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Synthesis and Photopolymerization of Bifunctional Liquid Crystalline Vinyl Ether Monomers

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Highly ordered densely crosslinked liquid crystalline poly(vinyl ether) films have been prepared by *in situ* photopolymerization of oriented bifunctional mesogenic vinyl ether monomers. Orientation was achieved by a simple surface treatment, using a unidirectionally rubbed polyimide film. Polymerization from various monomer phases resulted in LC polymer network films with different molecular organizations. The films were analyzed with small-angle x-ray scattering, polarized light microscopy and infrared-dichroism measurements. It was shown that films with nematic, smectic A and smectic B structures were obtained, the latter having a very high degree of orientation.

Keywords: orientation, networks, liquid crystalline polymers, vinyl ethers, bifunctional monomers

INTRODUCTION

Oriented liquid crystalline network polymers are an interesting class of materials with potential use in optical, electrical and mechanical applications. From an industrial viewpoint, oriented polymer networks are of great interest mostly due to their mechanical and thermal stability.[1–4]

Several methods have been used to obtain oriented and more or less crosslinked systems. Orientation can be achieved by allowing an external field to align either the already made polymer or, prior to polymerization, the monomer. In the first case, cold drawing is the common process. In the second case, the low viscosity of the monomers simplifies the orientation process which can be induced by contacting the monomer with a pretreated surface or by exposing it to an electric or a magnetic field. Subsequent *in situ* polymerization of the ordered monomer system results in an ordered polymer. The use of this technique has been reported earlier.[5,6]

Crosslinking may be achieved by the use of bifunctional non-mesogenic or me-

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sogenic monomers. When using non-mesogenic crosslinkers, extensive crosslinking results in an amorphous polymer. Lightly crosslinked LC polymers have elastomeric properties and can be stretched to produce oriented systems.[7-11] As reported earlier, photopolymerization of an oriented mixture of a monofunctional mesogenic vinyl ether monomer and a bifunctional mesogenic vinyl ether monomer resulted in a highly ordered polymer with a thermally stable mesophase.[12] The use of a purely bifunctional acrylate monomer system produced oriented LC polymer networks, with anisotropic optical and mechanical properties.[13]

Photopolymerization has the advantage over thermal polymerization that the reaction temperature can be chosen relatively freely. As reported earlier,[14] the use of cationic bulk polymerization at elevated temperatures, initiated with low concentrations of sulfonium salts, produced high molar mass polymers with a low amount of impurities. Reactions were fast and gave high yields. This paper presents data from *in situ* photopolymerization of oriented bifunctional liquid crystalline vinyl ether monomers. The oriented LC polymer networks were studied by small-angle x-ray scattering and infrared-dichroism measurements. The materials are not liquid crystalline in a general sense, because unlike a liquid they cannot be sheared. However, they exhibit the molecular organization characteristic of liquid crystals and will therefore be called LC polymers.

EXPERIMENTAL

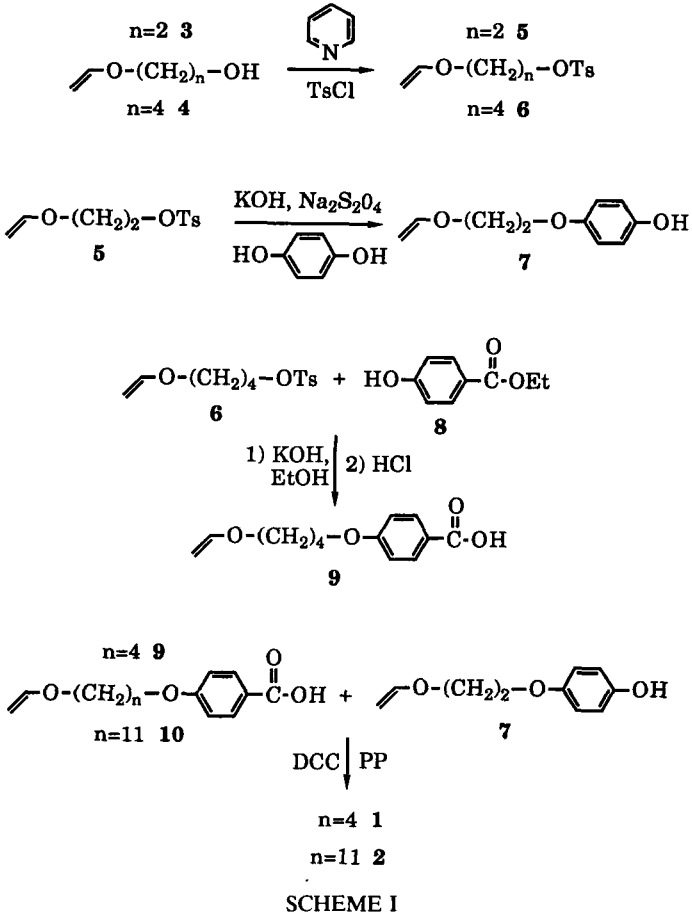
Materials

Phenacyltetramethylenesulfonium hexafluoroantimonate was used as photoinitiator and phenothaizine as photosensitizer. The sulfonium salt was synthesized as described previously[15] and the sensitizer was purchased from Aldrich. 4-[11-(Vinyloxy)undecyloxy]benzoic acid **10**, was synthesized as reported earlier.[16] 2-Hydroxyethyl vinyl ether **3** and 4-hydroxybutyl vinyl ether **4** was kindly supplied by Nisso Maruzen Chemical Co. All other reagents and solvents were obtained from Aldrich and MERCK.

Synthesis of Monomers

4-[11-(vinyloxy)undecyloxy]-4-[2-(vinyloxy)ethyloxy]phenylbenzoate **2**. 4-Toluenesulfonyl chloride (21.4 g, 112 mmol) was dissolved in pyridine (42 ml, 520 mmol). The solution was added dropwise to 2-hydroxyethyl vinyl ether **3** at 0°C and the mixture was allowed to react for 1 h. The product was extracted with diethyl ether and NH_4Cl (aq). The organic phase was washed several times with water and Na_2CO_3 (aq). After evaporating the organic solvent the product was purified by column chromatography (silica gel) using CH_2Cl_2 to yield 22 g (90%) of **5**.

Sodiumdithionite (27 mg, 0.16 mmol) and hydroquinone (11.36 g, 103.3 mmol) were dissolved in 50 ml ethanol. **5** (5.0 g, 20.7 mmol) was added and the mixture was heated to reflux temperature. KOH (1.99 g, 31.05 mmol), dissolved in 25 ml ethanol, was added slowly to the reaction mixture. The resulting precipitate was



SCHEME I

filtered off and the solvent evaporated in a rotavapor. The resulting solid was extracted with $NaHCO_3$ (aq) and CH_2Cl_2. The organic phase was washed several times with water and $NaHCO_3$ (aq). After evaporating the organic solvent the product was purified by column chromatography (silica gel) using a gradient of hexane/ethyl acetate. Recrystallization from ethyl acetate/hexane gave 1.4 g (38%) of white crystals **7**.

To a solution of **7** (0.81 g, 4.49 mmol) and **10** (1.5 g, 4.49 mmol) in 60 ml dry CH_2Cl_2 at 0°C were added 1,3-dicyclohexylcarbodiimide (1.02 g, 4.93 mmol) and 4-pyrrolidinopyridine (0.67 g, 4.49 mmol). The reaction mixture was heated at reflux temperature for 5 days. The resulting precipitate was filtered off and the solvent was evaporated in a rotavapor. The resulting solid was purified by column chromatography (silica gel) using a gradient of hexane/ethyl acetate. Recrystallization from ethanol gave 0.9 g (41%) of white crystals **2**. ^{1}H-NMR ($CDCl_3$, TMS, d, ppm): 1.28–1.55 (14 protons, —($C\underline{H}_2$)$_7$—, m), 1.62–1.74 (2 protons, —$C\underline{H}_2$—CH_2—O—CH=CH_2, p), 1.78–1.91 (2 protons, —$C\underline{H}_2$—CH_2—OPh, p), 3.69 (2 protons, —$C\underline{H}_2$—O—CH=CH_2, t), 3.96–4.32 (10 protons, 2 from PhO—$C\underline{H}_2$—CH_2—O—CH=CH_2, 2 from PhO—CH_2—$C\underline{H}_2$—O—CH=CH_2, 2

from —$C\underline{H}_2$—OPh, 2 from $C\underline{H}_2$=CH—O— trans and 2 from $C\underline{H}_2$=CH—O— cis, m), 6.43–6.60 (2 protons, CH_2=$C\underline{H}$—O—, m), 6.98 (4 aromatic protons, 0 from —O— of ether groups, d), 7.12 (2 aromatic protons, 0 from —O— of ester group, d) 8.13 (2 aromatic protons, 0 from —C— in ester groups, d).

4-[4-(vinyloxy)butyloxy]-4-[2-(vinyloxy)ethyloxy]phenylbenzoate **1**. 4-Hydroxybutyl vinyl ether **4** was tosylated, using the procedure described earlier, to give **6**.

Ethyl-4-hydroxybenzoate **8** (6.8 g, 40.7 mmol), **6** (10.0 g, 37 mmol) and KOH 2.2 g, 40.7 mmol) were co-dissolved in 60 ml ethanol. The reaction mixture was kept at reflux temperature for 12 h. Following the addition of KOH (3.1 g, 55.6 mmol) the reaction was continued for another 24 h. After cooling to room temperature the mixture was neutralized with 1 M HCl. The resulting precipitate was filtered off, washed with water and recrystallized from ethanol to yield 6.0 g (69%) of white crystals **9**.

Reacting **7** and **9**, using the esterification procedure described earlier, gave white crystals **1**. ^{1}H-NMR ($CDCl_3$, TMS, d, ppm): 1.80–1.98 (4 protons, 2 from —$C\underline{H}_2$—CH_2—O—CH=CH_2 and 2 from —2$C\underline{H}_2$—CH_2—OPh, m), 3.72 (2 protons, —$C\underline{H}_2$—O—CH=CH_2, t), 4.00–4.29 (10 protons, 2 from PhO—$C\underline{H}_2$—CH_2—O—CH=CH_2, 2 from PhO—CH_2—$C\underline{H}_2$—O—CH=CH_2, 2 from —$C\underline{H}_2$—OPh, 2 from $C\underline{H}_2$=CH—O— trans and 2 from $C\underline{H}_2$=CH—O— cis, m), 6.43–6.60 (2 protons, CH_2=$C\underline{H}$—O—, m), 6.97 (4 aromatic protons, 0 from —O— of ether groups, d), 7.11 (2 aromatic protons, 0 from —O— of ester group, d) 8.13 (2 aromatic protons, 0 from —C— in ester group, d).

Methods

The initiator was added to the monomer as a dilute methylene chloride solution. The monomer-initiator blend was then dissolved in methylene chloride and thoroughly mixed while allowing the solvent to evaporate. The resulting solid was then dried in vacuum overnight. The monomer to initiator concentration was unanimously 500. Polymerizations were performed under isothermal conditions between glass slides in a microscope hot-stage. Polymerizations of the monomer in the mesomorphic state were performed by heating the monomer-initiator blend over the isotropization temperature and subsequently cooling it down to the polymerization temperature.

Orientation of the liquid crystalline monomer was achieved by contacting it with a rubbed polyimide film. The sample and the polyimide film was kept between glass slides. Polyethylene fiber (Spectra) was used as a spacer between the glass slides to give the polymerization cell a uniform thickness of 30 μm.

Since the polymerizations were performed in the microscope hot-stage, optical investigations could be made before, during and after completion of the reaction. Prior to x-ray and infrared-dichroism analysis, the films were pealed off from the glass slides.

Instrumentation

A differential scanning calorimeter (Perkin Elmer DSC-7, scanning rate 10°C/min) was used for the thermal characterizations. Hot-stage polarized light microscopy

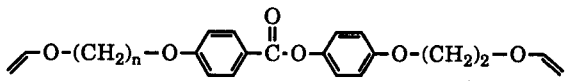
(Leitz Ortholux POL BKII equipped with a Mettler Hot Stage FP 82) was used for the morphological and thermal characterizations. An OSRAM Ultra-Vitalux lamp (300 W) served as UV-source for photopolymerizations. Small-angle x-ray scattering (SAXS) patterns were recorded by a Statton camera, using Cu K_α radiation from a Philips PW 1830 Generator. ^{1}H-NMR was performed on a BRUKER 250 MHz. A Perkin Elmer 1760X FTIR was used for the infrared-dichroic measurements.

RESULTS AND DISCUSSION

The structures of the bifunctional mesogenic vinyl ether monomers used in this study are described in Figure 1. They are relatively similar, with the rigid phenylbenzoate mesogenic group, substituted in both *p*-positions with spacers of different lengths and at the ends polymerizable vinyl ether groups. Data of the thermal transitions are presented in Table I and Figure 2. Monomer **2**, having 11 methylene groups in the spacer unit, exhibits a nematic, a smetic A and a smectic B liquid crystalline phase on cooling. Monomer **1**, with 4 methylene groups in the spacer, only shows a nematic mesophase. It is well known that an increase in spacer length promotes smectic molecular organization.

The different molecular structure of the monomers and also the different mesophases of monomer **2** were believed to give possibilities of preparing LC polymer films of varying molecular architecture, since it was reported by Broer *et al.*[11] that *in situ* photopolymerization of a mesomorphic bifunctional acrylate monomer resulted in polymer network samples, in which the monomer organization was frozen-in.

Results from optical investigations of the polymers obtained by photopolymerization of monomers **1** and **2** from the different mesophases are shown in Table II. It can be seen that polymerization of **1** at 70°C from the nematic phase resulted in a nematic polymer network. Polymerization from the nematic state of monomer **2** at 65°C did not result in a polymer with a nematic structure but surprisingly a network with a smectic A molecular organization was formed. This indicates that



n=4 **1** n=11 **2**

FIGURE 1

TABLE I

Thermal behaviour of monomers **1** and **2**

Monomer	Heating	Cooling
1	k88i	i78n58k
2	$k64s_A66n70i$	$i66n63s_A48s_B25k$

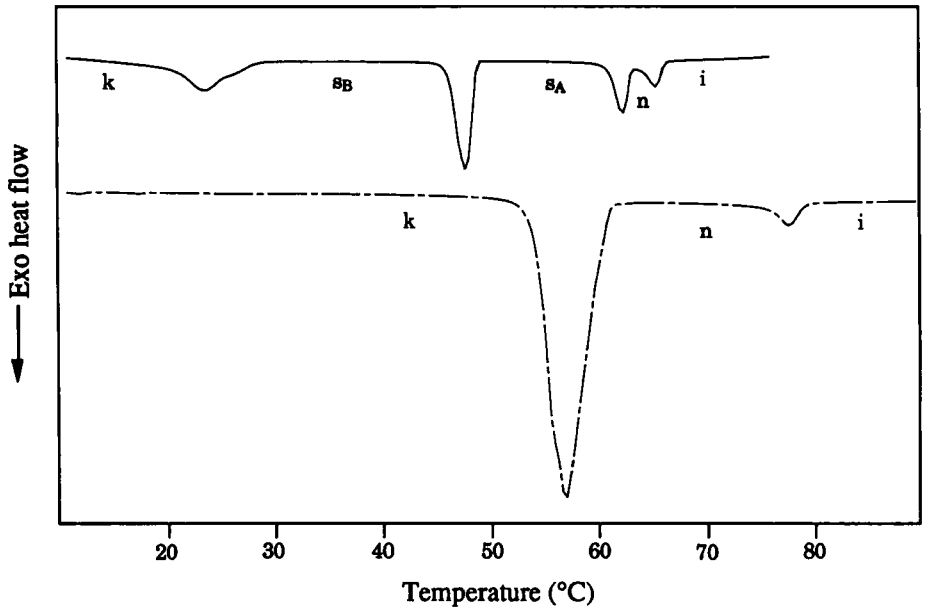


FIGURE 2

TABLE II

Results from polarized light microscopy and x-ray investigations of the monomers and corresponding polymers

Monomer	T_p (°C)	Monomer phase	Polymer structure	Spacings (nm)
1	70	nematic	nematic	0.45
2	65	nematic	smectic A	0.44 3.4
2	57	smectic A	smectic A	0.44 3.4
2	45	smectic B	smectic B	0.44 3.4

the long spacer unit present in **2** strongly promotes smectic layer formation. Polymerization from the smectic A phase of **2** at 57°C gave a polymer with a smectic A organization, quite as expected. Finally, the highly ordered smectic B liquid crystalline phase of monomer **2** could be frozen-in by photopolymerization at 45°C. Hot-stage polarized microscopy showed that the materials obtained using this technique were stable from room temperature up to 200°C.

Small-angle x-ray scattering analysis confirmed the observations and phase assignments made by polarized light microscopy (Table II and Figure 3). The diffraction pattern of the nematic network poly(**1**) is shown in Figure 3(a) and the presence of broad wide-angle reflections and the absence of sharp small-angle reflections clearly indicate a nematic structure. Polymerization of monomer **2** from both the nematic and the smectic A phase resulted in polymer networks with identical structures and a representative pattern can be seen in Figure 3(b). As opposed to the one shown in Figure 3(a) the presence of sharp small-angle reflections clearly indicates a smectic layerlike organization and the assignment of a

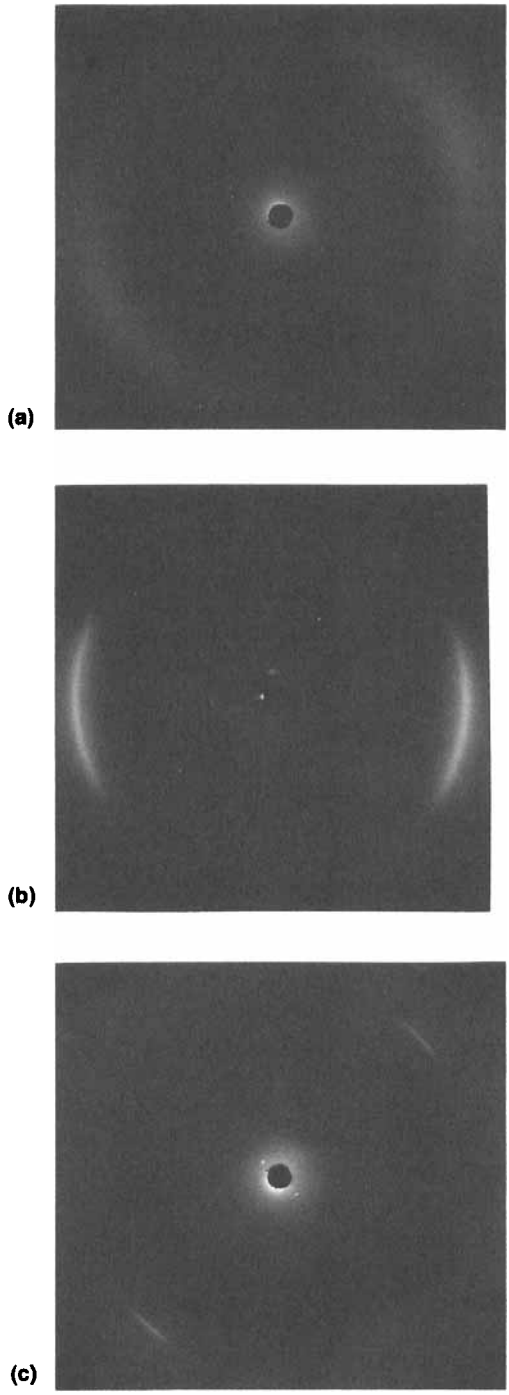


FIGURE 3

smectic A structure is confirmed. Figure 3(c) shows the diffraction pattern of the polymer obtained by polymerization of monomer **2** from the smectic B phase. The presence of sharp reflections both at wide and small angles indicate a highly ordered smectic structure. Together with the optical investigations it can be concluded that by polymerization, the mesophase of the monomer was frozen-in, producing a material with a smectic B structure. As can be seen from the wide-angle reflections, corresponding to an intermesogenic distance of 0.44 nm, the LC network has a high degree of uniaxial orientation. Directly from the photograph, a value of the Herman orientation function was estimated to be approximately 0.9. Figures 3(b) and (c) both show small-angle reflections, corresponding to the thickness of the smectic layers. The measured layer thickness was 3.4 nm indicating the formation of smectic monolayers.

Figure 4 shows a typical FTIR absorbance spectrum of poly(**2**), obtained from photopolymerization at 65°C. The peak at 2927 cm^{-1} corresponds to the asymmetric C—H stretch (—CH_2—) and the one at 2854 cm^{-1} to the symmetric equivalent. The peaks represent the spacer group, containing 11 methylene units. The spectrum with the electrical vector of the polarized light perpendicular to the direction of orientation is shown to the left and to the right the corresponding spectrum with the light polarized parallel to the direction of orientation. Since the C—H bonds in the spacer unit have a direction that is almost perpendicular to the spacer, when considered as an extended chain, the strong dichroism shown in Figure 3 clearly indicates orientation of the spacer unit. This is also verified by the results obtained from x-ray measurements. The smectic layer thickness approximately corresponds to the fully extended length of the monomer, indicating an extended spacer unit.

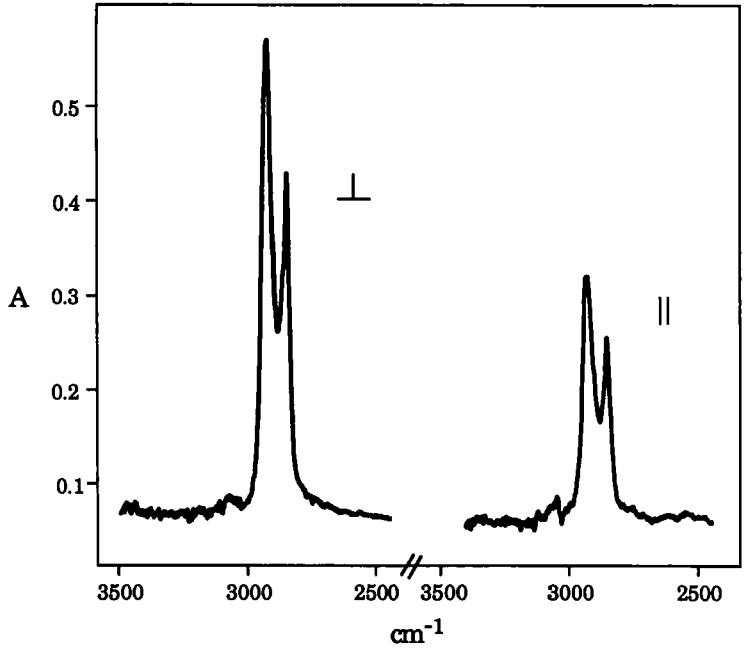


FIGURE 4

Subsequently, if the mesogenic groups have a uniaxial orientation the spacer unites will be ordered as well, even though not to the extent of the rigid aromatic arrangement.

CONCLUSION

It has been shown that highly ordered LC polymer networks with different molecular structure can be prepared by the *in situ* photopolymerization of bifunctional mesogenic vinyl ether monomers, possessing various mesophases. Polymer films with nematic, smectic A and smectic B structures were obtained.

Acknowledgment

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References

1. B. Vorländer, *Trans. Faraday Soc.*, **29**, 907 (1933).
2. L. Strzelecki and L. Liebert, *Bull. Soc. Chim. Fr.*, 597 (1973).
3. R. A. M. Hikmet and D. J. Broer, *Polymer*, **32**, 1627 (1991).
4. A. E. Hoyt and B. C. Benicewicz, *J. Polym. Sci., Part A: Polym. Chem.*, **28**, 3403 (1991).
5. D. J. Broer, H. Finkelmann and K. Kondo, *Makromol. Chem.*, **189**, 185 (1988).
6. H. Jonsson, H. Andersson, P.-E. Sundell, U. W. Gedde and A. Hult, *Polym. Bull.*, **25**, 641 (1991).
7. H. Finkelmann, H.-J. Kock and G. Rehage, *Makromol. Chem., Rapid. Commun.*, **2**, 317 (1981).
8. J. Schätzle and H. Finkelmann, *Mol. Cryst. Liq. Cryst.*, **142**, 85 (1987).
9. J. Küpfer and H. Finkelmann, *Makromol. Chem., Rapid. Commun.*, **12**, 717 (1991).
10. F. J. Davis and G. R. Mitchell, *Polym. Commun.*, **28**, 8 (1987).
11. K.-H. Hanus, W. Pechhold, F. Soergel, B. Stoll and R. Zentel, *Colloid. Polym. Sci.*, **268**, 222 (1990).
12. H. Andersson, U. W. Gedde and A. Hult, *Polymer*, in press.
13. D. J. Broer, J. Boven, G. N. Mol and G. Challa, *Makromol. Chem.*, **190**, 2255 (1989).
14. H. Jonsson, P.-E. Sundell, V. Percec, U. W. Gedde and A. Hult, *Polym. Bull.*, **25**, 649 (1991).
15. P.-E. Sundell, S. Jönsson and A. Hult, *Radiation Curing of Polymeric Materials*, C. E. Hoyle and J. F. Kinstle Eds, (American Chemical Society, Washington DC, 1990), ACS Symp. Ser., **417**, Ch. 32.
16. H. Jonsson, V. Percec and A. Hult, *Polym. Bull.*, **25**, 115 (1991).