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# Liquid crystalline copoly(vinylether)s containing 4(4')-methoxy-4' (4)-hydroxy-α-methylstilbene constitutional isomers as side groups

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## SUMMARY

Ethoxy vinyl ethers containing 4-methoxy-4'-hydroxy-α-methylstilbene and 4-hydroxy-4'-methoxy-α-methylstilbene constitutional isomers as side groups were synthesized by phase transfer catalyzed etherification of a mixture containing the above mentioned isomers with 2-chloroethyl vinyl ether. Cationic copolymerization of various ratios between the two constitutional isomeric monomers led to a mixture of two copolymers which were separated by fractional precipitation. One copolymer exhibits a nematic mesophase, the other exhibits two smectic mesophases.

## INTRODUCTION

The synthesis of liquid crystalline polymers (LCP) containing mesogenic units which exhibit either constitutional (1, 2) or conformational (3, 4) isomerism is of current interest to our laboratory. The copolymerization of monomer-pairs containing mesogenic units which exhibit constitutional isomerism is of interest both because it can be used to tailor phase transitions (1) and because it can provide qualitative information on the degree of decoupling of the side-groups from the main chain (2).

This paper presents our first results on the synthesis and cationic copolymerization of ethoxy vinyl ethers containing 4-methoxy-4'-hydroxy-α-methylstilbene and 4-hydroxy-4'-methoxy -α- methylstilbene constitutional isomers as side-groups.

## EXPERIMENTAL

### Materials

All the reagents were commercially available and were used as received unless otherwise specified. Methylene chloride used in the polymerization reaction was purified by conventional techniques used to achieve the purity required for carbocationic polymerization. 4,4'-Dihydroxy-α-methylstilbene (HMS) was synthesized and purified as previously reported (5). Its purity was higher

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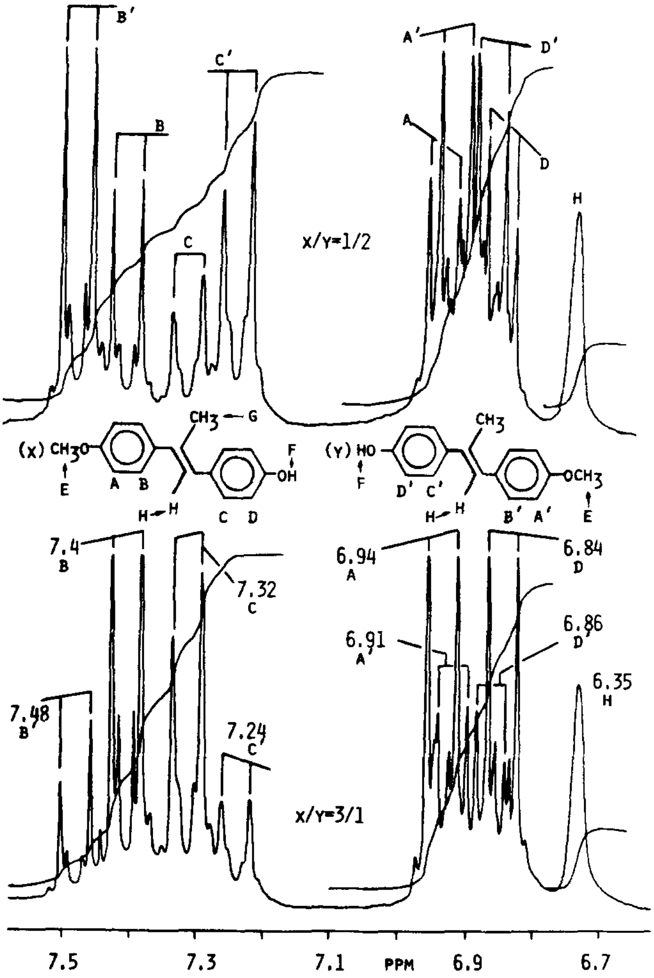


Figure 1. 200 MHz $^1$H-NMR spectra of two representative samples of MHMS ($(CD_3)_2CO$, TMS)

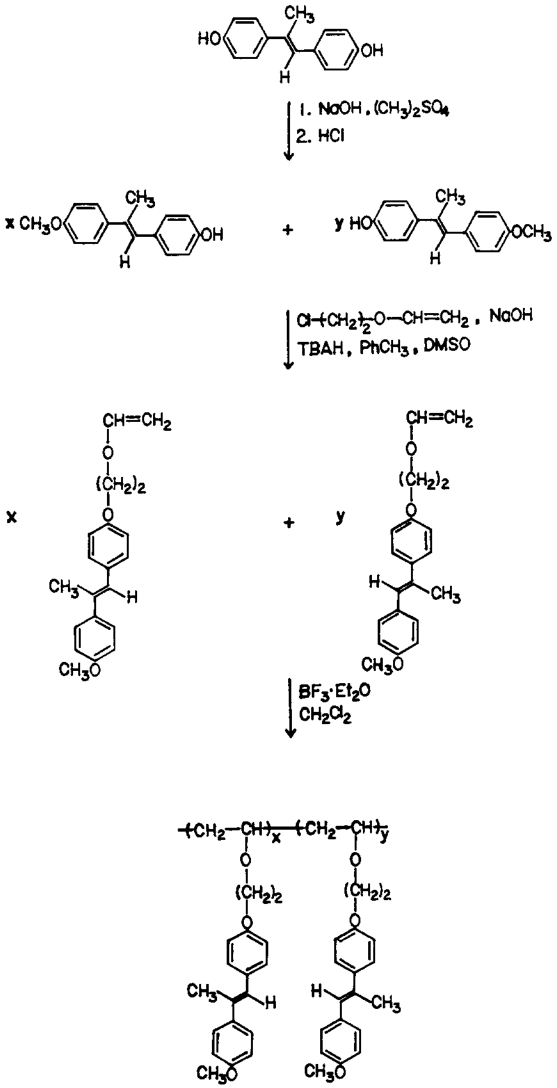
than 99.5% (HPLC). 4(4')-Methoxy-4'(4)-hydroxy-α-methylstilbene (MHMS) was synthesized as previously reported (1). Its composition was determined by 200 MHz $^1$H-NMR spectroscopy (Fig. 1).

### Synthesis of Monomers and Polymers

Scheme 1 describes the synthesis of monomers and polymers.

### Synthesis of Vinyl Ethers (VE)

Ethoxy vinyl ethers were prepared by a general procedure previously used for the synthesis of various vinyl ethers (6). An example follows. To a stirred mixture containing MHMS (2.0 g, $8.3x10^{-3}$ mole), 2-chloroethyl vinyl ether (2.1 ml, $2.1x10^{-2}$ mole), NaOH (0.42 g, $1.1x10^{-2}$ mole), toluene (15 ml) and DMSO (1 ml) and heated at 80°C, was added tetrabutylammonium hydrogen sulfate (TBAH, 0.1 g, $2.9x10^{-4}$ mole). The temperature was increased to 95°C and the reaction mixture was stirred overnight. After cooling to room temperature, the reaction



Scheme 1. Synthesis of Monomers and Polymers

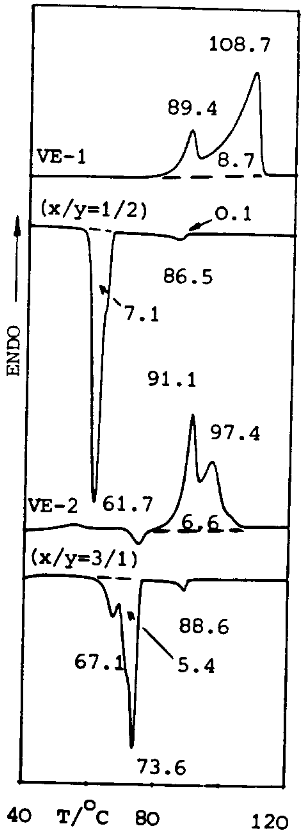


Figure 2. DSC thermograms of VE-1 and VE-2 (heating and cooling rates, 20°/min).

TABLE I: CATIONIC COPOLYMERIZATION OF VINYL ETHERS BY $BF_3.Et_2O$
SOLVENT, $CH_2Cl_2$; POLYMERIZATION TIME, 1 HR.

| MONOMER AND COMPOSITION | [M] (MOLE/L) | $[I].10^3$ (MOLE/L) | POLYMERIZATION TEMP. (°C) | CONV. % | $Mn.10^{-3}$ | Mw/Mn |
|---|---|---|---|---|---|---|
| VE-1(x/y=1/2) | 0.147 | 7.4 | -10 | 88.0 | 3.7 | 1.97 |
| VE-2(x/y=3/1) | 0.147 | 7.4 | -20 | 88.0 | 4.2 | 1.95 |
| VE-3(x/y=1.3/1) | 0.141 | 7.4 | -10 | 83.3 | 3.2 | 2.16 |

mixture was washed with NaOH 10% aqueous solution, water, dried over $MgSO_4$ and the solvent was evaporated in a rotavapor. The obtained solid was recrystallized once from methanol and once from heptane to yield 1.65 g (64%) of white crystals. Purity was higher than 99.0% (HPLC). DSC traces of two different monomer compositions are presented in Fig. 2. 200 MHz $^1H$-NMR ($CDCl_3$, $\delta$, TMS, ppm): 2.24 (s, $-CH_3$), 3.84 (s, $CH_3O-$), 4.07 (t, $-CH_2O-$), 4.23 (t, $-C\underline{H}_2OPh$), 4.10 and 4.30 (m, $CH_2=$), 6.50 - 6.60 (d of d, $-CH=$), 6.71 (s, $Ph-C\underline{H}=$), 6.89 - 7.47 (m, 8 aromatic protons).

### Polymerizations

The copolymerization of the monomers was performed in methylene chloride by using $BF_3.Et_2O$ as initiator. Experimental details are as previously reported (6). Table I presents the polymerization results.

### Techniques

The experimental techniques used in the characterization of monomers and polymers were previously described (3, 5).

## RESULTS AND DISCUSSION

Figure 1 presents the NMR spectra of two different compositions of MHMS. MHMS-1 (less soluble than MHMS-2) has a 1/2 mole ratio between the x and y isomers (i.e., x/y=1/2), while MHMS-2 has x/y=3/1. The DSC thermograms of the corresponding vinyl ethers are shown in Figure 2. Both mixtures exhibit two meltings due to the two individual isomers present in the mixture, and a monotropic nematic mesophase.

The DSC thermograms of three different copolymers (compositions are available on the figure) show in each case a glass transition temperature and three liquid crystalline transitions. With the exception of the cooling scan of PVE-1 and heating scan of PVE-2, it is difficult to separate the enthalpy changes associated with each transition in part. Nevertheless, an inspection of the heating and cooling thermograms, shows that the second LC transition from the heating scan is less suppercooled on the cooling scan than the last transition. The enthalpies associated with these two transitions (Fig. 3 cooling scans) would suggest two nematic mesophases.

However, the GPC traces of all three polymers exhibit a bimodal molecular weight distribution. The two fractions of these polymers can be separated by precipitation in acetone (giving PVE-i with $\overline{M}n$ of about 7,000) and by evaporating the acetone layer (giving PVE-s with $\overline{M}n$ of about 2,000 - 3,000). Figure 4 presents typical GPC traces for the unfractionated and fractionated PVE-2. A reinvestigation by DSC of the PVE-i

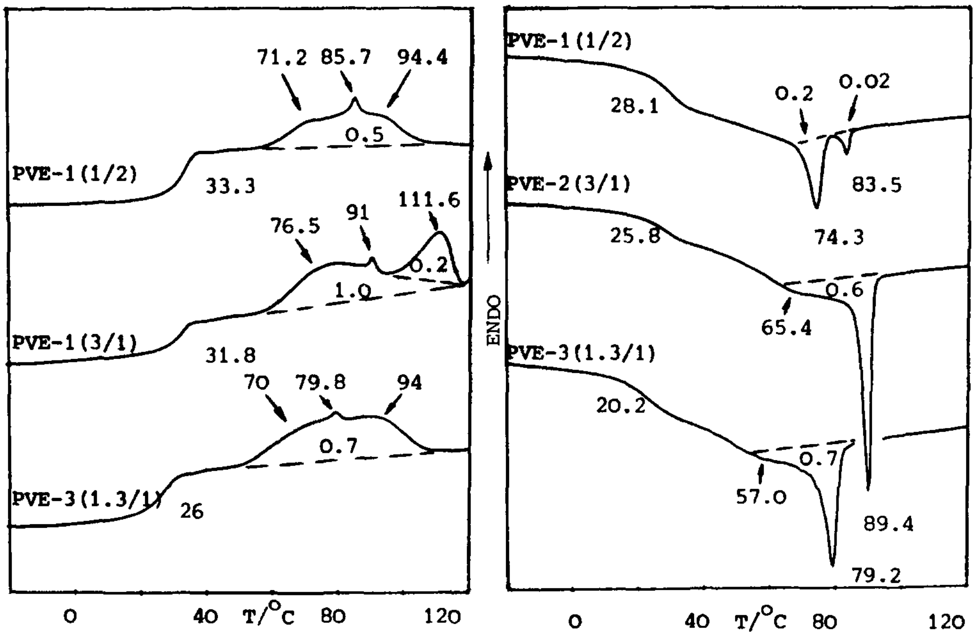


Figure 3. Heating (left side) and cooling (right side) DSC thermograms of unfractionated PVE. Enthalpy changes are in kcal/mru or mole in all figures.

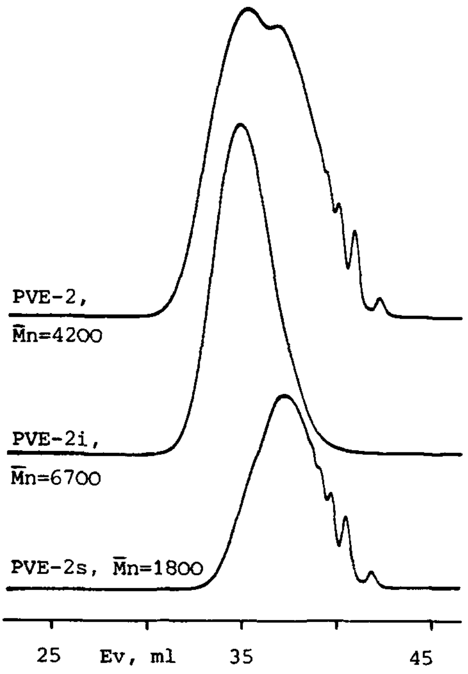


Figure 4. GPC curves of an unfractionated PVE (PVE-2), and of the high molecular weight (PVE-2i), and low molecular weight (PVE-2s) samples obtained by fractionation.

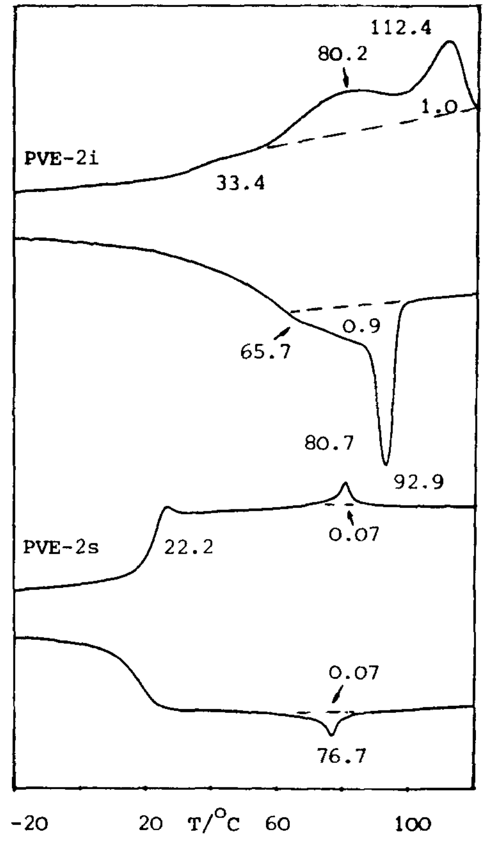


Figure 5. DSC thermograms of the fractionated samples of PVE-2.

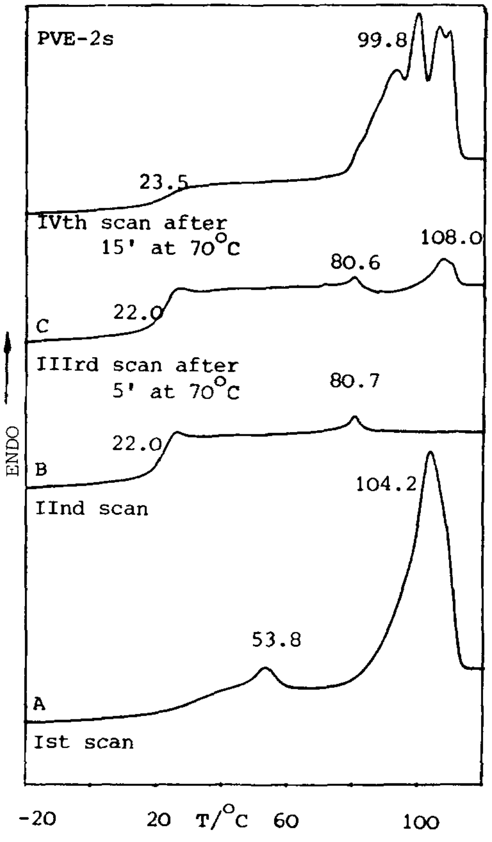


Figure 7. DSC thermograms of the PVE-2s as a function of sample thermal history.

and PVE-s shows clearly that all three copolymers consist of a mixture of two copolymers (Fig. 5). The low molecular weight fraction (PVE-s) is always nematic. The high molecular weight fraction (PVE-i) exhibits two smectic mesophases. Although the enthalpy change associated with the isotropization of the smectic mesophase (Fig. 5, PVE-2i) is lower than the expected values, the optical polarization microscopy reveals a texture which is characteristic for smectic mesophases i.e., batonnets (Fig. 6). This result is not unexpected since we have previously reported that smectic mesophases obtained from copolymers containing constitutional isomeric mesogens present low isotropization enthalpies (2). Optical polarized micrographs of the low molecular weight fractions exhibit textures characteristic for nematic mesophases (Fig. 6).

An additional interesting behavior of the low molecular weight fractions is presented in Fig. 7. As obtained by solvent evaporation, the polymer presents two meltings (Fig. 7A). The subsequent heating and cooling scans present only the nematic mesophase (curve B). This is due to the kinetically controlled crystallization process. On annealing at 70°C, the polymer crystallizes, and the melting transitions are overlapping the isotropization temperature (curves C, D). Nevertheless, when the polymer is stirred in acetone and filtered, the acetone insoluble fraction does not undergo crystallization anymore. The acetone soluble fraction contains oligomers which do not exhibit liquid crystallinity even after quenching, but it crystallizes very fast. Its $\bar{M}n$ is always about 1,000.

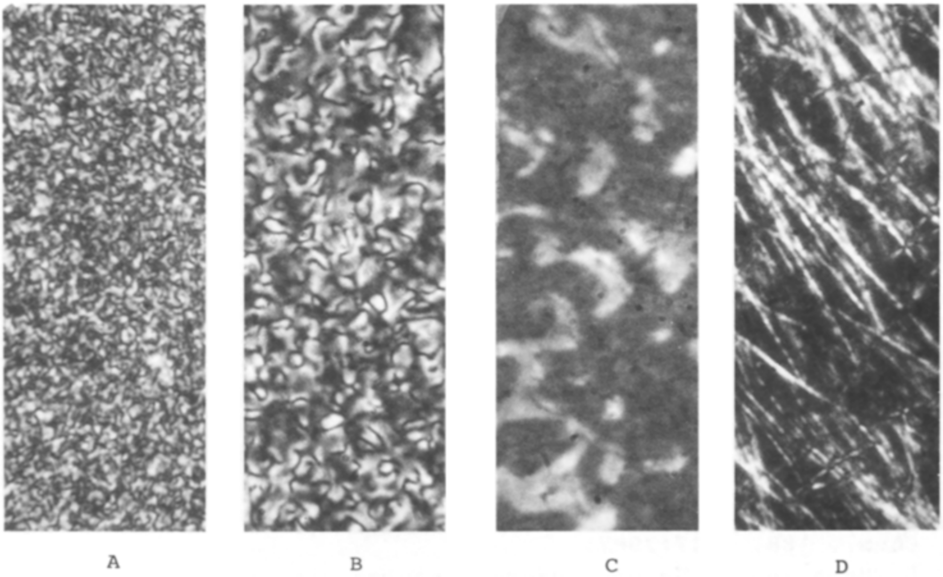


Figure 6. Typical optical polarization micrographs (magnification, 300x) of the nematic texture exhibited by PVE-2s after extraction with acetone: A) after 1 second at 78°C; B) after 1 min at 78°C; C) after 3 min at 78°C; and D) the smectic texture exhibited by PVE-2i after 2 hr at 112°C on cooling scans.

Although at the first site this copolymerization system looks unusual, in our oppinion it does not represent an unexpected result. It is well documented that carbocationic polymerization induced by undefined initiators like $BF_3.Et_2O$ can give rise to multiple initiating systems which initiate and propagate with different rate constants (i.e., at least ion-pairs and free ions) (7). Two sets of rate constants are certainly going to give rise to two different sets of reactivity ratios for the same monomer pair, and therefore, a single copolymerization experiment can provide two copolymers with different compositions. In this particular case , one composition gives a nematic copolymer while the other composition gives a smectic copolymer. Since smectics are not miscible with nematics they can be easily separated by fractionation. This supposition requires additional experiments, eventually with two different individual constitutional isomers, since $^1$H-NMR spectroscopy can not discriminate between the two isomers of the disubstituted HMS.

Last but not least, it is interesting to mention that the copolyacrylates and the copolymethacrylates containing the same mesogenic units and two methylenic units in the flexible spacer give only nematic mesophases, independent on their composition (2). The formation of smectic polymers by replacing the ester interconnecting group with an ether one, supports our previous statement that the degree of decoupling of the side-groups from the main chain is not dependent on the spacer length only, but also on the nature of the backbone-spacer interconnecting group, and on the nature of the polymer backbone (6, 8).

## ACKNOWLEDGEMENTS

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## REFERENCES

1. V. Percec, J. M. Rodriguez-Parada, C. Ericsson and H. Nava, Polym. Bull., 17, 353(1987)
2. V. Percec, C. S. Hsu and D. Tomazos, J. Polym. Sci: Part A: Polym. Chem., submitted
3. C. S. Hsu, J. M. Rodriguez-Parada and V. Percec, Makromol. Chem., 188, 1017(1987)
4. B. Hahn and V. Percec, Macromolecules, in press
5. V. Percec, H. Nava and H. Jonsson, J. Polym. Sci: Part A: Polym. Chem., 25, 1943(1987)
6. J. M. Rodriguez-Parada and V. Percec, J. Polym. Sci: Part A: Polym. Chem., 24, 1363(1986)
7. J. P. Kennedy and E. Marechal, " Carbocationic Polymerization", J. Wiley, New York, 1982
8. C. S. Hsu and V. Percec, Makromol. Chem., Rapid Commun., in press

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