

Synthesis and characterization of poly (11-(4'-cyano-*trans*-4-stilbenyloxy)undecanyl vinyl ether)

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SUMMARY

Polymers based on 11-(4'-cyano-*trans*-4-stilbenyloxy)undecanyl vinyl ether have been synthesized by living cationic polymerization, photo-initiated cationic polymerization using onium salts and thermal initiated cationic polymerization using onium salts. The polymers have been characterized by size exclusion chromatography, nuclear magnetic resonance spectroscopy, differential scanning calorimetry and polarized light microscopy. Living cationic polymerization resulted in a polymer of low molecular mass $M_n \leq 3\,600$, with a uniformity index (D) of 1.2 displaying a focal conic texture indicative of smectic A (s_A) phase with preserved cyanogroup and *trans*-configuration. Photo-initiation using 2,4,6-trimethylbenzoylthoxyphenylphosphine oxide and diphenyliodonium hexafluorophosphate resulted in an insoluble polymer exhibiting only vague liquid crystalline textures. Initiation with phenothiazine and phenacyltetramethylenesulfonium hexafluoroantimonate also yielded a partly insoluble polymer with a disturbed s_A phase. It is suggested that the monomer and polymer are sensitive towards radicals leading to cross-linking and branching. The thermal initiation on systems with α -methylbenzyltetramethylenesulfonium hexafluorophosphate and *p*-methoxybenzyltetramethylenesulfonium hexafluorophosphate resulted in completely soluble mesomorphic polymers of $M_n \leq 13\,000$, $D = 1.7$ and $M_n \leq 26\,000$, $D = 2.8$ respectively, in both cases with a preserved cyanogroup and a *trans*-configuration. Polarized light microscopy revealed a distinct focal conic structure indicative of s_A in both cases.

INTRODUCTION

Interest in functional liquid crystalline side-chain polymers has grown in recent years due to their potential use in electro-optical devices (1-3). Low molecular mass liquid crystal materials with terminal cyano groups have proved to be of technological importance (4). Their polymer analogues have been successfully made with the polyacrylates and polymethacrylates (5-6). Highly ordered films potentially useful for various electro-optical applications have been made by *in situ* photopolymerization of mono- and bifunctional acrylates (7-10). A high degree of orientational order of the system requires not only control of ordering but also a regular chain structure. Living cationic polymerization is one of the most promising techniques in this context. Living cationic polymerization was invented by Higashimura and Sawamoto (11) in 1984. The nucleophilic stabilization of the propagating carbenium ion eliminates chain transfer and termination, and regular almost monodisperse polymers can be made. The system can be stabilized with a nucleophilic counter ion in combination with a Lewis acid or by an externally added base (12). It has been shown that the cyano group tolerates cationic polymerization with a non-nucleophilic counterion and a Lewis base (13).

Cationic bulk polymerization, which can be initiated by photochemical and thermal means has been shown to give polymers with a regular chain structure (14-15).

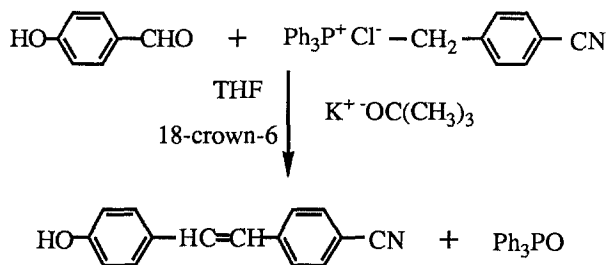
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Photo-initiated polymerization can be carried out over a broad temperature range. This is an important advantage of this technique compared with thermally induced polymerization. Polymerization may be performed in the narrow temperature range where the monomer exhibits mesomorphic behaviour. The initiating system here used was a photoredox system based on onium salts. Photosensitizers and free radical photoinitiators have been used to broaden the spectral response of the onium salt. This paper presents data on the polymerization and structure of side-chain liquid crystalline polymers based on 11-(4'-cyano-*trans*-4-stilbenyloxy)undecanyl vinyl ether. Comparison is made between the structure of polymers synthesized by living cationic polymerization, by photo-initiated cationic polymerization with onium salts and by thermally initiated cationic polymerization using onium salts.

EXPERIMENTAL

Synthesis of the mesogen.

Scheme 1. Synthesis of the mesogen.



Materials: (4-Cyanobenzyl)-triphenylphosphonium chloride(Aldrich), 4-hydroxybenzaldehyde (Merck), potassium tert-butoxide (Merck) and 18-crown-6 ether (Aldrich) were used without further purification. The solvent (THF) was purified by distillation.

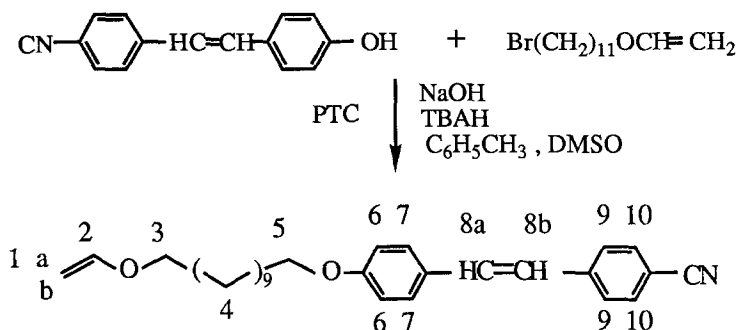
All equipment was dried and purged with dry nitrogen throughout the reaction. The reaction mixtures were continuously stirred, 50 ml THF was added and dried with nitrogen for 30 min. A catalytic amount of 18-crown-6 was dispersed in THF. (4-cyanobenzyltriphenylphosphonium-chloride (20 g; 48 mmol) was added to the mixture and was stirred for 20 min. The mixture was kept at 0°C. Potassium tert-butoxide (5.97 g; 53 mmol) was added slowly to the white slurry. The yellow suspension formed was allowed to react for 30 min. The reaction mixture was heated to 50 °C, and p-hydroxybenzaldehyde (5.9 g;48 mmol) were dispersed in THF was added. The reaction was followed by thin-layer chromatography (TLC) with eluent hexane:ethylacetate 1:1. The plates used were silica gel 60 (Merck). The reaction mixture was centrifugated and then evaporated on silicagel 60 (Merck). Column chromatography was used with a gradient of hexane and ethylacetate. The yield after chromatography was 70 %. The product was characterized by ¹H-NMR (deuterated acetone) and infrared (FTIR) spectroscopy.

Synthesis of the spacer.

11-bromoundecanyl vinyl ether was synthesized according to reference (16).

Synthesis of the monomer.

Scheme 2. Synthesis of the monomer.



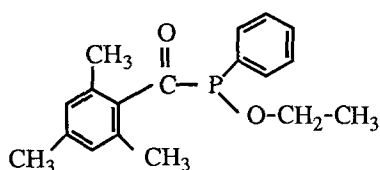
Materials: NaOH , tetrabutylammonium hydrogen sulfate (TBAH) Merck, toluene , DMSO. Synthesized as described in paper (17). Yield 65%. Thermal characterization of the monomer : k 92 i ; i 83 n 54 k. The purity of the monomer was according to HPLC 99.9%.

$^1\text{H-NMR}$ of the monomer:

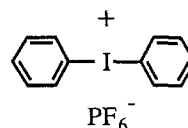
$^1\text{H-NMR}$ (CDCl_3 , TMS, δ , ppm) ; 1.15-1.80 (18 H, 4, m), 3.55-3.65 (2 H, 3, t), 3.9-4.0 (3 H, 1 a and 5, m), 4.05-4.2 (1 H, 1 b, dd), 6.35-6.5 (1 H, 2, q), 6.89-6.93 (2 H, 6, d), 6.98-6.93 (1 H, 8a, d), 7.14-7.26 (1 H, 8b, d), 7.45-7.49 (2 H, 7, d.), 7.53-7.57 (2 H, 9, d), 7.61-7.64 (2 H, 10, d). $J_{\text{H8a-H8b}} = 16.33$ Hz, which indicates trans configuration, (trans $J=12-19$ Hz and cis $J=7-11$ Hz). FTIR spectroscopy revealed the presence of cyano group (2286 cm^{-1}).

Initiators.

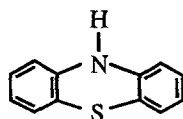
The following cationic photo-redox initiating systems were used:



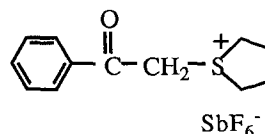
2,4,6-Trimethylbenzoyl ethoxyphenylphosphine oxide (BASF).



Diphenyliodonium hexafluorophosphate (18).

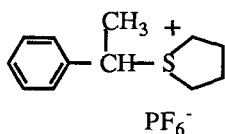


Phenothiazine (Aldrich).

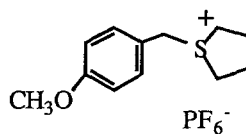


Phenacyltetramethylenesulfonium hexafluoroantimonate (19).

The following sulfonium salts were used for thermal initiation:



α -Methylbenzyltetramethylene-sulfonium hexafluorophosphate (20).



p-Methoxybenzyltetramethylene-sulfonium hexafluorophosphate (19).

Polymerization.

Living cationic polymerization: the monomer was polymerized by a living cationic mechanism as described in refs (17, 21). See Table 1.

Photo-initiated cationic bulk polymerization (onium salts): A solution of the initiator (20-50 mM) in 1ml methylene chloride was prepared. The monomer (0.1 g) and 20 μ l of the initiator solution was dissolved under agitation in methylene chloride. The solvent was evaporated and the mixture dried in a vacuum oven. The polymerization was performed in aluminium 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 395 nm cut-off filter. The light intensity was 0.58 mW/cm² according to International Light IL 1700 Radiometer with a SED 038 detector. The monomer was polymerized both in the isotropic and mesomorphic states. Polymerization experiments were also performed between cover and object glass slides in a Mettler hot-stage while being examined in a Leitz Pol BK II optical microscope. The monomer was either macroscopically randomly oriented or oriented in a 30-50 μ m thick cell coated with rubbed polyimide film. The UV-source in this case was an ICI Luxor 4 000 with THORN Tungsten lamp 150 W emitting in the wave length range 380-520 nm.

Cationically bulk polymerization with thermal initiation (onium salts): A solution of the initiator (20-50 mM) in 1 ml methylene chloride was prepared. The monomer (0.1 g) and 20 μ l of the initiator solution were dissolved in methylene chloride and mixed thoroughly. The solvent was evaporated and the mixture dried in a vacuum oven. The polymerization was performed in aluminium pans in a Perkin- Elmer DSC-7 and between cover and object glass slides in the microscope hot-stage. Further details of polymerizations conditions are given in Table 1.

Characterization.

Thermal transitions were detected in a temperature- and energy-calibrated Perkin Elmer DSC-7 and by hot-stage polarized light microscopy studies in a Leitz Ortholux POL BKII optical microscope equipped with a Mettler Hot Stage FP 82 controlled by Mettler FP80 Central Processor, in both cases at heating and cooling rates of 20°C/min in. ¹HNMR, 250 MHZ, spectra were recorded in a Bruker AC-250 spectrometer in deuterated acetone for the mesogen and CDCl₃ for the monomer and polymer. IR spectra were taken using a Perkin Elmer 1700 FTIR spectrometer.

RESULT AND DISCUSSION

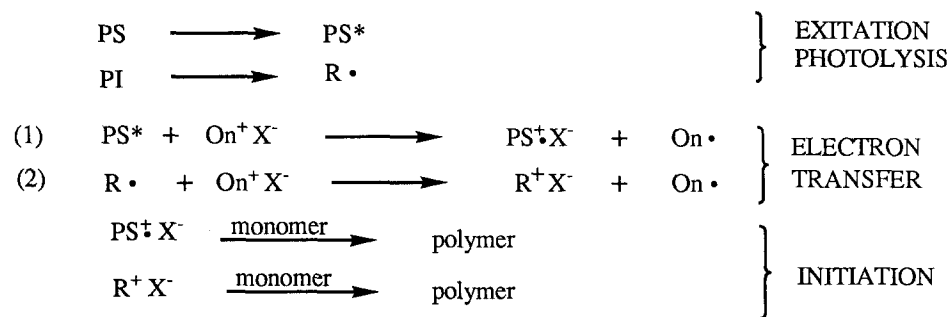
Polymerisation by a living cationic mechanism resulted in a regular polymer which was completely soluble. NMR showed that the trans-stilbene configuration and the cyano group were maintained after polymerization. Polarized light microscopy revealed focal conic textures indicative of a smectic A phase, Figure 1. Narrow molecular mass samples, uniformity index = 1.19, of comparatively low molecular mass were produced, $M_n \leq 3.600$. Table 1 summarizes the polymerizations results and characterization of the polymer.

The monomer was bulk polymerized cationically in a photo DSC-7 using onium salts for photochemical initiation. The DSC thermograms indicated that polymerization occurs within 40 s. Onium salts are latent sources of Brønsted acids. The latent acidity can be released by ultraviolet (UV) light or thermally. As free radical photoinitiator 2,4,6-trimethylbenzoylhexoxyphenylphosphine oxide was used together with diphenyliodonium hexafluorophosphate. The synthesized polymer was insoluble (crosslinked) and no thermal transitions were revealed by DSC.

Polymerization initiated by photochemical means with phenacyltetramethyleulfonium hexafluoroantimonate and phenothiazine resulted in partially a soluble polymer. Polarized light microscopy confirmed that this polymer was mesomorphic. Vague focal conic structures indicative of s_A were observed. A portion of the birefringence remained in the sample even after it was heated above the major isotropization temperature. The latter phenomenon may indicate "permanent" crosslinked liquid crystallinity. DSC revealed two minor first order transitions. Table 1. Macroscopically oriented polymer was obtained by polymerizing oriented monomer. This polymer was also only partially soluble, i.e. the same as in the non-oriented case.

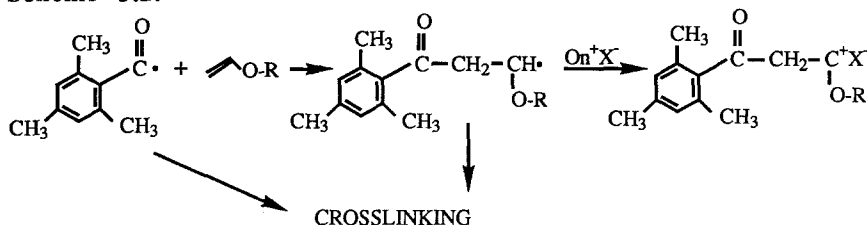
The photolysis of free radical photoinitiators yields radicals. Addition to the alpha vinyl ether double bond or hydrogen abstraction from the monomer produces an aliphatic alpha-ether radical (22). The radical either produces a cation so that polymerization can take place in the presence of an onium salt or reacts with the stilbene double bond to give a crosslinked polymer. The principle of the induced electron transfer reduction of onium salts resulting in the initiation of cationic polymerization (22) is as follows:

Scheme 3.1. Principle of the initiation of cationic polymerization through photoinitiated electron transfer reduction of onium salts.



The overall process consists of (a) the generation of electron-donating free radicals or an excited state photo-sensitizer, (b) electron transfer from these species to suitable oxidizing agents, e. g. onium salts, producing the corresponding cation or radical cation and (c) the initiation of cationic polymerization by these species (23). An additional effect of using free radical photoinitiators as radical sources is that the radicals derived from the photoinitiator may also be oxidized by the onium salt (23). Phenothiazine is less apt to form crosslinked polymers (1) than to 2,4,6-trimethylbenzoylhexoxyphenylphosphine oxide according to reaction (2) and as described in scheme 3.2. Two different radicals could here produce a crosslinked polymer.

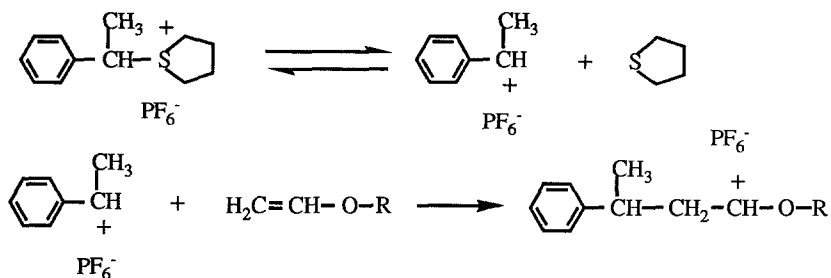
Scheme 3.2.



Stilbenes are known to trans-cis isomerize and dimerize photolytically by free radical polymerization (23). Photodimerization of the stilbene double bond can take place either before polymerization with the monomer or during polymerization with the polymer or after polymerization and can give crosslinked polymers. Dimerization is potentially favoured in the solid state (24). The polymer can also be branched or crosslinked due to polymerization through the stilbene double bond. It has been shown (25) that free radical polymerization can give insoluble stilbene side-chain polymers.

In order to avoid radicals in the system, the monomer was polymerized with thermal initiation using α -methylbenzyltetramethylenesulfonium hexafluorophosphate. The monomer was polymerized in the isotropic state at 95°C. The polymer was completely soluble with a molecular mass, $M_n = 13\ 100$ and an uniformity index of 1.7. Polarized light microscopy showed the presence of focal conic structures (s_A). Table 1 summarizes the results from the characterization of the polymer. The polymer was not crosslinked since no radicals were present in the system, compare scheme 3 and 4.

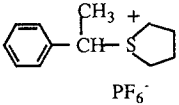
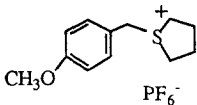
Scheme 4. Mechanism for initiation by thermal decomposition of α -methylbenzyltetramethylenesulfonium hexafluorophosphate.



Polymerization was also carried out with p-methoxybenzyltetramethylenesulfonium hexafluorophosphate as initiator. The polymerization temperature was 95°C. The molecular mass of the polymer was $M_n \leq 26\ 000$ and the uniformity index 2.7. Polarized light microscopy showed focal conic structures indicative of s_A . Table 1 summarizes the polymerization results and characterization of the polymer. The polymer is sensitive towards heat; rearrangement of the stilbene double bond and discoloration occurs. Since p-methoxybenzyltetramethylenesulfonium hexafluorophosphate has a faster decomposition rate than α -methylbenzyltetramethylenesulfonium hexafluorophosphate, it will also give a higher polymerization rate than in the previous case. Faster polymerization produces a higher exotherm in the sample and chain transfer increases, resulting in lower conversion and a higher uniformity index (D). The time to complete the polymerization reaction according to DSC is 0.8 min for p-methoxybenzyltetramethylenesulfonium hexafluorophosphate and 4 min for α -methylbenzyltetramethylenesulfonium hexafluorophosphate. In cationic polymerization of vinyl ethers, propagation must be faster than chain transfer or termination. Termination determines the ultimate degree of conversion and the molecular

mass determining reaction is chain transfer. In these systems the growing centers must have been stabilized in order to explain the high molecular mass of the synthesized polymers at 95°C. The stabilization may be due to steric hindrance caused by the bulky side group and to the large size of the counter-ion.

Table 1. Cationic polymerization and characterization of 11-(4'-cyano-*trans*-4-stilbenyloxy)-undecanyl vinyl ether.

| | T_{poly} (°C) | $t_{\text{poly}}^{\text{a}}$ (min) | Conv. (%) ^b | M_n (g/mol) | M_w/M_n | Thermal transitions (°C) and corresponding enthalpy changes J/g for the polymer ^c . Heating/Cooling |
|---|---------------------------|---------------------------------------|---------------------------|------------------|-----------|---|
| <u>Living polymerization:</u> | 0 | 240 | 100 | 3624 | 1.19 | k13(5.0)k32(1.4)s _A 144(6.5)i i133(5.9)s _A 23(12)k |
| <u>Thermal polymerization.</u> | | | | | | |
| [Monomer]/[Initiator] (mol/mol) = 500 | | | | | | |
| Thermal initiators: | | | | | | |
|  | 95 | 4 | 71 | 13126 | 1.70 | k49(5.1)s _A 145(1.3)i i168(6.3)s _A 37(3.3)k |
|  | 95 | 0.8 | 57 | 25715 | 2.78 | k50(5.4)s _A 147(1.4)i i156(3.7)s _A 36(6.2)k |

^a Time to complete reaction according to DSC. ^b Conversion calculated from SEC. ^c Calculated from 2nd heating and 1st cooling scan. Giving the peak temp.

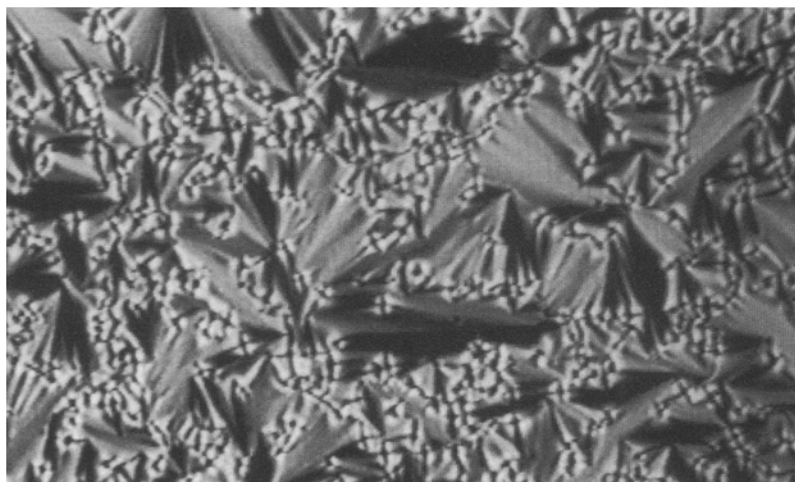


Figure 1. Polarized photo micrograph showing the smectic A (s_A) phase of the polymer polymerized by living mechanism.

CONCLUSIONS

Side reactions and crosslinking may occur when monomers sensitive towards radicals are polymerized according to a cationic mechanism. The higher radical concentration prevailing in bulk polymerization compared with that of solution polymerization enhances these side reactions and causes a lowering of mesomorphility in the polymers produced by the former technique.

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