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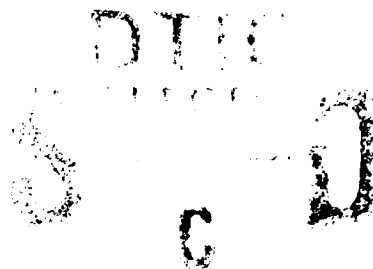


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Cationic Bulk Polymerization of Vinyl Ethers in the Liquid Crystalline Phase

by

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CATIONIC BULK POLYMERIZATION OF VINYL ETHERS IN THE LIQUID CRYSTALLINE PHASE

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Abstract: Cationic bulk polymerization of liquid crystalline phenyl benzoate and biphenyl vinyl ethers was performed using either thermal or photochemical initiation by onium salts. High molecular mass polymers having narrow molecular mass distribution were produced in high yields at very high temperatures (i.e., $\leq 120^\circ$).

Seemingly, the polymerization system could stabilize the growing species and thus reduce the amount of chain transfer reactions. Thin films of the monomers were oriented in their liquid crystalline state by the use of conventional ordering techniques used for low molar mass liquid crystals. On subsequent polymerization the orientation was preserved giving liquid crystalline thin films having a very high degree of order.

INTRODUCTION

Even though there has been a considerable amount of research performed on polymerization in the liquid crystalline (LC) state, the knowledge of the effect of monomer and polymer organization on the course of polymerization is still rather limited. A number of reviews have been published (e.g. Refs. 1, 2) and they usually conclude that polymerizations performed in organized media affect both the polymerization kinetics and the polymer structure. Unfortunately, they also agree that it is difficult to predict the nature and the degree of this effect, partly because the results reported in the literature often are contradictory. Erroneously assigned mesophases and phase separation between monomer and polymer are examples of things that complicate the evaluation of the results. In the case of reactions between low molar mass molecules in ordered media the systems are much less complicated, and clear and significant effects have been reported (for a review see Ref. 3). Nevertheless, organization of the monomer prior to polymerization could in principle change the polymerization characteristics and hence affect polymer structure. This could lead to a different stereo-regularity than that resulting from polymerization in non-organized media, or could mean that a "frozen-in" structure is achieved.

A very interesting application of mesophase polymerization is the in-situ photo polymerization of oriented LC mono- and bifunctional acrylates described by Broer et al. (e.g. Refs. 4-7). The monomers were oriented prior to polymerization and then the polymerization was initiated with uv-radiation with subsequent freezing-in of the structure.

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In this way, oriented thin films were produced with a higher degree of order than films resulting from the conventional ordering of polymers.

This paper describes the cationic bulk polymerization of vinyl ethers in the LC phase, using onium salts as initiators. For several reasons vinyl ethers represent a very interesting group of liquid crystalline monomers. Cationic polymerization of vinyl ethers is fast and gives high yields with a low concentration of initiator. It has also been shown that vinyl ethers can be polymerized by a living cationic mechanism, giving well-defined polymers with narrow molecular mass distributions and tailored molecular masses (Refs. 8-20). If initiating systems based on ethylaluminumdichloride and dimethylsulfide or triflic acid and dimethylsulfide (Refs. 21, 22) are used, the polymerization has been shown to tolerate a large number of functional groups (Refs. 14, 15, 18-20). In addition, the flexible poly(vinyl ether) chain represents a suitable backbone for LC polymers since its flexibility tolerates its fast distortion at various phase transitions. The use of onium salts as initiators made it possible to study the cationic bulk polymerization with thermal as well as photochemical initiation. As will be shown, this type of polymerization represents a route for the synthesis of well-defined high molecular mass side chain LC polymers at temperatures where cationic polymerization usually produces only oligomers.

EXPERIMENTAL

Experimental details are presented elsewhere (Refs. 25, 26).

RESULTS AND DISCUSSION

The phenylbenzoate and biphenyl vinyl ether monomers used were synthesized according to a novel procedure that allows the preparation of mesogenic vinyl ethers containing two or more methylene units in the flexible spacer (Refs. 14, 15). Figure 1 shows a typical example of a phenylbenzoate vinyl ether synthesis. The monomers exhibited nematic and/or smectic mesophases, which made possible the study of the effect of the initial state of the monomer, anisotropic or isotropic melt, on the course of polymerization.

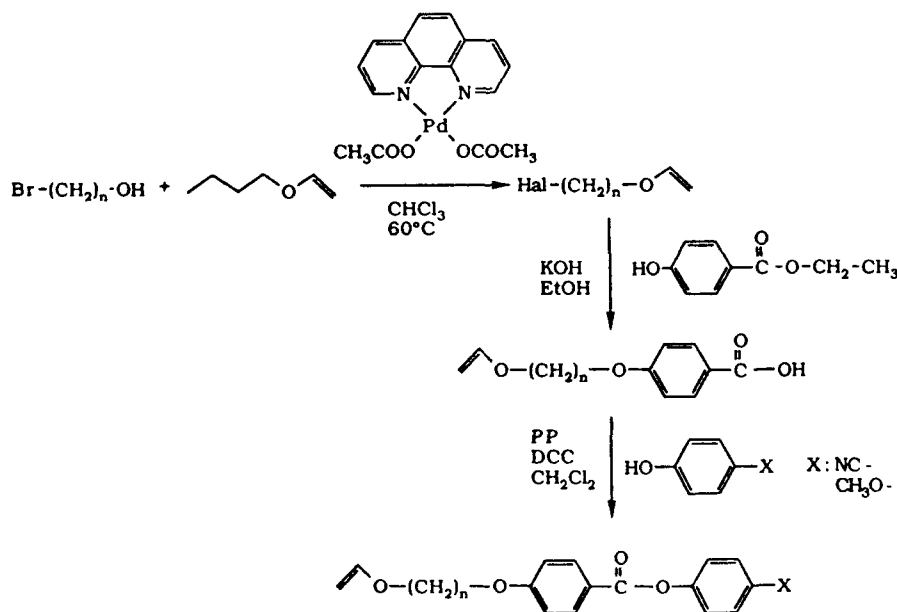


Figure 1. Synthetic route used for the preparation of mesogenic vinyl ether monomers.

One example of the thermal behaviour of the monomer can be seen in Figure 2 which shows the DSC cooling curves of 11-[p-(methoxyphenylbenzoate)oxy]undecanyl vinyl ether and its corresponding polymer. The monomer exhibits a nematic and a smectic A mesophase and the polymer a smectic A phase.

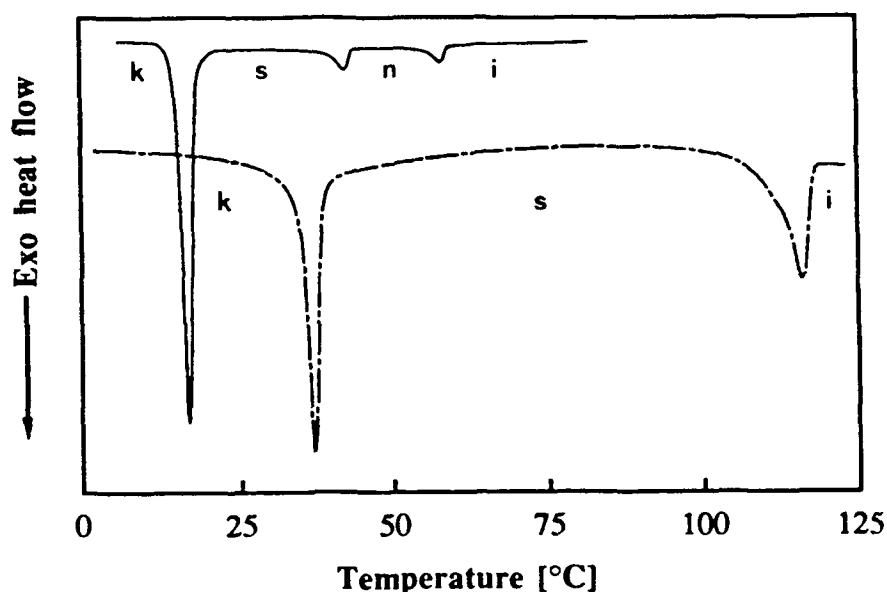


Figure 2. DSC cooling curves for 11-[p-(methoxyphenylbenzoate)-oxy] undecanyl vinyl ether (solid line) and its corresponding polymer (broken line). k = crystalline, s = smectic, n = nematic and i = isotropic.

Two types of initiators were used: The first one generates the active species by thermally while the second one by photochemically induced dealkylation of theonium salt. Figure 3 shows the mechanism for thermal initiation of vinyl ethers by a benzylic sulfonium salt. The initiation proceeds mainly by a S_N1 mechanism, i.e. a reversible generation of the α -methyl benzyl cation that is stabilized by the non-nucleophilic hexafluorophosphate anion. Then the benzyl cation is responsible for the initiation of the polymerization by addition to the nucleophilic vinyl ether bond. To a smaller extent initiation also takes place by β -elimination, i.e. addition of a β -proton from the benzyl cation to the vinyl monomer. Due to the fact that the initiator is formed through an equilibrium reaction, initiating species are formed during the whole polymerization. This increases the molecular mass distribution and results in residual initiator at the end of the polymerization.

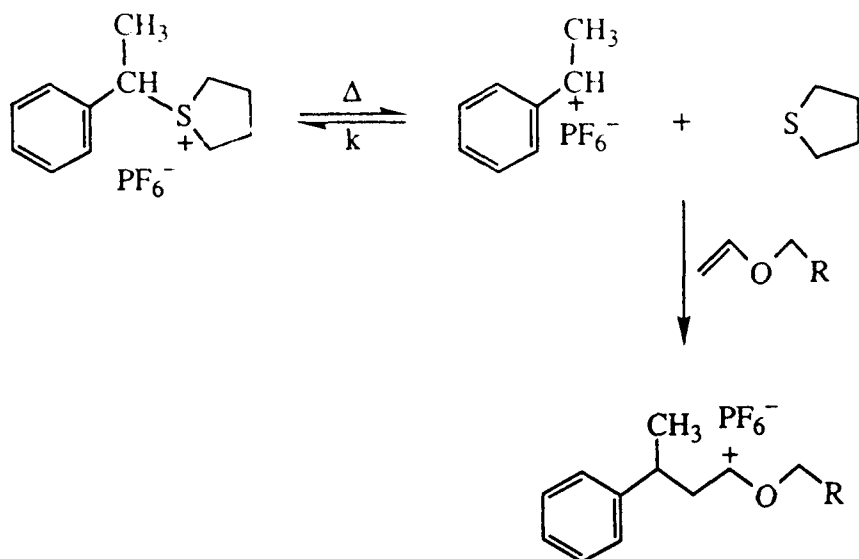


Figure 3. Mechanism for thermal initiation of vinyl ethers by α -methylbenzyltetramethylenesulfonium hexafluorophosphate.

The onium salt based initiator system for photochemical initiation was of the photoredox type, i.e. the spectral response of the onium salt was broadened by a photosensitizer, in this case phenothiazine. A mechanism for the initiation has been proposed by Crivello (Refs. 23, 24) (Figure 4). The initiation starts with excitation of phenothiazine followed by transfer of an electron from this specie to the phenacyl sulfonium salt leading to the formation of the corresponding radical cation. Then this radical cation is responsible for the initiation of the polymerization.

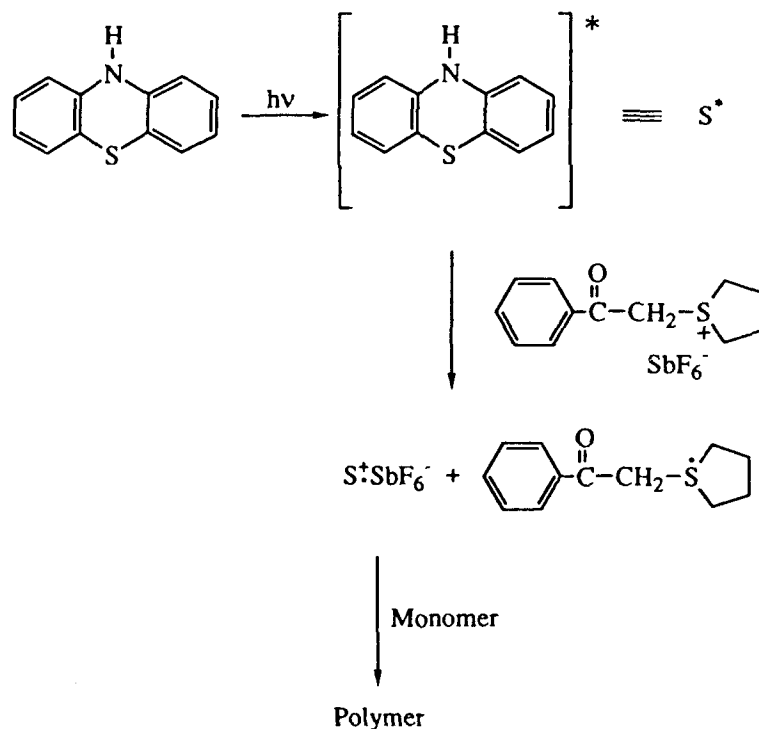


Figure 4. Mechanism for photoredox initiation of vinyl ethers by phenacyltetramethylenesulfonium hexafluoroantimonate using phenothiazine as photosensitizer.

One advantage of photoinitiated over thermally initiated polymerization is the ease with which the polymerization temperature is chosen and the onset of polymerization directed. These are very important parameters when the polymerization is to be carried out in a monomer LC phase which is 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 of photoinitiation is that it is possible to change the polymerization rate by merely changing the intensity of the light.

The experimental set-up used is shown in Figure 5. The polymerizations were performed under isothermal conditions in either a Perkin Elmer DSC-7 equipped with a differential photo-accessory (high pressure Xe-lamp, 366 nm narrow bandpass filter), or in 30 or 50 μm thick cells coated with a thin poly(imide) film and placed in an optical microscope equipped with a hot-stage that was illuminated with a uv-lamp (Tungsten halogen lamp, 380-520 nm).

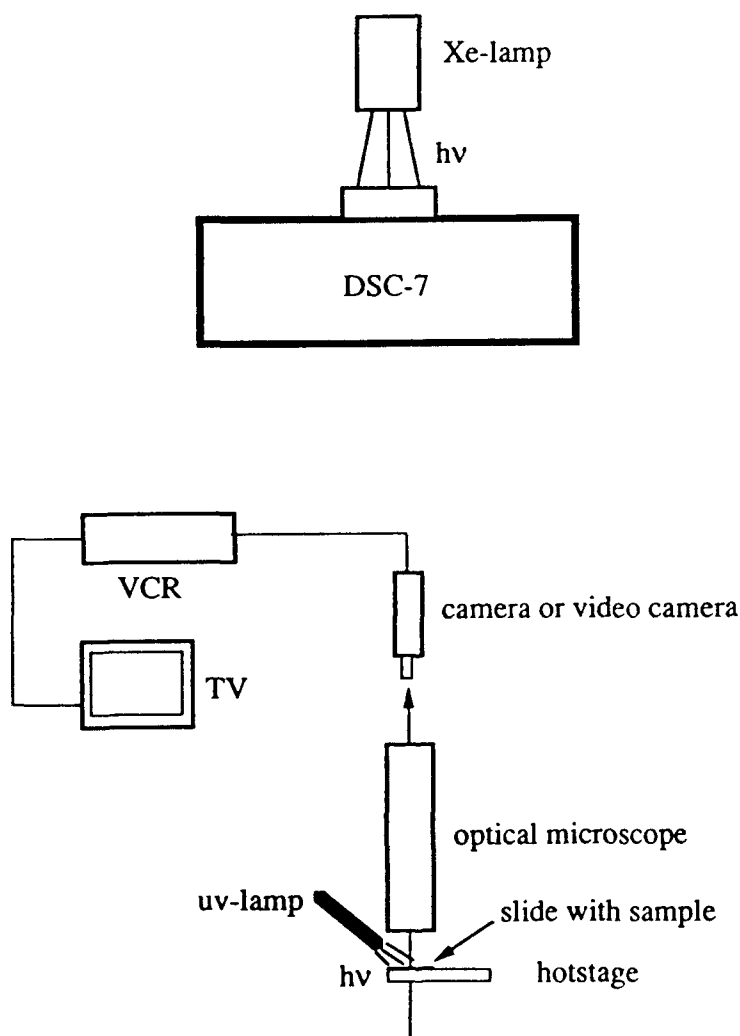
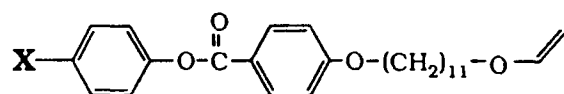


Figure 5. Experimental set-up for thermal and photoinduced polymerizations.

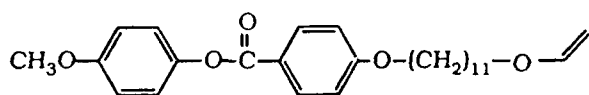
In order to obtain high molecular mass polymers by cationic polymerization, propagation must be much faster than any side reaction such as rearrangement, chain transfer or termination. The termination is the reaction that determines the ultimate degree of conversion, and both termination and chain transfer reactions determine the molecular mass of the polymer. Due to the instability of the propagating species, extensive chain transfer takes place when vinyl ethers are polymerized at room temperature, and only low molecular mass polymers are obtained. If higher polymerization temperatures are to be reached, the growing cation has to be stabilized like in living cationic polymerization. With this in mind, the results in Table 1 (DSC polymerization results) and in Table 2 (thin film polymerization results) are quite surprising and therefore very interesting. Even though the polymerizations were performed at high temperatures, the molecular masses were high and at the same time the molecular mass distribution were kept narrow. This was valid for both thermal and photochemical polymerizations performed in the DSC, as well as in the microscope. Polymerizations in the microscope produced polymers with a lower molecular mass than polymers resulting from photo-DSC polymerizations. This result is probably due partly to the greater difficulty to carry out the polymerizations under dry conditions in the former case, and partly to the large difference in optical density, giving a much larger amount of initiating species in the thin film polymerizations. No effect of the mesophase was observed on polymerization rate, polymer molecular mass or molecular mass distribution.

Table 1. Thermally and photochemically initiated polymerization of 11-[p-(methoxyphenylbenzoate)oxy]undecanyl vinyl ether and 11-[p-(cyanophenylbenzoate)oxy]undecanyl vinyl ether.



X	[M] ₀ /[I] ₀	T _{poly} [°C]	Conv [%]	M _n [g/mol]	M _w /M _n	DP _n
Thermal initiation						
NC-	250	90	97	32 400	1.83	74
	500	92	90	83 300	1.87	191
CH ₃ O-	250	90	97	28 600	2.01	65
Photochemical initiation						
NC-	500	68	96	36 400	2.04	84
NC-	500	80	98	37 200	1.95	85
CH ₃ O-	500	80	98	21 200	2.01	48

Table 2. Photochemically initiated polymerization of thin films of 11-[p-(methoxyphenylbenzoate)oxy]undecanyl vinyl ether carried out in the microscope.



30-50 μm thick films

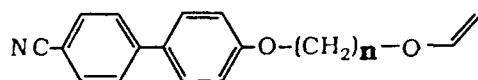
Monomer state	T_{poly} [$^{\circ}\text{C}$]	$[\text{M}]_0/[\text{I}]_0$	M_n [g/mol]	M_w/M_n
<i>Unoriented</i>				
isotropic	80	500	18 100	2.35
nematic	54	500	16 500	2.21
smectic	41	500	20 500	2.02
<i>Oriented</i>				
isotropic	80	500	13 700	2.04
nematic	54	500	13 200	1.99
smectic	41	500	11 600	1.95

Polymer films from the polymerization of oriented monomer films had a much higher degree of order than polymer films obtained from the non-oriented monomer films. These oriented polymer films 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.

These polymerization results show that this polymerization system can stabilize the propagating cation and suppress chain transfer. To evaluate the possible effect of the mesophase of the formed polymer on this stabilization, two cyanobiphenyl vinyl ether monomers that only differed in the length of the flexible spacer, i.e. 2-[(4-cyano-4'-biphenyl)oxy]ethyl vinyl ether and 10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether, were synthesized (Table 3). The monomer with the ethylene spacer produces only a glassy polymer, whereas the monomer with the long decanyl spacer gives a polymer which exhibits a smectic A phase. Even though the degree of polymerization of the latter was about twice that of the former, the glassy polymer still had a high molecular mass and a narrow molecular mass distribution, considering the high polymerization temperature used.

Apparently, the effect of the mesophase, if any, cannot alone be responsible for the unusual results obtained in this study.

Table 3. Polymerization of 2-[(4-cyano-4'-biphenyl)oxy]ethyl vinyl ether and 10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether in the glassy and the liquid crystalline state respectively.



n	$[M]_0/[I]_0$	$T_{poly} [^{\circ}C]$	Conv [%]	M_n [g/mol]	M_w/M_n	DP_n
2	500	120	96	14 200	1.82	54
10	500	120	99	41 500	2.11	110

This statement is supported by the results of a solution polymerization of 11-[p-(cyanophenylbenzoate)oxy]undecanyl vinyl ether in 1,1,2,2-tetrachloroethane at 92°C using the same benzylic sulfonium salt that was used in the thermal bulk polymerizations as initiator. Even though the yield was only 7 %, a degree of polymerization of 48 and a molecular mass distribution of 1.53 strongly supports that the liquid crystalline phase alone is not responsible for these polymerization results. However, one cannot rule out the possibility of the existence of some degree of organization of the polymer in the isotropic melt, as well as in the isotropic solution. Another explanation for the reduced tendency towards chain transfer reactions is that the growing carbenium center is stabilized by the nucleophilic tetramethylene sulfide released during the initiation process. As already demonstrated (Refs. 21, 22), sulfides are used for stabilization of the propagating carbocation and thus generate living cationic polymerization of vinyl ethers. Finally, the possibility that the predominant chain transfer reaction is to counteranion and not, as usually assumed, to monomer should be considered. Figure 6 shows the main chain transfer and termination reactions believed to take place in this system.

The very low basicity of the hexafluoroantimonate counteranion may most probably be responsible for the small extent of chain transfer reactions. Both transfer to monomer ($k_{tr,m}$) and to counteranion ($k_{tr,c}$) produces unsaturated chain ends which should be detectable with 1H -NMR spectroscopy if the molecular mass of the polymer is not too high. The termination reaction (k_t) proceeds via the reversible intramolecular generation of an onium propagating chain end which is attacked by the nucleophilic counterion or monomer to produce a polymer containing an aldehyde chain end. In order to investigate the nature of the polymer chain ends 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether was thermally polymerized in bulk, under conditions which led to a polymer with a degree of polymerization of 10. The molecular mass distribution of this polymer was 1.20. The resulting 200 MHz 1H -NMR spectra is shown in Figure 7.

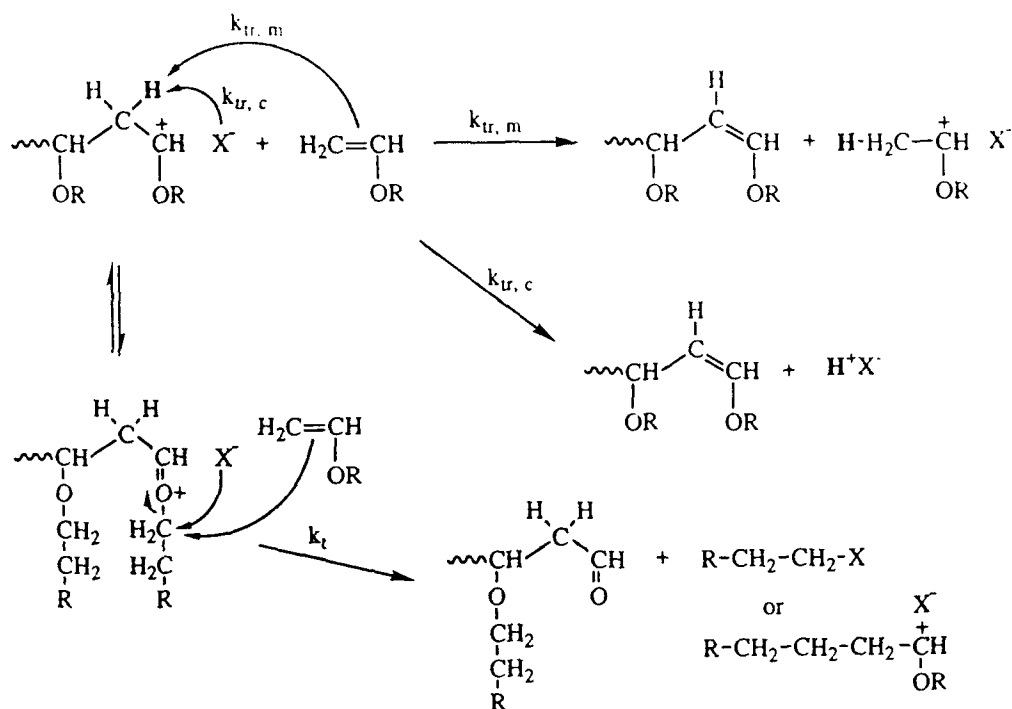
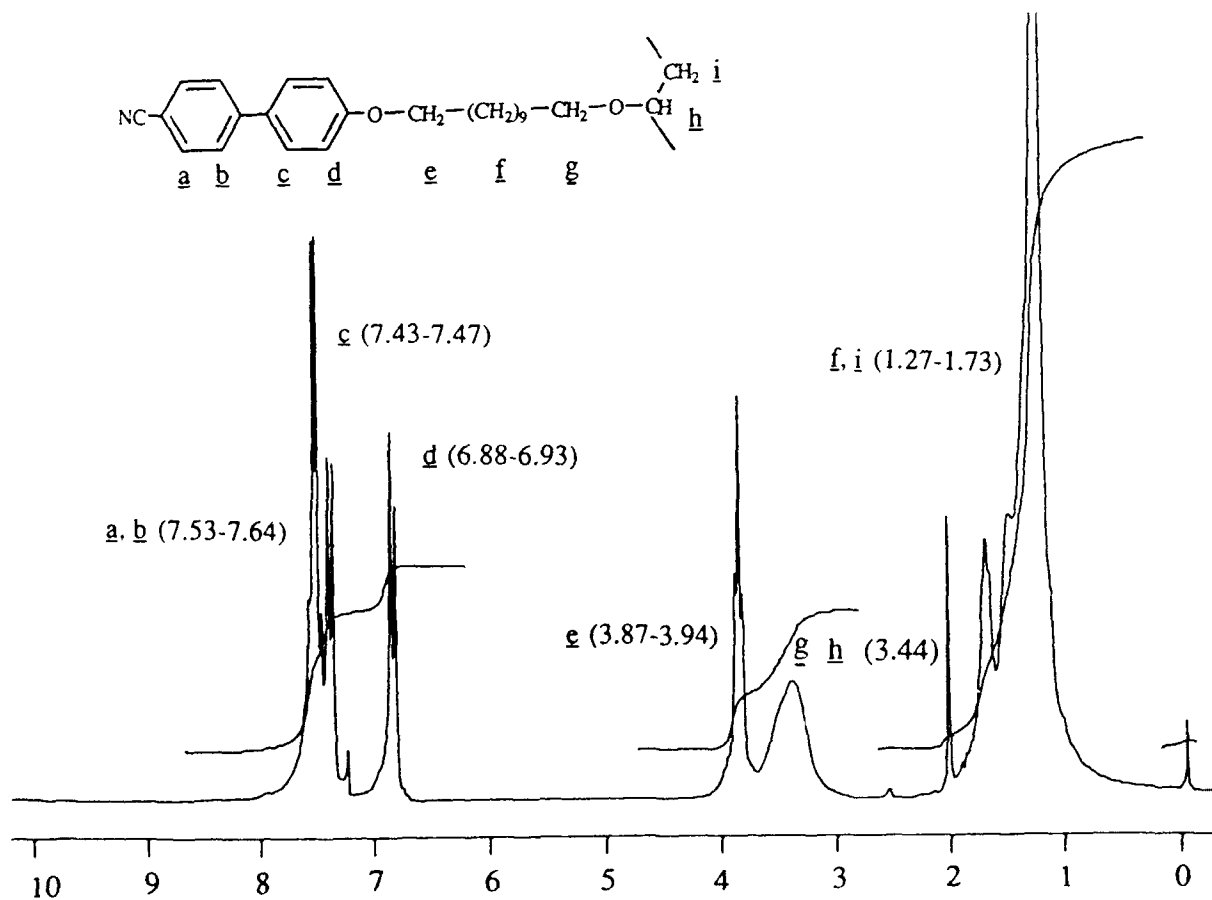


Figure 6. Chain transfer and termination reactions.

Figure 7. 200 MHz ¹H-NMR spectrum of poly{11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether} with a number average molecular mass of 3 800.

Using this equipment no chain ends containing double bonds or aldehyde groups could be detected. This is also an indication of the "living character" of this system. The only chain end that could be detected was the initiator end. Figure 8 shows the multiplet of the methine proton of the initiator fragment in an expansion of the ^1H -NMR spectrum of Figure 7.

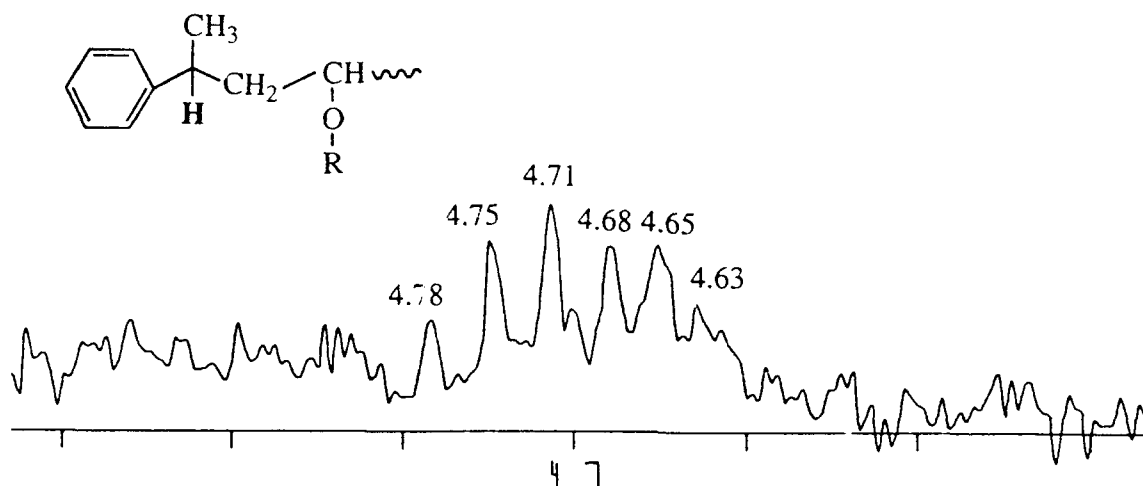


Figure 8. 200 MHz ^1H -NMR spectrum of the aliphatic region of the poly{11-[(4-cyano-4'-biphenyl)-oxy] undecanyl vinyl ether} (number average molecular mass 3 800) showing the multiplet of the methine proton of the initiator fragment at the chain end.

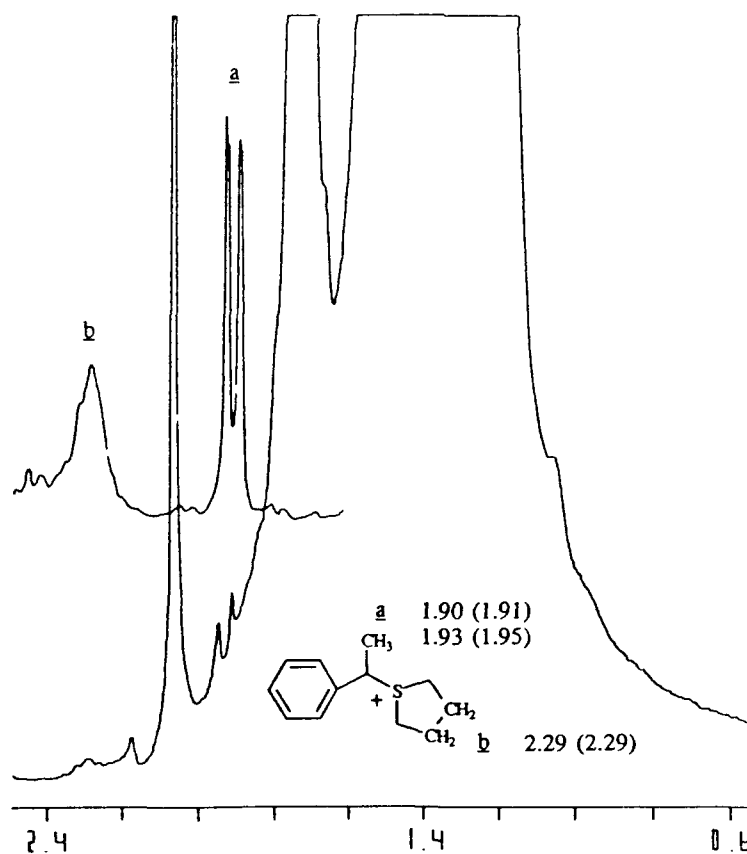


Figure 9. 200 MHz ^1H -NMR spectrum of poly{11-[(4-cyano-4'-biphenyl)oxy] undecanyl vinyl ether} (number average molecular mass 3 800) showing the unreacted benzylic sulfonium salt found in the polymer and its corresponding chemical shifts (in parentheses). Included is also the same portion of a spectrum of pure initiator and its chemical shifts.

As mentioned earlier, due to the fact that the initiator is formed through an equilibrium reaction, initiating species are formed during the whole polymerization process and residual initiator can be found at the end. This is shown in Figure 9 that presents another enlarged part of the spectrum from Figure 7. Included in the figure is also part of the spectrum of the onium salt, α -methylbenzyltetramethylenesulfonium hexafluorophosphate. There is a good resemblance between the chemical shifts of the pure initiator and those of the initiator left in the polymer.

CONCLUSIONS

It has been shown that cationic bulk polymerization of liquid crystalline vinyl ethers using thermal or photochemical initiation by onium salts, gives high molecular mass polymers of high uniformity index when the cationic polymerization is carried out at very high temperatures (i.e., $\leq 120^\circ\text{C}$). The mechanism is not fully elucidated but apparently the polymerization system is able to stabilize the propagating cation and thus reduce chain transfer reactions. One possible reason is that the predominant chain transfer reaction is to counter anion and not to monomer. The very non-nucleophilic character of the hexafluoroantimonate anion may be responsible for the small extent of chain transfer. Another possibility is that the tetramethylene sulfide generated from the onium salt during initiation stabilizes the growing cation, like in living cationic polymerization of vinyl ethers. Regardless of the present state of understanding of this polymerization reaction, these results suggest that living cationic polymerization of vinyl ethers can be accomplished at temperatures as high as more than 100°C .

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