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Synthesis and characterization of poly(vinylether)s with pendant mesogenic groups

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ABSTRACT

Two different methods of synthesis were examined for the preparation of poly(alkylvinylether)s with pendant 4'-cyano-4-oxy-biphenyl mesogenic groups attached to side chains of different length : a) anchoring of the mesogenic group onto an alkylvinylether monomer followed by polymerization or b) synthesis of the corresponding poly(chloroalkylvinylether)s and chemical substitution of the pendant chlorine by the mesogenic groups. Polymerization were performed with initiating systems based on activated iodide. Much better control of MW and MWD of the final polyvinylether chains was obtained when process b) was applied. Polymers with 2 and 4 carbons in the spacer do not show liquid crystalline properties. It is only with polymers having six carbon atoms in the spacer that mesophases were observed. Those issued from process b) give two distinct mesophases: a smectic A phase in the high temperature range and a smectic C phase for the low one. Polymers synthetized from process a) present only the smectic A phase. The effects of molecular weights and molecular weight distributions on the liquid crystalline properties have been examined and are discussed.

INTRODUCTION

Studies on side-chain liquid crystalline polymers have focused, for a long time, on the influence of size, nature, and structure of mesogenic side chains on liquid crystalline properties. Incidentally, the role of the main polymer chain just started to be examined in some detail, very recently. In order to understand better the contribution of the polymer backbone to the mesogenic properties, the interest in well defined new polymeric structures has grown rapidly . The synthesis and properties of liquid crystalline side-chain polymers with 1,2 -polybutadiene (1), poly-olefin (2), polystyrene (3), polysulfone (4), polyether (5), and polyvinylether (6-9) backbones have been reported recently.

New developments in cationic polymerization of vinylethers (8-11) have made this class of polymers very attractive. Particularly because of the discovery of conditions for living polymerization which allows the synthesis of well-defined polymeric structures and the control of molecular weight (MW) and molecular weight distribution (MWD) of the polymers. The application of this polymerization procedure to the synthesis of poly(ethylvinylether)s with 4'-methoxy-4-oxy-biphenyl and 4'-cyano-4-oxy-biphenyl mesogenic groups has recently been reported (8, 9).

This paper presents our first results on the synthesis and characterization of poly(n-alkylvinylether)s with 4'-cyano-4-oxy-biphenyl pendant side groups. Two synthetic methods have been used and re compared : anchoring

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*To whom offprint requests should be sent of the mesogenic group on chloroalkylvinylether prior to polymerization and chemical substitution of the corresponding poly(chloroalkylvinylether)s. The influence on liquid crystalline properties of the mode of synthesis, of the spacer length and of the MW and MWD of the polymers are also discussed.

EXPERIMENTAL SECTION

Synthesis of monomers

Chloroalkylvinylethers were prepared from ethylvinylether and chloroalcohols by transetherification reaction catalyzed by mercuric acetate. An example of this procedure is given : ethylvinylether in quantity (2 moles) and chlorobutanol (0.12 mole), previously dried over molecular sieves, were reacted overnight at room temperature in the presence of mercuric acetate in a schlenk apparatus. The reaction was stopped by adding sodium carbonate, and the mixture was passed through a silica column. After evaporation of the residual ethylvinylether, chlorobutylvinylether (purity >99%) was obtained in 90% yield.

The n(4'-cyano-4-oxy-biphenyl)alkylvinylether (n = 2,6) were synthetized by the phase transfer catalyzed Williamson etherification. For example, a mixture of chlorohexylvinylether (0.01 mole) and 4'-cyano-4-hydroxy-biphenyl (in slight excess) were reacted in 50 ml DMF in the presence of tetrabutylammonium bromide (0.005 mole) and potassium carbonate at 90°C. After 20 hours, water and methylene dichloride were added to the reaction mixture. The organic layer containing the substituted vinylether was dried over $MgSO_4$ and the solvent evaporated under vacuum. The solid obtained was recrystallized from methanol to give white crystals, in 80% yield.

Polymerization

Purification procedure

Solvents (toluene, hexane, and methylene dichloride) and chloroalkylvinylethers monomers were purified and dried according to conventional procedure used in cationic polymerization (14). Solid monomers were degassed and kept under vacuum.

Hydrogen iodide was obtained from a 57% aqueous solution by dehydration in toluene or hexane with phosphorus pentoxide. The organic HI solution was twice cryodistilled and stored under dry nitrogen at -30°C in the dark. Iodine was sublimed under vacuum and stored in hexane or toluene in the dark, under nitrogen. Tetrabutylammonium perchlorate was degassed under vacuum and dissolved in dry toluene or methylene dichloride.

Polymerization experiments

Polymerizations were performed under dry nitrogen in glass flasks equipped with teflon stopcocks and septa.

Solid monomers were first introduced and degassed overnight. Liquid monomers were introduced just before use. Then, solvent and HI solution were successively introduced. Polymerizations were finally started by adding the co-initiator solution. Reactions were stopped by adding ammoniacal methanol. The reacting medium was washed by a 10% sodium thiosulfate solution and dried over $MgSO_4$. Polymers were recovered by precipitation into methanol and dried under vacuum.

Characterization of the products

Molecular weights and molecular weight distributions were determined by GPC in THF on a Varian 5500 chromatograph fitted with 4 TSK gel columns calibrated with polystyrene standards.

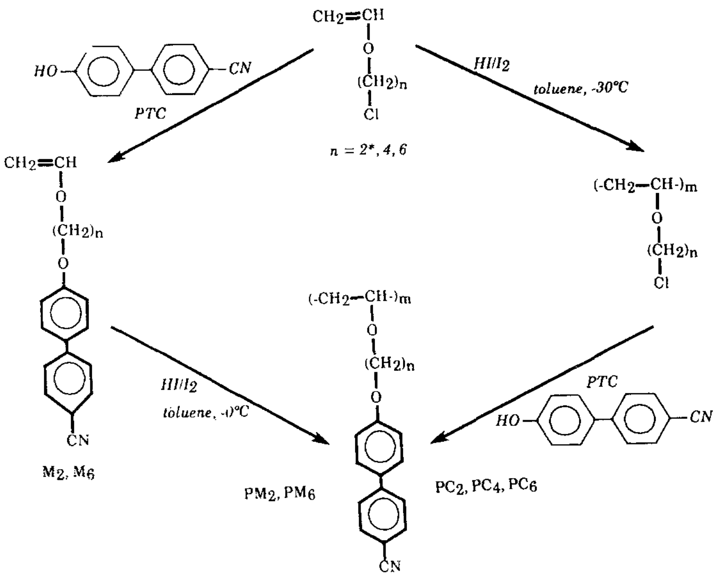
Proton and ^{13}C NMR spectra were recorded on a BRUKER AC 250 spectrophotometer in $CDCl_3$ at room temperature.

Thermal analysis was carried out on a METTLER DSC apparatus with polymer samples of about 10 mg and at a scanning rate of 10°C/mn. Transition temperatures were measured at the second heating cycle.

Visual observations of textures were made on a polarizing microscope equipped with polarizers and a hot stage.

RESULTS AND DISCUSSION

The two synthetic methods used for the synthesis of poly(4'-cyano-4-oxy-biphenyl)alkylvinylether are outlined in scheme 1.



scheme 1

* commercial product

Chloroalkylvinylethers (n = 4,6) were prepared by transetherification of ethylvinylether with n-chloroalcohols in one step (11). The corresponding (4'-cyano-4-oxy-biphenyl)alkylvinylethers where obtained by chemical substitution of the chlorine atoms with 4'-cyano-4-hydroxy-biphenyl by PTC. The ^{13}C NMR spectra of the substituted monomers M_2 and M_6 (2 and 6 are the number of carbon atoms in the spacer) are given in figure 1. The M_2 derivative presents a melting peak at 126°C on its DSC curve but does not exhibit LC properties. For M_6 an endothermal peak at 77°C corresponding to a nematic-isotrope transition is observed.

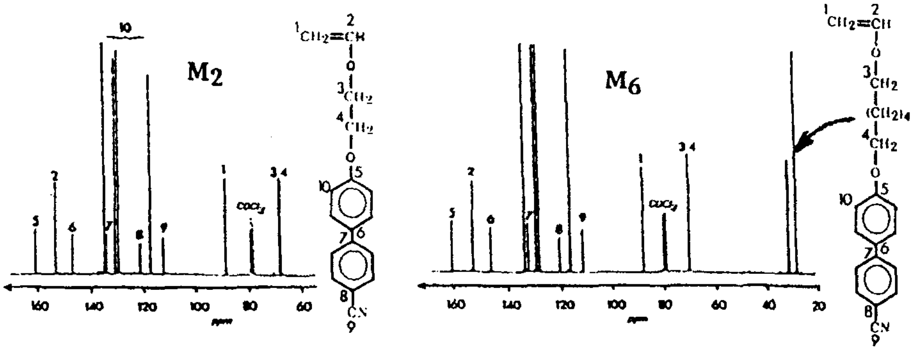


Figure 1 62,25 MHz ^{13}C NMR spectra of (4'-cyano-4-oxy-biphenyl) alkylvinylethers. Solvent $CDCl_3$ alkyl= ethyl (M_2) and hexyl (M_6)

Polymerizations of M_2 and M_6 in the presence of HI/I_2 as initiating system were performed in toluene. At low temperature, the monomer is only slightly soluble in toluene and reactions were conducted at 0°C. In these conditions a slow precipitation of the polymers was also observed when the chains reached a certain $\overline{Dp}_n$ and conversions were incomplete. Typical polymerization data are given in Table 1. Polymers obtained under these conditions had relatively broad molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = 1.6-1.9) and experimental $\overline{M}_n$, determined by GPC on the basis of a polystyrene calibration, were lower than predicted by the [monomer consumed]/[HI] ratio. Insofar as a living polymerization process in CH_2Cl_2 has been claimed by SAGANE and al. (9) for (4'-cyano-4-oxy-biphenyl)ethylvinylether , our data might be explained by the precipitation process of the growing polymer in toluene.

Table 1 :
Polymerization of (4'-cyano-4-oxy-biphenyl)alkylvinylethers in presence of HI/I_2 in toluene, at 0°C, $[HI]=[I_2]=3.10^{-2}$ $mol.l^{-1}$, $[M_6]=[M_2]=0.4$ $mol.l^{-1}$.

monomer	[M]/[HI]	conversion (%)	$10^{-3}\,\overline{M}_n$		$\overline{M}_w/\overline{M}_n$	$\overline{Dp}_n$
			obs.	calcd.		
M_2	70	#70	5.1	18.3	1.6	16
M_6	70	#70	4.3	22.4	1.9	14

The cationic polymerization of long-chain chloroalkyl-vinylethers initiated by activated iodide systems has not been reported yet; however, it has been shown that the polymerization of chloroethylvinylether initiated by HI/I_2 (13,14) proceeds according to a truly living process. The cationic polymerization of chloro-4-nbutyl and chloro-6-nhexylvinylethers (C_4 and C_6) has been examined using similar experimental conditions. Co-initiators used were either iodine or tetrabutylamonnium perchlorate (15). Typical polymerization data are presented in Table 2. Polymerization of chloroalkylvinylether leads to polymers of narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n$<1.2) and with experimental $\overline{M}_n$ which closely corresponds to those calculated from the initial [monomer]/[HI] ratio, even in the case of experiments leading to polymers of relatively high $\overline{Dp}_n$(60). GPC of chlorinated poly(vinylether)s are shown in figure 2.

Table II :

Polymerization of chloroalkylvinylethers in presence of activated iodide in toluene or methylene dichloride, at -20°C, $[HI]=[I_2]=2.10^{-2}$ mol.l^{-1}, $[HI]=[Bu_4N^+ClO_4^-]=8.10^{-2}$ mol.l^{-1}.

monomer	[M]/[HI]	conversion (%)	$10^{-3}\overline{M}_n$ obs.	$10^{-3}\overline{M}_n$ calcd.	$\overline{M}_w/\overline{M}_n$	$\overline{D}p_n$
C_2	100	92	14	11	1.15	127
C_4	20	96	3.9	2.7	1.3	21
C_6	14	100	2	2.3	1.2	12
	25	100	3.5	4	1.2	22
	38	100	6.3	6.2	1.2	37
	54	100	8.9	8.8	1.2	55

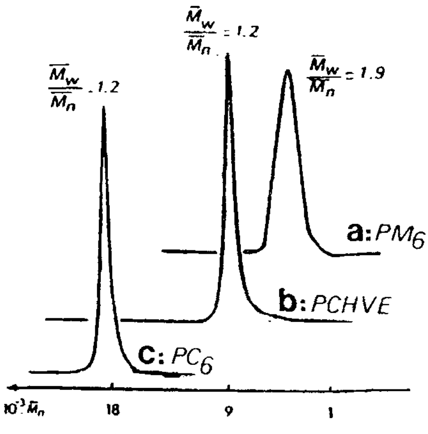


Figure 2

Gel permeation chromatograms of poly(vinylether)s obtained by:
a) polymerization of the monomer bearing a mesogenic group
b) polymerization of chloroalkylvinylether
c) after substitution of b) by the mesogenic group

The chlorine substitution of poly(chloroalkylvinylether)s (n = 2,4,6) by 4'-cyano-4-hydroxy-biphenyl was performed under phase transfer catalysis conditions. The reaction proceeds readily and cleanly. Complete substitution of Cl atoms was achieved without occurrence of detectable elimination or other side processes (16).

The ^{13}C NMR spectra of a chemically modified polymer PC_2 and of the corresponding polymer obtained by polymerization of the vinylether monomer bearing the mesogenic group PM_2 are shown in figure 3. They are in agreement with the same chemical composition and structure for the two samples. Signals of the methylene carbons of the vinylether chains are resolved into two signals resulting from configurational effects. If we assume a similar placement for m and r sequences in the poly(n-alkylvinylether) series the resonance peaks at 39.9 and 41.9 ppm respectively can be attributed to meso and racemic diads (17). Polymers prepared by the two synthetic routes, figure 4, exhibit different m/r diads ratio indicating that there is probably some stereoregulating effect of the side groups during polymerization. No such effect was observed for PM_6 and PC_6 polymers. GPC of chemically modified polymers are shown in figure 2. Molecular weights are in close agreement with MW calculated from the corresponding chlorinated polymers and the weight increase of monomer units. Their MWD remains narrow and in the range 1.2 to 1.3. These results show that the synthesis of poly(chloroalkylvinylether)s followed by anchoring of mesogenic groups on polymer chains is an interesting alternative for the preparation of well defined and high molecular weight poly(vinylether)s with pendant mesogenic groups.

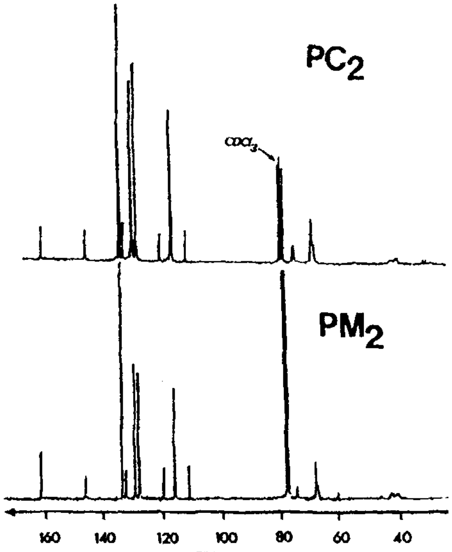


Figure 3

62,25 MHz ^{13}C NMR spectra of poly((4'cyano-4-oxy- biphenyl)ethylvinyl)ether, PM_6 and PC_6. Solvent $CDCl_3$

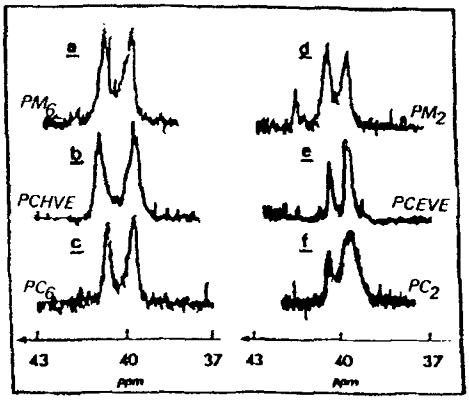


Figure 4

Expanded spectra of the main chain methylene carbon of poly(alkylvinylether)s
a) PM_6, b) poly(chlorohexyl)vinylether (PCHVE),
c) PC_6, d) PM_2,
e) poly(chloroethyl)vinylether (PCEVE),
f) PC_2

THERMAL PROPERTIES OF THE POLYMERS

Typical DSC thermograms of polymers obtained by the two synthetic methodes are presented in figure 5. Polymers with two carbons in the spacer PM_2 and PC_2, as well as those with four carbons, PC_4, show only Tg transitions. No indication of the presence of a crystalline or liquid crystalline endotherm could be observed even after repeated thermal cycles and annealing. According to SAGANE (9) only the very low molecular weights (4'-cyano-4-oxy-biphenyl)ethylvinylether, of $\overline{Dp}_n<10$, exhibit liquid crystal properties, while those of higher MW, among which PM_2 and PC_2 can be included, do not. Similar behaviour could be postulated also for the PC_4 series.

It is only with poly(vinylether)s having 6 carbon atoms in the spacer, PM_6 and PC_6, that liquid crystalline properties were observed in the whole molecular weight range of the synthesized polymers. However, the observed liquid crystalline properties were found to be strongly dependent on the polymer MW and MWD.

For polymer PM_6 of low $\overline{Dp}_n$ (≈ 15) and broad MWD (≈ 1.9) a smectic A phase is observed. In contrast, all PC_6 polymers exhibit on their DSC thermograms, figure 6, two endothermic peaks corresponding to two distincts mesophases. Optical observations made on a polarizing microscope show on cooling from the isotropic state, first the formation of fan-shape textures, identical to those observed with PM_6 and characteristics to a smectic A phase. At lower temperature transition to a schlieren texture is then observed. This was attributed to the formation of a smectic C phase. Isotropization temperatures, S_A-S_C transitions and glass transition temperatures of PM_6 and PC_6 polymers of different MW are collected in table 3. Dependence of thermal properties on MW is shown on figure 7. The stability temperature range of the S_C phase is drastically reduced for low MW compounds, however this cannot satisfactorily explain the absence of a S_C phase in the PM_6 sample. It is very likely that the presence of oligomers of low $\overline{Dp}_n$ indicated by the broader MWD of this sample, and the higher dispersity in polymer chain length, play an important role in this phenomenon. Further studies are in progress in this field.

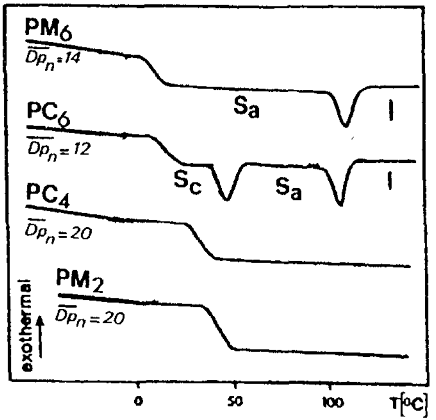


Figure 5

DSC thermograms of poly(4'-cyano-4-oxy-biphenyl)alkylvinylether of various spacer length ($\overline{Dp}_n$ = 10-20), second heating cycle

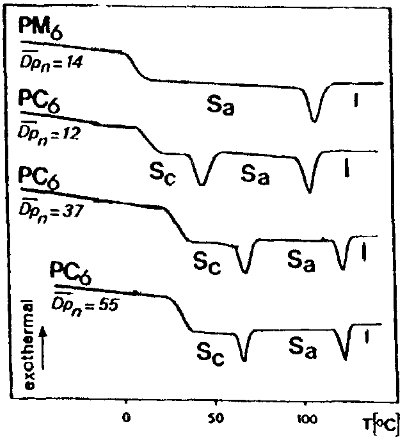


Figure 6

DSC thermograms of poly(4'-cyano-4-oxy-biphenyl)hexylvinylether of differents $\overline{Dp}_n$, second heating cycle

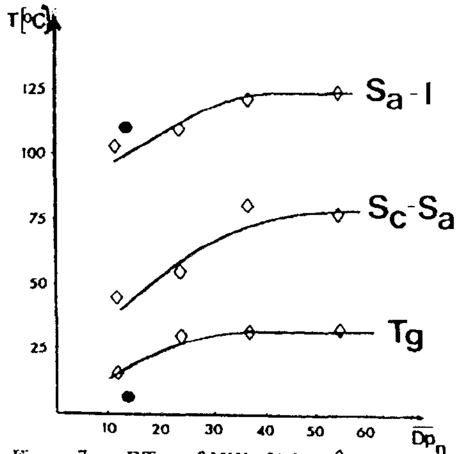


Figure 7 Effect of MW of PC_6 (◇) and PM_6 (●) polymers on their thermal transition temperatures

Table III :
Thermal transitions (°C)
of (4'-cyano-4-oxy-biphenyl)alkylvinylethers.

polymer	$\overline{Dp}_n$	T_g	$T_{Sc.Sa}$	T_i
PM_2	20	43	-	-
PC_2	100	73	-	-
PC_4	20	34	-	-
PM_6	15	15	-	110
PC_6	12	16	45	105
	24	27	56	110
	37	34	82	125
	55	33	78	126

In conclusion, in this first paper, we have examined two different ways for the synthesis of liquid crystalline poly(alkylvinylether)s with pendant 4'-cyano-4-oxy-biphenyl groups : anchoring of the mesogenic group on the monomer prior the polymerization step and chemical substitution of the corresponding poly(chloroalkylvinylether)s. This latter procedure was found more convenient and appropriate for the preparation of polymers of well defined structure, controlable molecular weights and narrow molecular weight distributions. These are important structural parameters for the polymer chains since it has been shown that they strongly affect the liquid crystalline properties of the resulting polymers.

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