerization of 10 μm thin films of **4** was performed at room temperature by direct photolysis, without the presence of photoinitiators, using various UV sources. A xenon−mercury lamp, equipped with a 366 nm band-pass filter, was used in the first stage. The IR absorption of the maleimide group (Figure 5B), with an aromatic peak as an internal reference, was plotted as a function of irradiation time. The behavior of the vinyl ether group was also studied (Figure 5A). It is clearly seen that in this case the degree of conversion was around 45%, and the two monitored peaks showed good agreement, indicating a consumption of both vinyl ether and maleimide groups.

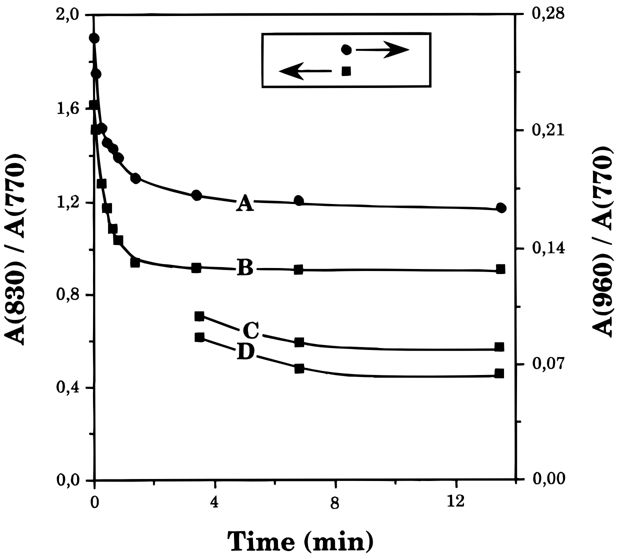

Figure 5. Infrared absorption decay *versus* irradiation time for the polymerization of **4** at room temperature. (A) shows the vinyl ether group at 960 cm^{-1} and (B), the maleimide group at 830 cm^{-1} using a 366 nm filter during polymerization. (C) represents polymerization without a filter, and (D), polymerization with 0.5 mol % photoinitiator present. The aromatic peak at 770 cm^{-1} was used as an internal reference.

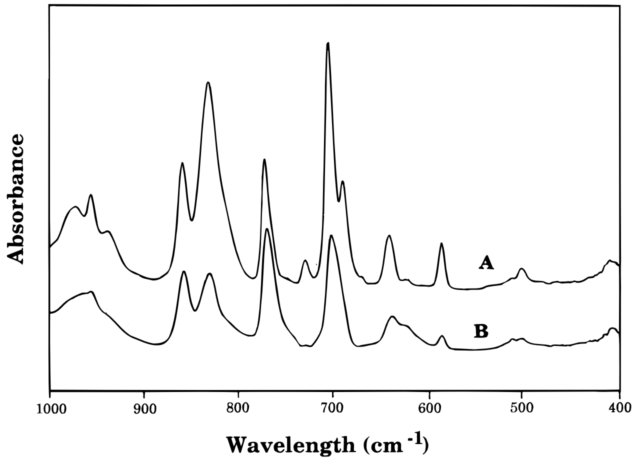

Figure 6. Infrared spectra of (A) **4** and (B) poly(**4**).

By the removal of the 366 nm filter, the degree of conversion was increased to around 65% (Figure 5C). Since no band-pass filter was used, the entire monomer absorption spectrum was illuminated. The addition of 0.5 mol % photoinitiator to the monomer increased the degree of conversion even more, to around 75% (Figure 5D). These two experiments indicate that the formation of an excited state complex and subsequent alternating copolymerization proceeds *via* both the excitation of a ground state complex (if present) and the excitation of either the donor or the acceptor followed by the association of these excited species with a ground state acceptor or donor, respectively. This was recently described by Jönsson et al.[17] Also, the increased curing efficiency when a photoinitiator was added supports the theory that a free radical mechanism is involved in the polymerization. Figure 6 shows a decrease in intensity for the IR peaks at 830 and 960 cm^{-1} (maleimide and vinyl ether, respectively) upon polymerization of **4**. The figure also shows the invariability of the aromatic peak at 770 cm^{-1}, which was used as an internal reference.

A high-power microwave irradiator was also utilized for the photopolymerization of monomer **4**. Two differ-

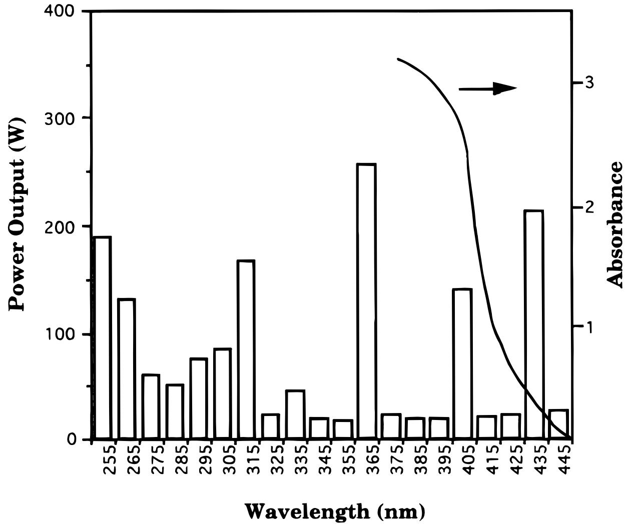

Figure 7. Spectral distribution of the H-bulb and the UV spectrum of a 10 μm thin film of monomer **4**.

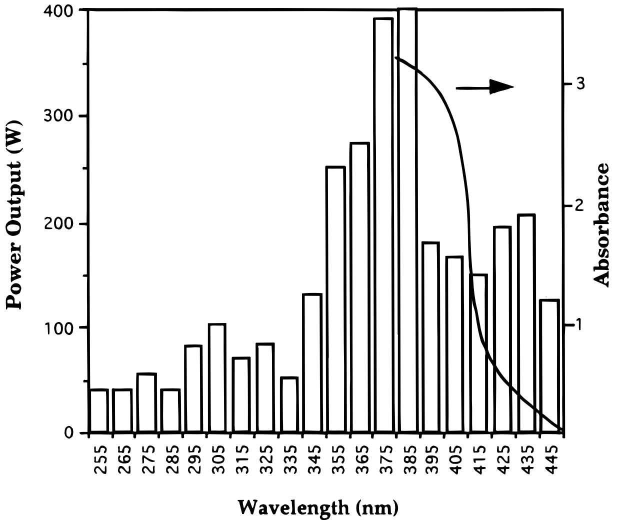

Figure 8. Spectral distribution of the D-bulb and the UV spectrum of a 10 μm thin film of monomer **4**.

ent bulbs, namely H and D, with different spectral distributions (Figures 7 and 8), were used. The efficiency of the polymerization is shown in Figures 9 and 10, by monitoring the peaks described earlier. Already during the first passage, both bulbs caused a conversion of 50% of the system and further runs on the belt resulted in a degree of conversion of 85% for the D-bulb and around 70% for the H-bulb. In this case, the monomer was exposed during 20 successive runs, resulting in a total exposure time of 2 s. The measurements described above using the xenon−mercury lamp resulted in a degree of conversion of maximum 65%, and here the system was illuminated for 12 min, 360 times longer than with the high-power microwave irradiator. The difference in the curing efficiency, when the two different types of radiation sources are compared, is a result of the different amount of power that is put into the system. For the xenon lamp around 5 mW/cm^2 was released and for the high-power lamps, between 150 and 400 times the amount of power was released, clearly giving more efficient polymerization.

The difference in the degree of conversion, using the D-bulb and the H-bulb, is a result of the different spectral distribution and output, being broader and higher for the D-bulb (Figure 7). The spectral distribution of the D-bulb fits the absorption spectra of monomer **4** in a better way than the spectral distribution from the H-bulb (Figure 8).

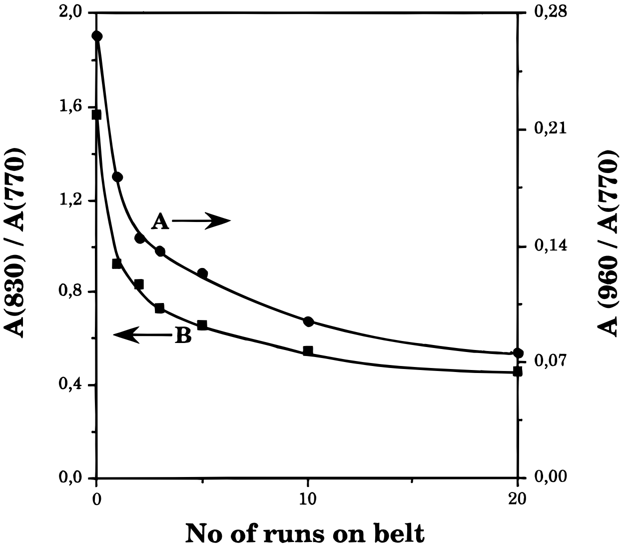

Figure 9. Infrared absorption ratio *versus* number of passages on the belt for curing of **4** using the H-bulb, monitoring the decay of the absorption at 960 cm^{-1} (A, vinyl ether) and 830 cm^{-1} (B, maleimide) relative to the absorption at 770 cm^{-1} (aromatic).

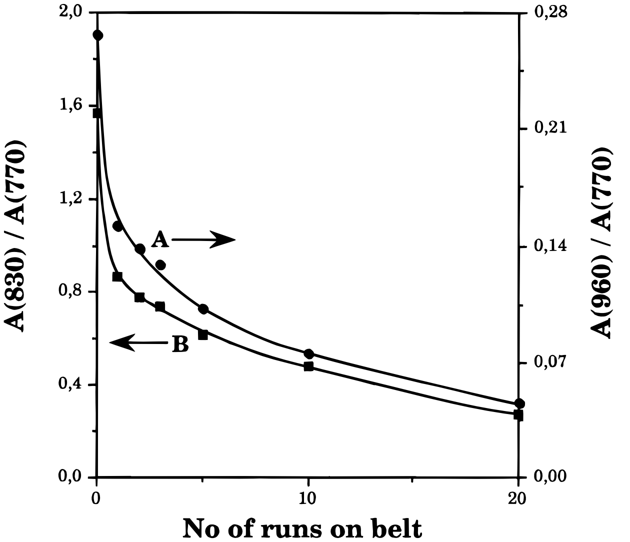

Figure 10. Infrared absorption ratio *versus* number of passages on the belt for curing of **4** using the D-bulb, monitoring the decay of the absorption at 960 cm^{-1} (A, vinyl ether) and 830 cm^{-1} (B, maleimide) relative to the absorption at 770 cm^{-1} (aromatic).

The liquid crystalline monomer **3** was also polymerized by direct photolysis without the presence of photoinitiators. However, due to the need for thermal control, the high-power microwave irradiators could not be used. The curing efficiency was investigated using the xenon lamp and a 366 nm band-pass filter, and polymerizations were performed at 80 °C in the isotropic state and at room temperature in the nematic phase. As can be seen in Figure 11, the degree of conversion at elevated temperatures (50%) was higher than at room temperature (45%), as expected since the glass transition temperature of this type of network is close to 80 °C.[18] At low polymerization temperatures some vitrification occurred, resulting in a lower degree of conversion. Removal of the band-pass filter increased the

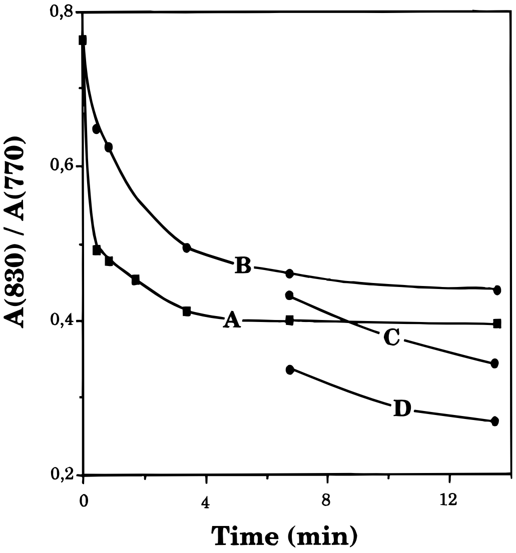

Figure 11. Infrared absorption decay for the maleimide group at 830 cm^{-1} *versus* irradiation time for the polymerization of **3**. Using a 366 nm filter, (A) shows polymerization at 80 °C and (B), polymerization at room temperature. (C) represents polymerization without a filter, and (D), polymerization with 0.5 mol % photoinitiator present, both performed at room temperature. The aromatic peak at 770 cm^{-1} was used as an internal reference.

room temperature degree of conversion to around 55% and the addition of 0.5 mol % photoinitiator resulted in 65% curing.

Mixtures of monomers **2** and **3** exhibited monotropic nematic mesophases (Table 1), potentially orientable and polymerizable. Oriented thin polymer films were prepared by *in-situ* photopolymerization of the preoriented monomer mixture **2**/**3** (30/70) at 45 °C in the nematic phase without the presence of initiators, illuminating with the xenon lamp for 12 min. As was observed by polarized light microscopy, the nematic texture as well as the order of the monomer was retained during the reaction. X-ray scattering analysis confirmed these observations, and the diffractogram (Figure 12) displayed only diffuse wide-angle reflections, indicative of a nematic organization.

Conclusions

This study showed that monomers containing a vinyl ether group (electron donor) and a maleimide group (electron acceptor) within the same molecule could be photopolymerized in the bulk state, without the presence of initiators. Fast and efficient polymerization, could be performed by the use of a high-power microwave irradiator. Oriented nematic networks were obtained by initiator-free polymerization of aligned liquid crystalline donor−acceptor monomers.

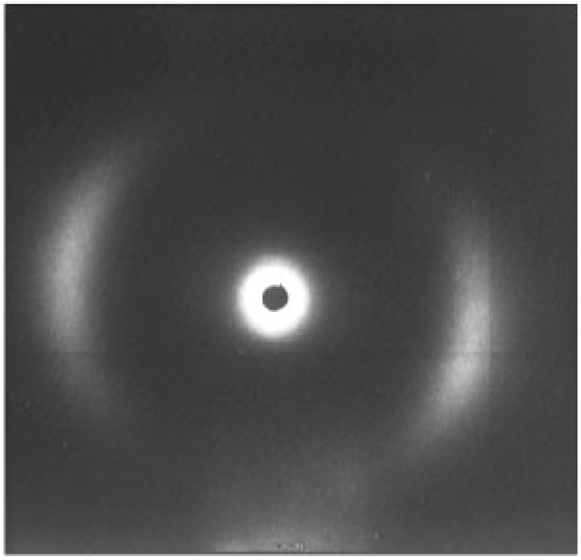

Figure 12. X-ray diffraction pattern for the oriented cross-linked network poly(**2**/**3**, 30/70) obtained by direct photolysis at 45 °C, without the presence of photoinitiators.

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