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Cationic bulk polymerization of mesogenic vinyl ethers induced by thermal decomposition of sulfonium salts

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SUMMARY

Liquid crystalline vinyl ethers have been bulk polymerized cationically in the mesophase using onium salts for thermal initiation. High molecular mass polymers ($M_n \leq 83\ 000$) with a narrow molecular mass distribution (around 2) were produced at very high temperatures (≤120°C). Apparently the polymerization system stabilizes the propagating cation and thus reduces chain transfer reactions that are determining the molecular mass. Possible reasons for this stabilization are e.g. influence of the mesophase of the formed polymer, interfacial polymerization, and nucleophilic stabilization by nucleophiles present in the monomer or produced by the initiators.

INTRODUCTION

Both academic and industrial research have in recent years brought the development of functional liquid crystalline side-chain polymers to a high level (see for example (1)). There are however still many fundamental questions that have to be answered, one of them being how to make highly ordered materials. Materials having a high degree of order are a crucial requirement for several applications in the electro-optical area. This, in turn, requires studies of well-defined polymer systems with respect to molecular mass, molecular mass distribution, tacticity etc., and how these factors affect the level of order that is obtainable in a material. One system that fulfils these requirements is living cationic polymerization of mesogenic vinyl ethers. We have in earlier publications shown that this polymerization technique gives well-defined poly(vinyl ether)s also in the presence of functionalities such as nucleophilic aromatic groups, cyano groups, aromatic esters, double bonds and acidic protons (2-3).

Another way to polymerize these mesogenic vinyl ethers that might make it possible to produce well-defined polymers is cationic bulk polymerization. Even though much research has been performed on polymerizations in the liquid crystalline phase initiated both thermally and by uv-radiation, there is very little agreement about its effect on polymer structure and morphology and on polymerization kinetics (4-14).

In order to evaluate the potential of this type of polymerization method in general and for producing high molecular mass polymers having well-defined structures in particular, a series of experiments on the cationic bulk polymerization of mesogenic vinyl ethers initiated by thermal decomposition of sulfonium salts have been performed. For comparison, the study included polymerization of monomers that do not give liquid crystalline polymers and also solution polymerization at high temperatures induced by sulfonium salts.

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EXPERIMENTAL

Synthesis of monomers and initiators

Monomers and initiators were synthesized as reported in previous publications;
11-[p-(Cyanophenylbenzoate)oxy]undecanyl vinyl ether (1) (3)
Thermal characterization: k68i; i64n50k (in the microscope, a nematic phase is observed between 65-68°C on heating and a smectic phase is observed between 52-50°C on cooling).
11-[p-(Methoxyphenylbenzoate)oxy]undecanyl vinyl ether (2) (3).
Thermal characterization: k72i; i56n39s_A12k
2-[(4-Cyano-4'-biphenyl)oxy]ethyl vinyl ether (3) (2)
Thermal characterization: k119i; i78k
10-[(4-Cyano-4'-biphenyl)oxy]decanyl vinyl ether (4) (2)
Thermal characterization:k67i; i62n48k (in the microscope a nematic phase is observed between 68-72°C on heating and a smectic phase is observed between 50-48°C on cooling).
α-Methylbenzyltetramethylenesulfonium hexafluorophosphate (5) (15)
p-Methoxybenzyltetramethylenesulfonium hexafluorophosphate (6) (16)

Polymerizations

The initiator was added to the monomer as 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.

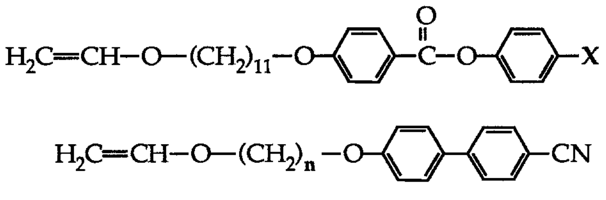
The polymerizations were performed under isothermal conditions either in aluminum pans in a DSC, or between glass slides in a microscope hot-stage. When polymerizations were performed in the mesophase of the monomer, the monomer-initiator blend was first heated to the isotropization temperature and then immediately cooled to the polymerization temperature.

Characterization

Molecular mass 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 with THF as eluent. Thermal characterizations were carried out with an 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.

RESULTS AND DISCUSSION

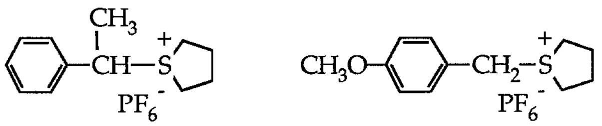
The mesogenic monomers used (Figure 1) were synthesized according to a novel procedure that allows the preparation of mesogenic vinyl ethers containing two or more methylene units in the flexible spacer (2-3). The monomers carried a number of functional groups, i. e., cyano groups, aromatic esters, and nucleophilic aromatic groups.



X = -CN, -OCH$_3$
1 2
n = 2, 10
3 4

Figure 1. Phenylbenzoate and cyanobiphenyl vinyl ether monomers.

The polymerizations were performed utilizing as initiators sulfonium salts with the structures shown in Figure 2.



5 6

Figure 2. Thermal sulfonium salt initiators.

The initiation by 5 probably proceeds by a S_N1 mechanism, i. e. a reversible generation of the α-methyl benzyl cation (7) that is stabilized by the non-nucleophilic anion, PF_6^- ((i) in Figure 3). Then 7 is responsible for the initiation of the polymerization by addition to the nucleophilic vinyl ether double bond (ii). Initiator 6 acts by a similar mechanism (15). The different activation temperatures of 5 and 6 made polymerizations at different temperature levels possible.

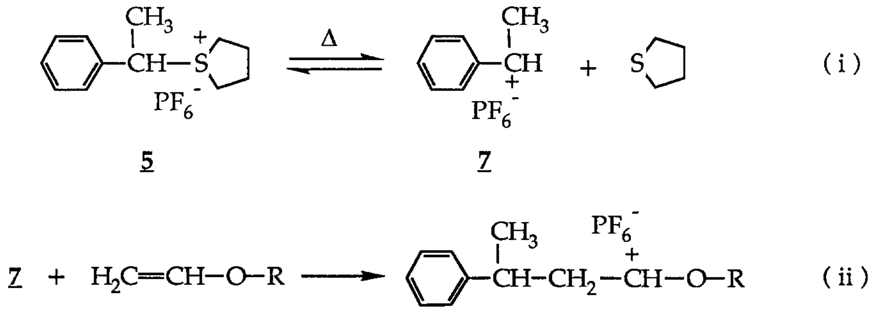


Figure 3. Mechanism for thermal initiation of vinyl ethers by 5.

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 the extent of chain transfer determines the molecular mass. Usually, extensive chain transfer occurs when vinyl ethers are polymerized at room temperature and only low molecular mass polymers are obtained. These facts make the results from this study quite remarkable. As can be seen in Table 1, where all polymerization data and data for the resulting polymers are summarized, high molecular mass polymers are produced at temperatures even above 100°C. Further, the molecular mass distribution is at the same time kept very narrow and the conversions are high. Apparently the propagating cation is stabilized and thus the amount of chain transfer reactions reduced. The good agreement between the [monomer] to [initiator] ratio and the resulting molecular mass is interesting since this should mean that "tailoring" of the polymer molecular mass is possible.

The first question that arises is whether or not the mesophase affect the route of polymerization. To evaluate this, 11-[p-(cyanophenylbenzoate)oxy]undecanyl vinyl ether (1) was polymerized in both its nematic and its isotropic state. No dissimilarities in rate (vinyl ether double bond consumption reflected in t_{poly} and in HF_{max} in Table 1) or molecular mass could however be detected other than those due to the differences in decomposition rate of the initiator at different temperatures. This was valid for almost all groups of polymerizations tested; higher polymerization temperatures give more initiating species and consequently a higher polymerization rate and a lower molecular mass. The lower viscosity of the polymer at a higher temperature should also increase the rate of polymerization due to higher monomer mobility.

A typical isothermal polymerization DSC thermogram is shown in Figure 4 together with the conversion vs. time plot derived from the thermogram. From such conversion plots, Arrhenius graphs can be made. The plot in Figure 5 is based on the time for 20% conversion, and is made from data obtained from the polymerization of 1 in its isotropic and nematic phases. These data fit a straight line almost perfectly, which indicates that there is no difference in activation energy in the two states, and this reflects the independence of the polymerization kinetics of the initial state of the monomer. This result is in line with those reported by e.g. Paleos and Labes (10) and Hsu and Blumstein (12), but contradicts that of Perplies et al. (11) who reported different activation energies in the isotropic and nematic phases.

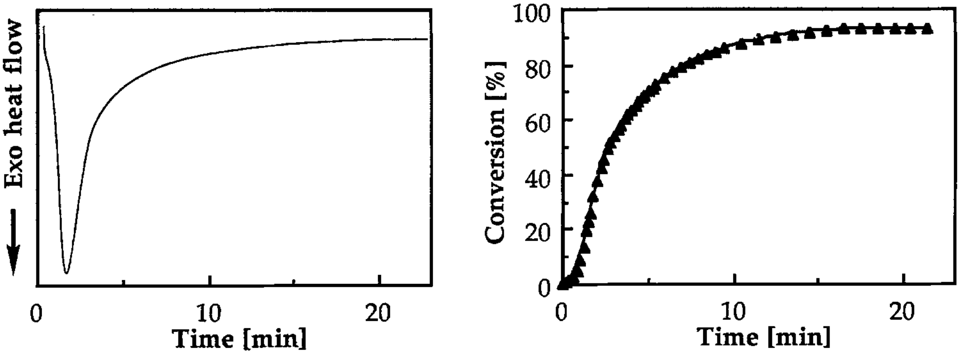


Figure 4. Polymerization thermogram for 1 polymerized at 68°C and the resulting conversion vs. time plot.

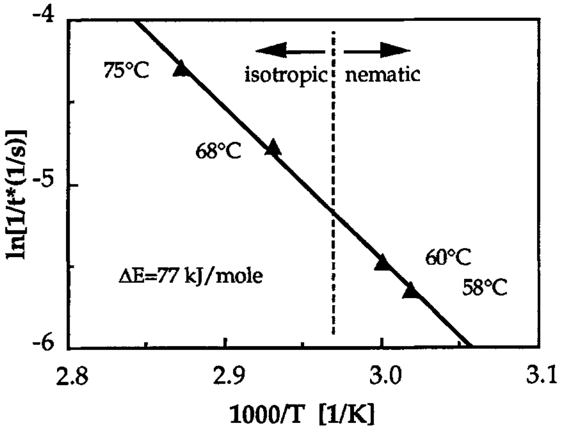


Figure 5. Arrhenius plot of the polymerization of 1 in the isotropic and nematic phases (t* is the time for 20% conversion).

Even though it appears that the state of the monomer (anisotropic or not) does not affect the polymerization kinetics, the mesophase of the resulting polymer might do so. As can be seen in Figures 6 and 7, the propagation reaction, regardless of whether the monomer is in the mesophase or not, occurs in, or at the interphase of, the s_A phase of the polymer. Even if the polymerization is initiated at a temperature above the isotropization of the monomer, the oligomers soon enter the mesophase. If it is possible for the monomer to dissolve and subsequently align in the polymer mesophase, the mesophase can be responsible for the stabilization of the propagating cation. If the monomer is insoluble, an interfacial polymerization probably takes place, and if so the effect of the mesophase is doubtful. It is however also possible that interfacial polymerization can suppress chain transfer reactions.

To further evaluate the effect of the mesophase, the monomers 3 and 4 were polymerized in their isotropic states (Table 1). 3 having only two methylene units in the spacer gives a glassy non-mesomorphic polymer. 4, on the other hand, with 10 methylene units gives a polymer with a s_A phase in the actual temperature range. Even though the degree of polymerization of poly(4) was about twice that of poly(3) (110 and 54 respectively), the latter still gave a high molecular mass polymer with a narrow molecular mass distribution, for a cationic polymerization carried out at 120°C. Apparently the mesophase effect is not the only reason for the extraordinary results obtained in this study. This was further illustrated in a solution polymerization of 1 in 1,1,2,2-tetrachloroethane at 92°C with 5 as initiator. Even though the yield was only 7%, a molecular mass of 21 000 and a molecular mass distribution of 1.53 strongly supports the previous discussion since, unless poly(1) aggregates and form a lyotropic solution, no mesophase exists in the solution. However, there was no sign of the existence of a lyotropic phase, e.g. turbidity.

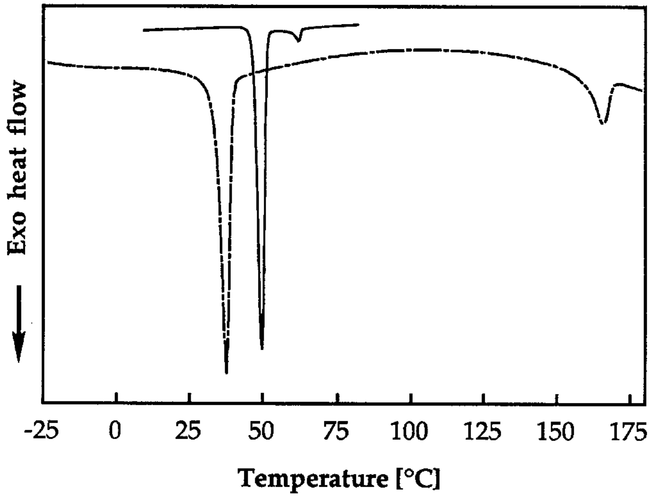
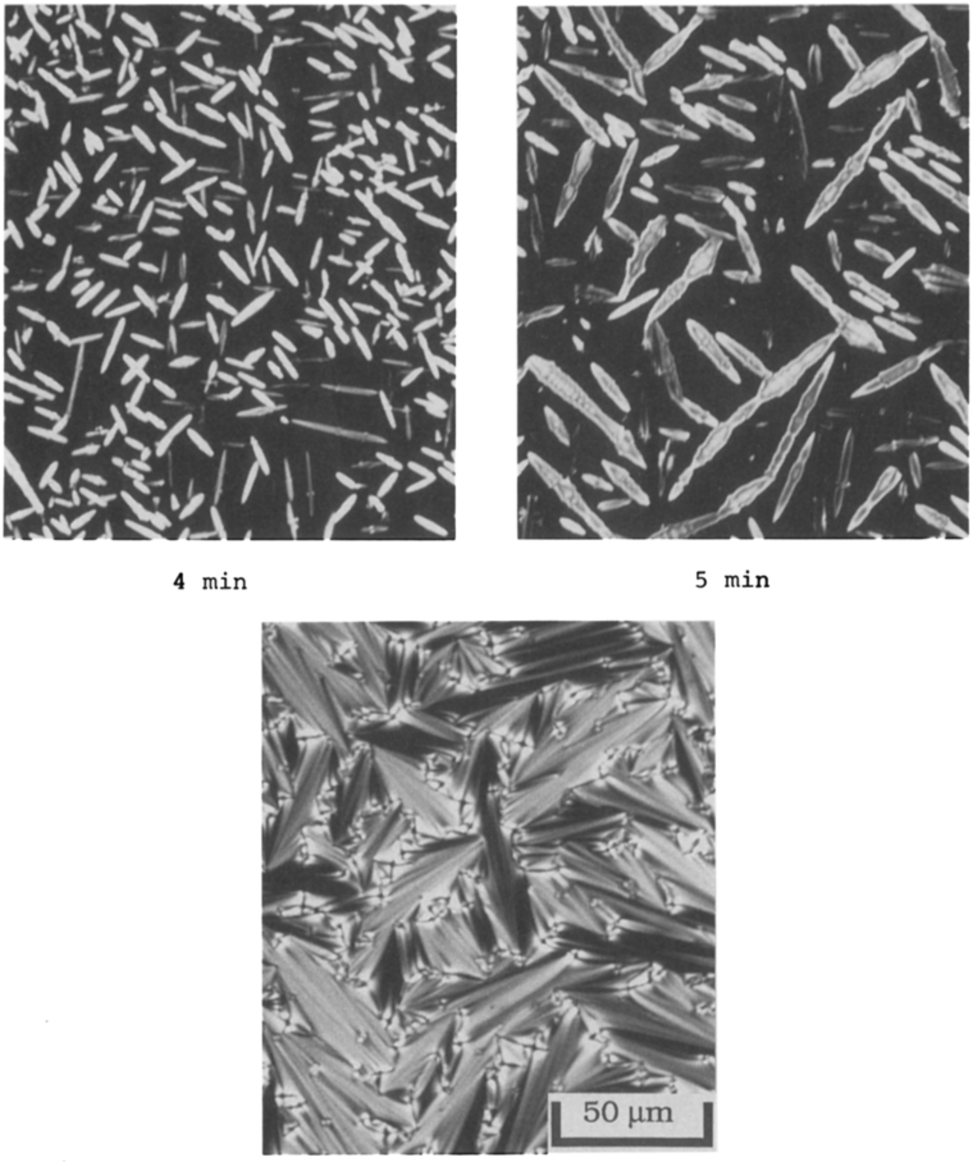


Figure 6. DSC cooling curves for 1 (solid line) and poly(1) (broken line).

Another possible explanation for the reduced chain transfer is that the growing centre is stabilized by one of the nucleophilic groups present in the system. Monomer 1 contains both an ester and a cyano group, 2 contains an ester group, and 3 and 4 contain cyano groups. Nucleophilic sulfides are also released during the initiation process (Figure 5). Both esters (17-18) and sulfides (2,3,19) have been used for stabilization of the propagating centre in order to achieve living cationic polymerization of vinyl ethers. In the case of ester stabilization, both added (intermolecular stabilization) and pendant (intramolecular stabilization) ester groups have been shown to function.

Finally the possibility that the predominant chain transfer reaction is to counteranion and not to monomer must also be considered. The low basicity of the PF_6^- and SbF_6^- counteranions may be responsible for the small extent of chain transfer reactions. In conclusion, additional experiments are required to determine whether polymerization in the mesophase, interfacial polymerization, or nucleophilic stabilization are suppressing chain transfer to monomer reactions, or whether the dominant chain transfer is to counteranion. However, it can be concluded that the effect, if any, of monomer alignment in the mesophase cannot alone be responsible for the reduced degree of chain transfer in this system.



4 min

5 min

11 min

Figure 7. Polarized photomicrographs showing the polymerization of 1 at 100°C using 5 as initiator at a [monomer] to [initiator] ratio of 500. Pictures taken at 4, 5, and 11 min from the onset of polymerization.

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

Monomer	Initiator	[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	6	500	60	23	0.06	87	54200	1.77	k38(3.2)k78(13.8)s_A160(2.4)i	i156(1.8)s_A38(11.4)k
1	6	500	68	23	0.30	96	49300	1.79	k38(3.1)k78(13.6)s_A161(2.5)i	i158(1.7)s_A39(11.3)k
1	6	500	75	12	0.66	98	38600	1.92	k38(3.2)k78(13.9)s_A162(2.5)i	i160(1.8)s_A39(11.3)k
1	5	250	80	28	0.08	97	32800	1.79	k36(2.0)k75(12.7)s_A144(2.2)i	i144(1.4)s_A39(12.2)k
1	5	250	85	15	0.16	97	31500	1.83	k36(1.5)k75(12.6)s_A150(1.9)i	i146(1.6)s_A37(12.0)k
1	5	250	90	8	0.29	97	32400	1.83	-	-
1	5	500	92	11	0.27	90	83300	1.87	-	-
1	5	500	95	11	0.34	92	78300	1.85	k41(3.6)k81(14.0)s_A175(1.8)i	i171(2.1)s_A42(10.6)k
1	5	500	100	6	0.62	98	60100	2.09	k40(3.8)k80(14.2)s_A172(2.0)i	i169(1.9)s_A42(11.0)k
1[e]	5	500	92	-	-	7[f]	21200	1.53	k35(2.1)k76(11.9)s_A161(2.4)i	i158(1.8)s_A34(9.5)k
2	5	250	80	20	0.15	94	34300	2.10	k38(2.7)k55(8.0)s_A123(3.5)i	i119(3.2)s_A32(3.4)k
2	5	250	85	15	0.18	94	30200	2.07	k39(1.3)k55(7.8)s_A121(3.3)i	i118(3.2)s_A33(3.6)k
2	5	250	90	9	0.27	93	28600	2.01	k37(1.1)k53(6.5)s_A119(3.0)i	i116(2.9)s_A31(4.0)k
3	5	500	120	1	10.38	96	14200	1.82	g73i	i71g
4	5	500	92	17	0.40	98	59300	2.16	-	-
4	5	500	120	3	2.84	99	41500	2.11	g15s_X53(1.3)s_A159(2.6)i	i154(1.9)s_A49(1.1)s_X10

[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). [e] Solution polymerization in 1,1,2,2-tetrachloroethane, polymerization time 30 min, [monomer] = 0.459M. [f] Yield.

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