Polymer Bulletin 25, 641–648 (1991)

Polymer Bulletin

# Photoinitiated cationic bulk polymerization of mesogenic vinyl ethers

**H. Jonsson, H. Andersson, P.-E. Sundell, U. W. Gedde, and A. Hult***

Department of Polymer Technology, Royal Institute of Technology, S-10044 Stockholm, Sweden

## SUMMARY

Mesogenic vinyl ethers have been bulk polymerized cationically in the liquid crystalline phase, using onium salt redox systems for photochemical initiation. High molecular mass polymers ($M_n \leq 41\,000$) with a narrow molecular mass distribution (around 2) were obtained at high temperatures (≤80°C). Apparently the polymerization system stabilizes the propagating cation and thus reduces the tendency for chain transfer to occur. Highly ordered thin (30-50 µm) films were produced by the polymerization of monomers oriented in their nematic phase. Despite the fact that they were in the $s_A$ phase, the films were completely transparent.

## INTRODUCTION

One part of the vast field of mesomorphic polymers that has received quite a lot of attention are polymerizations performed in the liquid crystalline (LC) phase (1-2). Nevertheless, knowledge of the effects this type of polymerization has on e. g. polymer structure and morphology and on polymerization kinetics, is rather limited. The reported results also differ remarkably and one example of this is the effect on polymerization rate. Hoyle et al. reported a rate enhancement in the LC phase upon photo-polymerization of cholesterol containing acrylate and methacrylate monomers (3-4). The reverse, a decrease, was described by Perplies et al. for the thermally initiated polymerization of Schiff base based acrylates and methacrylates (5). Mesophase polymerization of styrene monomers carrying Schiff base moieties gave, on the other hand, no change in rate compared to polymerization in the isotropic phase, according to Paleos and Labes (6). It is apparently difficult to compare directly systems with different monomers, initiators, mesophases etc. at this level of understanding.

A very interesting application of mesophase polymerization is the *in situ* photopolymerization of oriented LC mono- and bifunctional acrylates described by Broer et al. (7-10). The monomers were oriented in their mesophase by conventional techniques used for low molar mass liquid crystals and then polymerized with uv-radiation with subsequent freezing-in of the structure. In this way, oriented thin films were produced with a higher degree of order than films resulting from the ordering of polymers. Thin macroscopically ordered polymer films are a very important group of materials for the realization of several proposed applications for functional LC polymers such as non-linear optics.

In a previous paper (11) we showed that thermally initiated cationic polymerization of vinyl ethers in the LC phase produced high molecular mass polymers ($M_n \leq 83\,000$) with a narrow molecular mass distribution (around 2) at, for cationic polymerization very high temperatures (≤120°C).

This paper presents data on the sulfonium salt initiated photopolymerization of phenylbenzoate based LC vinyl ethers. It also shows how macroscopically ordered thin films of well-defined polymers can be made by polymerization of monomers preoriented in their LC state.

---

*To whom offprint requests should be sent

## EXPERIMENTAL

### Synthesis of monomers and initiators

Monomers and initiators were synthesized as reported in previous publications;
11-[p-(Cyanophenylbenzoate)oxy]undecanyl vinyl ether (1) (12)
Thermal characterization: k68i; i64n50k (in the microscope a nematic phase is observed on heating between 65-68°C and on cooling a smectic phase is observed between 52-50°C).
11-[p-(Methoxyphenylbenzoate)oxy]undecanyl vinyl ether (2) (12)
Thermal characterization: k72i; i56n39$s_A$12k
2,4,6-Trimethylbenzoylethoxyphenylphosphine oxide (3) (from BASF)
Diphenyliodonium hexafluorophosphate (4) (13)
Phenothiazine (5) (from Aldrich)
Phenacyltetramethylenesulfonium hexafluoroantimonate (6) (14)

### Polymerizations

The initiator was added to the monomer in a dilute methylene chloride solution (20-50 mM). The monomer-initiator blend was then dissolved in methylene chloride and mixed thoroughly and finally the solvent was evaporated. The resulting solid was dried *in vacuo* overnight.

The polymerizations were performed under isothermal conditions in two ways:
*i*) in aluminum pans in a Perkin Elmer DSC-7 equipped with a differential photo-accessory. The UV-radiation source was a XBO 450 W high pressure xenon lamp and the radiation was passed through an IR filter and a 366 nm narrow bandpass filter. A light intensity of 0.58 mW/cm$^2$ was measured by an International Light IL 1700 Radiometer with a SED 038 detector.
*ii*) in 30-50 μm thick cells coated with a rubbed poly(imide) film and placed in a microscope hot-stage. The uv-source was an ICI Luxor 4 000 with a THORN Tungsten halogen lamp 150 W 380-520 nm.

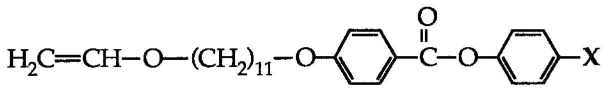
When polymerizations were performed in the mesophase of the monomer, the monomer-initiator blend was first heated to the isotropization temperature and then cooled to the polymerization temperature.

### Characterization

Molecular weight measurements were performed by gel permeation chromatography (Waters Model 510, WISP 710B, and Differential Refractometer 410), using Styragel® columns of 500, 10$^5$, 10$^4$, 10$^3$, and 100 Å and poly(styrene) standards and THF as eluent. Thermal characterization was carried out in a differential scanning calorimeter (Perkin Elmer DSC-7, scanning rate 10°C/min). Hot-stage polarized light microscopy (Leitz Ortholux POL BKII equipped with Mettler Hot Stage FP 82 controlled by Mettler FP80 Central Processor) was used for morphological characterization. Wide-angle X-ray scattering (WAXS) patterns were recorded by a Statton camera using Ni filtered Cu $K_\alpha$ radiation.

## RESULTS AND DISCUSSION

The benzoate vinyl ethers used in this study were the same as those that were polymerized thermally in a previous paper (Figure 1) (7), and made by the use of a novel route for the preparation of mesogenic vinyl ethers carrying long (and short) spacers (12,15).



X = -CN, -OCH$_3$
**1** **2**

Figure 1. Phenylbenzoate vinyl ether monomers.

The onium salt based initiatior systems were of the photo-redox type, i.e. the spectral response of the onium salt, 4 and 6 in Figure 2, is broadened by either a free radical photo-initiator 3 or a photosensitizer 5.

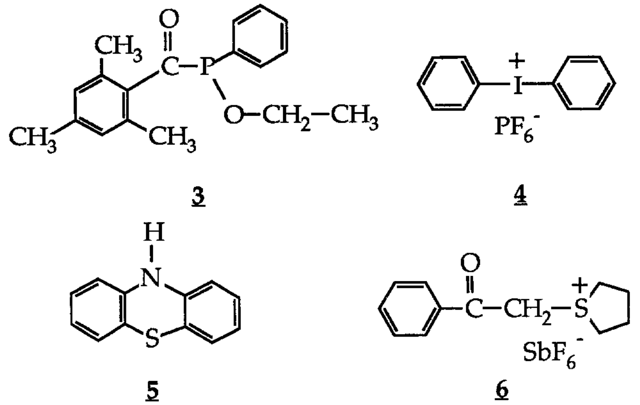


Figure 2. Cationic photo-redox initiating systems.

The overall process for the production of the cationic initiating species is shown in Figure 3. First, electron-donating free radicals are generated by photolysis *or* by excitation of a photosensitizer. Secondly, an electron is transferred from these species to the onium salt leading to the formation of the corresponding cation or radical cation, which in turn can initiate polymerization. The initiator system 3+4 possesses a much higher reactivity then 5+6, primarily due to the higher oxidizing capability of the diaryliodonium salt (4) compared with the phenacylsulfonium (6).

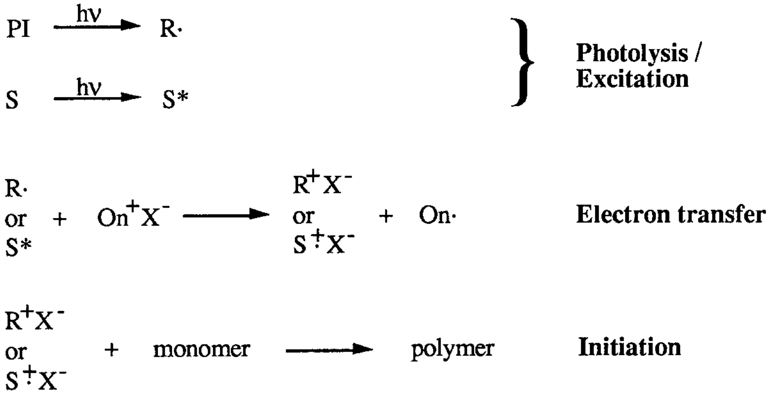


Figure 3. Initiation of cationic polymerization through photoinitiated electron transfer reduction of onium salts.

One advantage of photoinitiated over thermally-initiated polymerization is the ease with which the polymerization temperature is chosen and the onset of polymerization directed, a very important fact when e.g. the polymerization is to be carried out in a monomer LC phase stable only within a very narrow temperature range. In order to perform controlled isothermal polymerizations with thermal initiation, the initiator has to be selected with caution. Another advantage is that it is possible to change the polymerization rate merely by changing the intensity of the light.

Table 1 summarizes the polymerization results and the characterization of the polymers and, as can be seen, the remarkable results reported for the thermally initiated polymerizations, are repeated. High molecular mass, narrow molecular mass distribution, and high conversion characterize these polymerizations carried out at, for cationic polymerizations, high temperatures. The molecular masses of the polymers produced by photopolymerization are generally slightly lower than those obtained by thermally-initiated polymerizations. The results are expected because the production of initiating species is faster by photochemical initiation.

The higher polymerization rate and conversion (defined as vinyl ether double bond consumption and reflected in $HF_{max}$ and $t_{poly}$ in Table 1) at higher temperatures is probably due mostly to the fact that a lower viscosity of the formed polymer means an increased monomer mobility. In Figure 4, the conversion vs. dose plot for polymerization of 2 at three different temperatures is shown, and the temperature dependence of conversion and polymerization rate is clearly displayed.

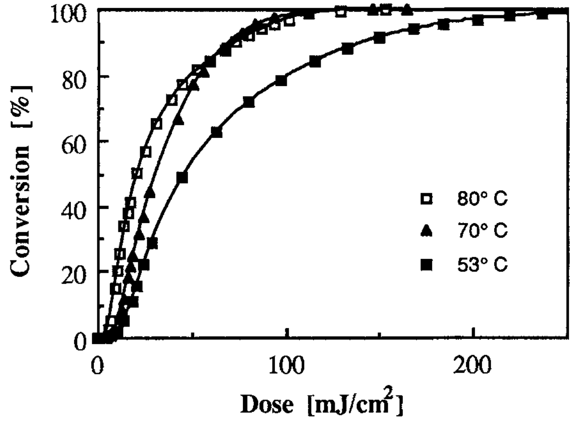


Figure 4. Conversion vs. dose plot for polymerization of 2 at different temperatures.

As was the case for the thermally initiated polymerizations, the initial state of the monomer, nematic or isotropic, did not affect the molecular mass, molecular mass distribution, or polymerization rate (Table 1). Broer et al. reported that there was no difference in kinetics at the onset of polymerization when mesogenic acrylates were polymerized in their monotropic $s_A$, enantiotropic nematic, or isotropic states (8). They also reported that polymerizations performed in the enantiotropic mesophase proceeded fast to completion, whereas polymerization in the monotropic phases resulted in significantly lower yields. They stated that the reason for this was a crystallization of the thermodynamically metastable mesophase resulting in an incomplete polymerization. In the present study, the anisotropic polymerizations were made in monotropic phases of the monomers. The polymerizations nevertheless resulted in high conversions, even though the conversions were higher at higher temperatures but this, as discussed above, we attribute to higher mobility of the monomer due to lower viscosity of the polymer, not to crystallization. The polymerization temperatures chosen were inside the mesophase of the formed polymer and this hinders crystallization. The polarized photomicrographs in Figure 5a and b show the transformation of the nematic phase of 2 to the $s_A$ phase of poly(2) during polymerization.

The reason for the change in common cationic polymerization characteristics in the present study, i.e. high molar mass polymers can only be formed at low temperatures, must be found in a strong reduction of chain transfer reactions, especially the proton eliminations very common for vinyl ethers. Chain transfer is the molecular-mass-determining side reaction in cationic polymerization and extensive chain transfer usually occurs already at room temperature in vinyl ether polymerizations. The growing center can apparently be stabilized in these systems. There are several possible reasons for this stabilization as discussed in an earlier paper (11): stabilization by the mesophase, stabilization through interfacial polymerization, or stabilization by nucleophilic interaction. Another alternative is that the predominant chain transfer reaction is to counteranion and not to monomer.

Table 1. Polymerization of vinyl ether monomers and thermal characterization of the polymers formed.

| Monomer | Initiator system | [Monomer]/ [Initiator] (mol/mol) | $T_{poly}$ (°C) | $t_{poly}$[a] (min) | $HF_{max}$[b] (kJ/(mol·s)) | Polymer |  |  | Thermal transitions (°C) and corresponding enthalpy changes (kJ/mru) for the polymer[d] |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | Conv. (%)[c] | $M_n$ (g/mol) | $M_w/M_n$ | Heating | Cooling |
| 1 | 3+4 | 260 | 59 | 0.4 | 13.28 | 97 | 45500 | 2.38 | k41(1.7)k81(13.2)$s_A$170(1.8)i | i165(1.7)$s_A$40(8.7)k |
| 1 | 3+4 | 260 | 68 | 0.3 | 17.94 | 98 | 41200 | 2.36 | k34(3.1)k78(12.2)$s_A$162(2.1)i | i158(1.8)$s_A$34(9.5)k |
| 1 | 5+6 | 500 | 62 | 25 | 0.34 | 98 | 37800 | 2.02 | k43(1.9)k82(13.7)$s_A$171(1.7)i | i168(1.2)$s_A$43(10.0)k |
| 1 | 5+6 | 500 | 68 | 23 | 0.39 | 96 | 36400 | 2.04 | k45(1.6)k83(13.7)$s_A$172(2.2)i | i168(1.7)$s_A$43(9.9)k |
| 1 | 5+6 | 500 | 80 | 9 | 0.62 | 98 | 37200 | 1.95 | k44(2.0)k83(14.3)$s_A$171(2.5)i | i167(2.1)$s_A$43(10.0)k |
| 2 | 5+6 | 500 | 53 | 9 | 0.75 | 98 | 22600 | 2.19 | k43(3.0)k70(4.8)$s_A$129(3.7)i | i125(3.4)$s_A$28(3.0)k |
| 2 | 5+6 | 500 | 70 | 5 | 1.12 | 98 | 21700 | 2.14 | - | - |
| 2 | 5+6 | 500 | 80 | 4 | 1.63 | 98 | 21200 | 2.01 | k43(2.7)k70(5.0)$s_A$130(3.7)i | i126(3.6)$s_A$26(3.1)k |

[a] Time to finished reaction (according to DSC). [b] Maximum rate of heat evolution, reflects the rate at which vinyl ether double bonds are consumed (from DSC). [c] Calculated from GPC traces. [d] Calculated from 2nd heating and 1st cooling scan (mru = mole of repeating unit).

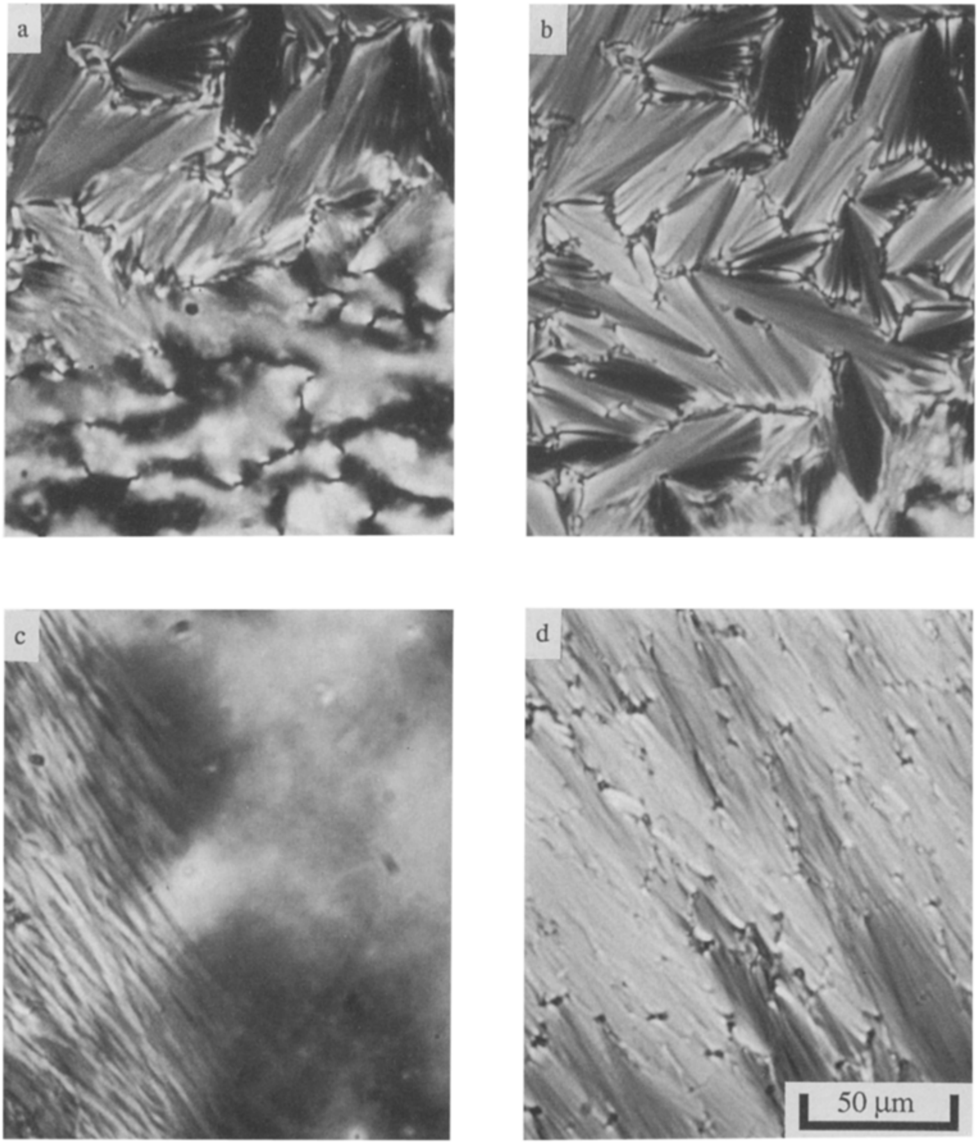


Figure 5. Polarized photomicrographs showing the polymerization of a 30 μm thick sample of 2 at 54°C using 5+6 as the initiating system at a [monomer] to [initiator] ratio of 500. a and b shows an unoriented system and c and d an oriented.

The monomers were also polymerized in 30-50 µm thick poly(imide) coated cells. By rubbing the poly(imide) film, the monomers could be oriented in their LC state and subsequently polymerized. Figures 5a and b show polarized photomicrographs of the system during the polymerization of 11-[p-(4-methoxyphenylbenzoate)oxy]undecanyl vinyl ether (2) from its unoriented nematic phase to the typical fan-shaped focal conic texture of the $s_A$ phase of poly(2). Figures 5c and d shows its ordered equivalent. As expected, the difference in texture is considerable. The films resulting from polymerization of ordered monomers were completely transparent also at room temperature, despite the fact that they were in the liquid crystalline state. Apparently the number of light scattering crystal boundaries are very few, which indicates the very high degree of order obtained in the material.

The phase of the polymer was determined using WAXS and Figures 6a and b show the typical pattern of a disordered and an ordered $s_A$ phase respectively. The measured layer thickness was 31 Å which is in good agreement with the calculated 30 Å (an all-trans conformation of the spacer assumed), and smectic monolayers are apparently formed. The reduction of the outer ring in Figure 6a to a short curve in Figure 6b, shows the very high degree of order that can be achieved in a polymer that result from the polymerization of a ordered monomer. From the equatorial wide angle peaks, a $d_{spacing}$ of 4.2 Å was measured, which corresponds to a nearest neighbour distance of 4.7 Å if a random arrangement of the mesogens is considered, and 4.9 Å if the arrangement is hexagonal.

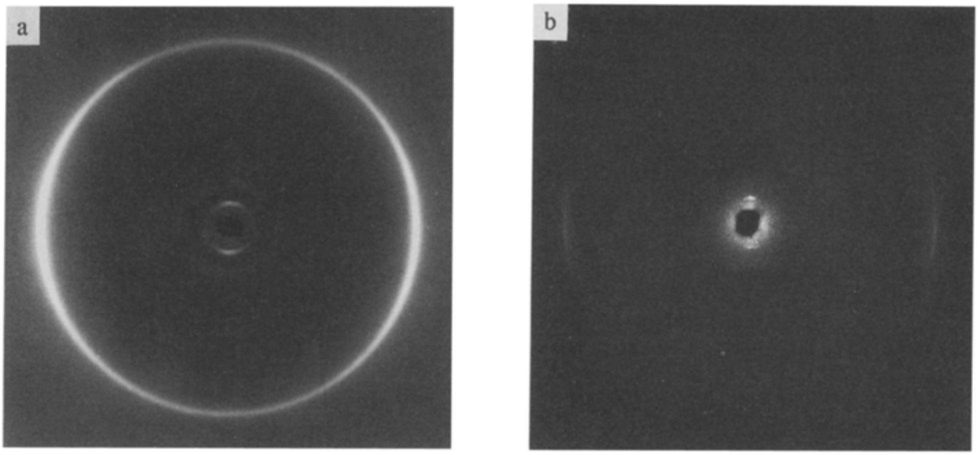


Figure 6. WAXS diffraction pattern of 50 µm thick samples of 2 polymerized at 55°C using 5+6 as the initiating system at a [monomer] to [initiator] ratio of 500. 6a shows the unordered $s_A$ phase that results from the polymerization of the unoriented nematic monomeric phase and 6b its ordered equivalent.

## ACKNOWLEDGMENT

Financial support from the National Swedish Board for Technical Development (STU), the Swedish Natural Science Research Council, and the Royal Institute of Technology (scholarship for H.J.) is gratefully acknowledged. The authors also want to thank Mr. Ronnie Palmgren for invaluable help with the GPC measurements, AB Wilhelm Becker R&D, Märsta, Sweden for supplying the Perkin Elmer Photo DSC-7, and Dr. Rifat A. M. Hikmet at Philips Research Laboratory, Eindhoven, The Netherlands for the WAXS analysis.

## REFERENCES

1. Barrall II E. M., Johnson J. F. *J. Macromol. Sci.-Rev. Macromol. Chem.* C17(1) 137 (1979).
2. Paleos C. M. *Chem. Soc. Rev.* 14, 45, (1985).
3. Hoyle C. E., Chawla C. P., Griffin A. C. *Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.* 157, 639, (1988).
4. Hoyle C. E., Chawla C. P., Griffin A. C. *Polymer* 60, 1909, (1989).
5. Perplies E., Ringsdorf H., Wendorff J. H. *Makromol. Chem.* 175, 553, (1974).
6. Paleos C. M., Labes M. M. *Mol. Cryst. Liq. Cryst.* 11, 385, (1970).
7. Broer D. J., Finkelmann H., Kondo K. *Makromol. Chem.* 189, 185, (1988).
8. Broer D. J., Mol G. N., Challa G. *Makromol. Chem.* 190, 19, (1989).
9. Broer D. J., Boven J., Mol G. N., Challa G. *Makromol. Chem.* 190, 2255, (1989).
10. Broer D. J., Hikmet R. A. M., Challa G. *Makromol. Chem.* 190, 3201, (1989).
11. Jonsson H., Percec V., Sundell P.-E., Gedde U. W., Hult A. *Polym. Bull.*Submitted.
12. Jonsson H., Percec V., Hult A. *Polym. Bull.* In press.
13. Crivello J. V., Lam J. H. W. *J. Org. Chem.* 43, 3055, (1978).
14. Sundell P.-E., Jönsson S., Hult A. In *Radiation Curing of Polymeric Materials*; Hoyle C. E., Kinstle J.F. Eds.; ACS Symposium Series No 417 Chapter 32; American Chemical Society: Washington, DC. 1990.
15. Percec V., Lee M., Jonsson H. *J. Polym. Sci., Part A: Polym. Chem.* In press.

Accepted January 23, 1991 K