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Stereospecific cationic polymerization of mesomorphic vinyl ethers characterized by ^{13}C-n.m.r., d.s.c. and X-ray diffraction

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Butylvinyl ether, 4-ethoxyphenyl 4-[4-(vinyloxy)butyloxy]benzoate and 4-ethoxyphenyl 4[11-(vinyloxy)-undecyloxy]benzoate have been polymerized using boron trifluoride diethyl etherate and tin tetrachloride as cationic initiator. Polymers produced at different temperatures and with different solvents exhibited different stereoregularities. Dyad resonances were assigned from the β-methylene absorption in a decoupled ^{13}C nuclear magnetic resonance spectrum, assuming that the polymerization proceeded according to the first-order Markovian trial. The liquid crystalline side-chain polymers were characterized by differential scanning calorimetry, hot-stage polarized light microscopy and X-ray diffraction in order to study the influence of tacticity on mesomorphism and organization. The polymers based on 4-ethoxyphenyl 4[11-(vinyloxy)undecyloxy]benzoate with different tacticities exhibited the same interdigitated smectic A and B structures. Recorded differences in isotropization temperatures could be attributed to differences in molar mass. Copyright © 1996 Elsevier Science Ltd.

(Keywords: liquid-crystalline polymer; side-chain polymer; cationic polymerization)

INTRODUCTION

Stereoregularity in vinyl monomers has been known since 1929 by the early work of Staudinger *et al.*[1]. Schildknecht *et al.*[2] investigated the cationic polymerization of vinyl ethers with boron trifluoride in different solvents and found that some of the polymers were semicrystalline, which according to the authors reflected a more regular tacticity in these polymers. Poly(vinyl ether)s with tacticities ranging from isotactic and syndiotactic to atactic have been prepared by changing the polarity of the solvent and the polymerization temperature[2–9]. This variability can be attributed to the fact that the degree of dissociation of the end-group ion pair affects the stereochemistry of the propagation reaction.

Side-chain liquid crystalline polymers have received considerable attention during the last 15 years due to their potential use in electro-optical applications[10–12]. Highly ordered films of liquid crystalline polymers are potentially useful in various electro-optical applications. A high degree of orientational order of the system requires not only control of the alignment but also a regular chain structure. Little attention has been given to the configuration of the backbone, and to the effect of tacticity of the polymer on the layer structure and morphology. Cationic stereospecific polymerization is one potential method, explored in this study, to achieve polymers with different tacticities.

This paper presents data on thermal transitions and morphology obtained by differential scanning calorimetry (d.s.c.), polarized light microscopy and X-ray diffraction on a series of poly(vinyl ether)s with different tacticities as revealed by ^{13}C-nuclear magnetic resonance (n.m.r.).

EXPERIMENTAL

Materials

Toluene-4-sulfonyl chloride (Merck), ethyl-4-hydroxybenzoate (Aldrich), 4-pyrrolidinopyridine (Aldrich), *N,N'*-dicyclohexylcarbodiimide (Aldrich) and 4-ethoxyphenol (Aldrich) were used without further purification. 4-Hydroxybutyl vinyl ether (GAF) and butylvinyl ether (**1**) (Aldrich) were distilled before use. Methylene chloride, CH_2Cl_2, was purified by stirring it with sulfuric acid (10:1) overnight, exchanging the sulfuric acid twice and then distilling it over CaH_2. 11-Bromundecanyl vinyl ether and 1,10-phenanthroline palladium (II)-diacetate complex were synthesized according to Percec *et al.*[13].

Synthesis of monomers

The synthesis of 4-ethoxyphenyl 4-[4-(vinyloxy)butyloxy] benzoate (**2**) was performed according to *Scheme 1*.

4-Hydroxybutyl vinyl ether (10 g; 86 mmol) was stirred at 0–5°C and toluene-4-sulfonyl chloride (18 g; 94.6 mmol) dissolved in pyridine (27.3 g; 345 mmol) was added slowly. The reaction mixture was stirred for 3 h, stored in a refrigerator overnight and then filtered. The solution was extracted 3× with water and dried over $MgSO_4$. Flash chromatography was used with CH_2Cl_2 as eluent to purify the tosylated product.

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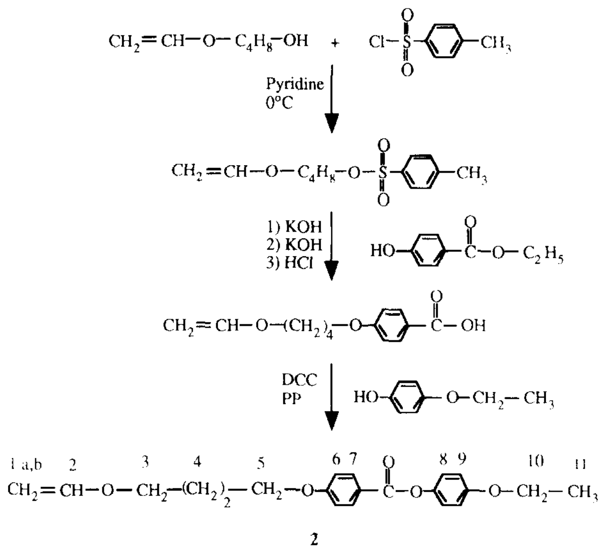
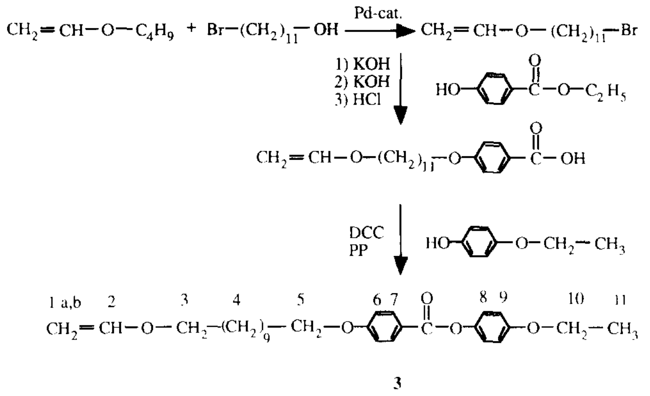
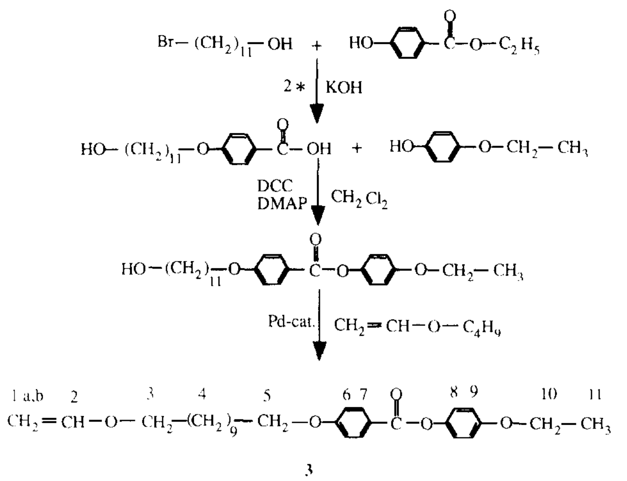


Scheme 1 Synthesis of (**2**)



Scheme 2 Synthesis of (**3**) with the butylvinyl ether added in the first step



Scheme 3 Synthesis of (**3**) with the butylvinyl ether added in the final step

Ethyl-4-hydroxybenzoate (6.8 g; 41 mmol) and potassium hydroxide (2.3 g; 41 mmol) was stirred at room temperature in ethanol (99.5%). Butylvinyl ether tosylate (10 g; 37 mmol) was added and the reaction mixture was heated under reflux for 24 h.

Potassium hydroxide (3.1 g; 56 mmol) was added to the reaction mixture which was kept at the reflux temperature for an additional 24 h. After being cooled to room temperature, the reaction mixture was neutralized with 1 M hydrochloric acid to pH 6. The acid was filtered and recrystallized from ethanol. Yield 80%.

The acid (10 g; 42.3 mmol) was then stirred in CH_2Cl_2 (15 ml g acid^{-1}) together with 4-ethoxyphenol (3.6 g; 30.2 mmol) at room temperature for 30 min. A solution of 4-pyrrolidinopyridine (PP) (4.5 g; 30.2 mmol) and 1,3-dicyclohexylcarbodiimide (DCC) (6.9 g; 33.2 mmol) in CH_2Cl_2 was added and the reaction mixture was kept at the reflux temperature for 4 days, then cooled and filtered. The mixture was then centrifuged and evaporated on silica gel 60 (Merck). Liquid chromatography with a gradient of hexane and ethyl acetate was used for purification. The yield after chromatography was 40%. The purity of the monomer according to h.p.l.c. was 99.9%. ^{1}H-n.m.r. ($CDCl_3$, TMS, δ (ppm)); 1.3–1.5 (3 H, 11, *t*), 1.8–2.1 (4 H, 4, *m*), 3.65–3.75 (2 H, 3, *t*), 3.9–4.1 (5 H 1*a*, 5 and 10, *m*), 4.1–4.3 (1 H, 1*b*, *dd*), 6.4–6.6 (1 H, 2, *q*), 6.85–7.1 (4 H, 6 and 9, *m*), 7.1–7.25 (2 H, 8, *d*), 8.15–8.3 (2 H, 7, *d*). Thermal characterization: k93i, i82n72k.

The synthesis of 4-ethoxyphenyl 4[11-(vinyloxy)undecyloxy]benzoate (**3**) with the butylvinyl ether added in the first step was performed according to *Scheme 2*.

Ethyl-4-hydroxybenzoate (6.6 g; 39.7 mmol) and potassium hydroxide (2.23 g; 39.7 mmol) were stirred at room temperature with ethanol (99.5%). 11-Bromundecanyl vinyl ether (10 g; 36 mmol) was added and the reaction mixture was kept at reflux temperature for 24 h. Potassium hydroxide (3.04 g; 54.1 mmol) was added and the mixture was refluxed for an additional 24 h. After it had cooled to room temperature, the reaction mixture was neutralized with 1 M hydrochloric acid to pH 6. The acid was filtered and recrystallized from ethanol. Yield 80%.

The acid (5 g; 14.9 mmol) was then stirred in CH_2Cl_2 (15 ml g^{-1}) together with 4-ethoxyphenol (1.88 g; 13.6 mmol) at room temperature. PP (2.03 g; 13.6 mmol) and DDC (3.09 g; 14.97 mmol) both dissolved in CH_2Cl_2 were added. The reaction mixture was heated at reflux temperature for 4 days, then cooled and filtered. The mixture was then centrifuged, evaporated on silica gel 60 (Merck) and purified using liquid column chromatography with a gradient of hexane and ethyl acetate. The yield after chromatography was 40%. The purity of the monomer according to h.p.l.c. was 99.9%. ^{1}H-n.m.r. ($CDCl_3$, TMS, δ (ppm)); 1.35–1.50 (3 H, 11, *t*), 1.50–1.95 (18 H, 4, *m*,), 3.60–3.80 (2 H, 3, *t*,), 3.95–4.10 (5 H, 10, 5 and 1*a*, *m*), 4.1–4.25 (1 H, 1*b*, *dd*), 6.40–6.55 (1 H, 2, *q*), 6.85–7.05 (4 H, 6 and 9, *m*), 7.05–7.20 (2 H, 8, *d*), 8.05–8.20 (2 H, 7, *d*). Thermal characterization: k67n76i, i70n59s_A 28k.

Synthesis of **3** with the butylvinyl added in the last step is presented in *Scheme 3*.

Ethyl-4-hydroxybenzoate (7.28 g; 44 mmol) and potassium hydroxide (2.47 g; 44 mmol) were stirred at room temperature in ethanol (99.5%). 11-Bromundecanol (10 g; 40 mmol) was added and the reaction mixture was heated at reflux for 48 h. Potassium hydroxide (3.35 g; 60 mmol) was added and the reaction was continued at reflux temperature for an additional 48 h. After cooling to room temperature, the reaction mixture was neutralized with 1 M hydrochloric acid to pH 2–3 to give the acid. The acid was filtered and recrystallized from ethanol.

The acid (5 g; 16.2 mmol) was then stirred in CH_2Cl_2 ($15\,ml\,g^{-1}$) together with 4-ethoxyphenol (2.04 g; 14.8 mmol) at room temperature. The acid was soluble in CH_2Cl_2 only at elevated temperatures. A solution of dimethylaminopyridine (DMAP) (0.27 g; 2.2 mmol) and 1, 3-DDC (3.34 g; 16.2 mmol) in CH_2Cl_2 was added. The reaction mixture was refluxed for 2–4 h, cooled and filtered. The white powder was precipitated from ethanol. Yield 75%.

1,10-Phenanthroline palladium(II)diacetate (0.2 g; 0.5 mmol) and chloroform (10 ml) were stirred for 1 h. Butylvinyl ether (30.3 g; 302 mmol) and hydroxyundecanyl (*p*-(4-ethoxy) phenyl) benzoate (2.8 g; 7 mmol) was added to the reaction mixture. The temperature was raised to 65°C and the reaction was continued for 16 h. The reaction mixture was evaporated on silica gel and liquid chromatography was performed using hexane as eluent. The solvent was evaporated and the product recrystallized from ethanol. Yield 80%. The purity of the monomer according to h.p.l.c. was 99.9%. ^1H-n.m.r. ($CDCl_3$, TMS, δ (ppm)); 1.20–1.58 (17 H, $\underline{9}$ and $\underline{2}$, *t*), 1.60–1.90 (4 H, $\underline{2}$, *m*), 3.60–3.75 (2 H, $\underline{1}$, *t*), 3.95–4.10 (5 H, $\underline{8}$ and $\underline{3}$, *m*), 6.85–7.02 (4 H, $\underline{4}$ and $\underline{7}$, *m*), 7.05–7.20 (2 H, $\underline{6}$, *d*), 8.1–8.20 (2 H, $\underline{5}$, *d*). Thermal characterization: k67n76i; i70n59s_A 28k.

Initiators

Boron trifluoride diethyl etherate, BF_3OEt_2 (Aldrich) and tin tetrachloride, $SnCl_4$ (Aldrich), were used without further purification.

Polymerization

All equipment was dried and purged with dry argon. Typically 0.1 g of the monomer was dissolved in 1.5 ml solvent. 2.5 mM of initiator solution was injected by syringe through a rubber septum vessel containing the stirred solution of the monomer and distilled solvent. The reaction mixture became violet directly after addition of the initiator, which indicated that the initiator was active. The polymerization was terminated after 30 min of reaction by injecting methanol and the mixture was then poured into a large excess of methanol. The precipitate was filtered and recrystallized from ethanol.

Characterization

Size exclusion chromatography (s.e.c.) using a Waters Model 510, WISP 710B, equipped with a Differential Refractometer 410 (THF as solvent; calibrated with polystyrene standards) was used for the assessment of molar mass distribution. The number average molar mass values presented in this paper are all given as polystyrene equivalents. Differential scanning calorimetry (d.s.c.) was performed using a temperature- and energy-calibrated Perkin Elmer DSC-7 at heating and cooling rates of $10°C\,min^{-1}$. Hot stage polarized light microscopy was carried out in a Leitz Ortholux POL BKII optical microscope equipped with a Mettler Hot Stage FP 82 controlled by a Mettler FP80 Central Processor. ^1H- n.m.r. and ^{13}C-n.m.r. (400 MHz) were performed on a Bruker AM-400 spectrometer using $CDCl_3$ as solvent. For tacticity evaluation, the spectra were measured with proton-decoupling, without NOE and with a delay time of 4 × spin-lattice relaxation time (T_1) between pulses. T_1s were measured with an inversion-recovery pulse sequence with different delays between pulses. The ^{13}C-n.m.r. spectra were integrated by measuring the integral under the β-methylene peak (38–42 ppm) giving the values for the *meso* and *racemic* sequences. Fourier transform infra-red (*FT* i.r.) spectra were obtained using a Perkin Elmer 1700 *FT* i.r. spectrometer. X-ray scattering patterns were recorded in a Statton camera, using Ni-filtered CuKα radiation from a Philips PW1830 Generator.

RESULTS AND DISCUSSION

The liquid crystalline monomers with two different spacer lengths, (**2**) and (**3**) were synthesized according to *Schemes 2* and *3*. A comparison between the two synthetic methods (*Schemes 2* and *3*) shows that when DMAP was used instead of PP in the last esterification step, the yield became higher, the required reaction time was shorter and fewer side reactions occurred. Also, as shown in *Scheme 3*, the precipitation of the acid was performed without the presence of acid-sensitive vinyl ether groups which is indeed favourable.

It has been found for the other vinyl ethers that polymers with different tacticities can be prepared by changing the polarity of the solvent, which indicates that the degree of dissociation of the end group ion pair influences the stereochemistry of the propagation reaction[2–9]. The penultimate group effect has been confirmed to exist in the cationic polymerization of vinyl ethers and the propagation steps were assumed to be expressed by the first-order Markovian statistics[14].

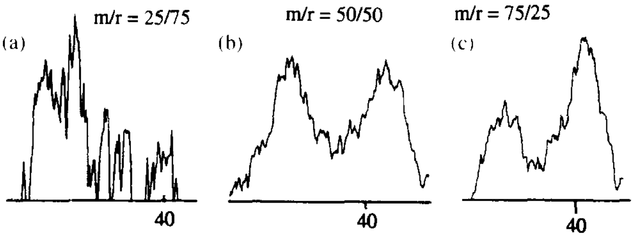


Figure 1 ^{13}C-n.m.r. spectra showing the β-methylene peak at 38–42 ppm for poly(**3**) prepared at (a) 25°C in C_7H_8; (b) 0°C in CH_2Cl_2; (c) −35°C in C_7H_8. The molar ratios of *meso* to *racemic* dyads are shown adjacent to each spectrum

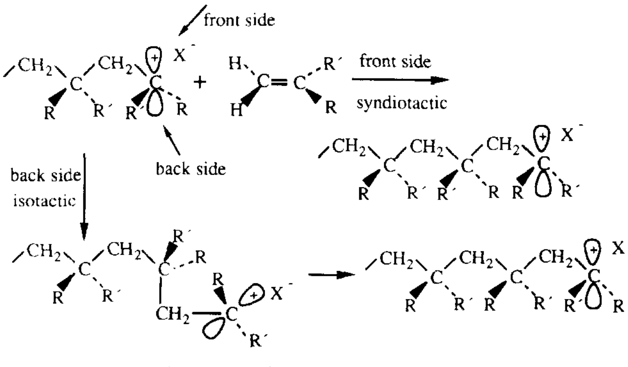


Figure 2 The steric course of stereospecific cationic propagation

Table 1 Tacticity and molar mass of synthesized polymers

[Monomer]/ [Initiator] (mol/mol)	Solvent	Temperature (°C)	*m/r*[a]	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$
(**1**) polymerized with boron trifluoride diethyl etherate					
400	C_7H_8	−78	83/17	69 100	2.0
400	C_7C_8	−35	72/28	86 400	2.2
400	C_7H_8	25	52/48	21 900	2.3
400	C_3H_6O	−78	50/50	6 100	2.3
(**1**) polymerized with tin tetrachloride					
400	CH_2Cl_2	0	52/48	9 700	2.6
20	CH_2Cl_2	−60	70/30	35 000	1.5
20	CH_2Cl_2	−35	50/50	15 600	2.4
20	CH_2Cl_2	25	43/57	15 700	2.9
(**2**) polymerized with boron trifluoride diethyl etherate					
400	C_7H_8	−35	64/36	10 200	2.0
400	CH_2Cl_2	0	64/36	14 300	2.6
400	C_6H_{14}/C_7H_8	−20	50/50	13 500	2.1
400	C_2H_3N	25	36/64	4 700	2.3
(**3**) polymerized with boron trifluoride diethyl etherate					
400	C_7H_8	−35	75/25	13 300	1.7
400	C_7H_8	−20	65/35	12 500	1.8
400	C_7H_8	25	50/50	11 700	1.8
400	CH_2Cl_2	0	50/50	12 600	1.7
400	C_2H_3N/CH_2Cl_2	−10	36/64	3 800	1.7
400	C_2H_3N	25	25/75	5 000	1.7

[a] *Meso*-to-*racemic* dyad molar ratio from ^{13}C-n.m.r. data; accuracy: ±5% (absolute)

The butylvinyl either (**1**) and the two liquid crystalline monomers (**2** and **3**) were polymerized at different temperatures in various solvents in order to obtain polymers with different tacticities. The spin-lattice relaxation times. T_1, were measured for all polymers, and T_1 showed only a weak dependence on tacticity and molar mass. Important structural features are the length and the flexibility of the side-chain which both have a pronounced effect on T_1. It was not possible to match the viscosities of poly(**1**) and poly(**3**) and it was not therefore possible to make a direct comparison of the T_1 values. T_1 for the β-methylene carbon was 0.5 s in poly(**1**) and 0.4 s in poly(**3**).

The ^{13}C-n.m.r. spectra of poly(**3**)s of different tacticity were essentially interpreted according to references 6–10, 15 and 16, analysing the β-methylene peak (*Figure 1*). The preparation of isotactic, atactic and syndiotactic polymers could be controlled by changing the polarity of the solvent, which indicates that the degree of dissociation of the end-group ion pair influences the stereochemistry of the propagation reaction (*Table 1*). These findings can be explained by a model which considers the sp^2 hybridization of the terminal chain carbon and the stability of the growing chain ion pair (*Figure 2*). Polar solvents would stabilize more separated ion pairs and favour front-side attack, thus minimizing steric repulsion between bulky groups present in the monomer and the growing polymer chain, leading to the formation of predominantly syndiotactic polymers. In unpolar solvents, on the other hand, the chain end exists as an ion pair. The dissociative bond strength is in this case expected to depend on the polarity of the solvent and on the polarity of the counterion. It may thus be assumed that considerable energy is required to separate the ion pair, and that the incoming monomer prefers back-side attack, i.e. a S_N2 reaction leading to isotactic placement. The fact that increasing temperature decreases stereoregularity can be explained by small differences in activation energy for front- and back-side attack as well as by the effect on the conformational mobility of the growing chain end.

Data for the dyad tacticities obtained by analysing the β-methylene peak area are presented in *Table 1*. These data are in accordance with earlier reports[3,7,8,15,16] on other poly(vinyl ether)s. Butylvinyl ether polymerized with BF_3OEt_2 in a non-polar solvent at low temperatures yielded a predominantly isotactic polymer. Syndiotacticity was not achieved when the polarity of the solvent and the reaction temperature were increased. It has been reported[5,17] that syndiotactic poly(vinyl ether)s were only obtained in a few cases, with monomers containing bulky substituents, e.g. trimethylvinylsilane, methylvinyl ether, *t*-butylvinyl ether in a polar solvent under homogeneous conditions. Murahashi *et al.*[18] reported

Table 2 Structural features of smectic structures of poly(**3**)s

m/r	Smectic structure	Layer spacing (Å)	Intermesogenic spacing (Å)
75/25	B	34.7	4.5
50/50	B	34.6	4.5
75/25	A	32.4	4.7–4.9
50/50	A	32.3	4.6–4.8

Table 3 Transition temperatures of (**3**) and poly(**3**)s

m/r	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$	Transition temperatures in °C and corresponding enthalpy changes in J g^{-1}; 2nd heading and cooling cycles[a] Heating	Cooling
(**3**)			k67 (70)n76(2.5)i	i70(2.6)n59(3.7)S_A28(60)k
Poly(**3**)				
75/25	13 300	1.7	S_B73(11)S_A142(10)i	i131(10.5)S_A60(12)S_B
50/50	12 600	1.7	S_B71(12)S_A145(11.4)i	i134(11)S_A62(11)S_B
36/64	3 750	1.7	S_B54(18.3)S_A99(11.1)i	i90(8.9)S_A43(15.5)S_B
25/75	5 000	1.7	S_B60(15)S_A115(11.4)i	i105(9)S_A51(14)S_B

[a] i, isotropic; n, nematic; S_A, smectic A; S_B, smectic B; k, crystalline; transition enthalpies are given within parentheses

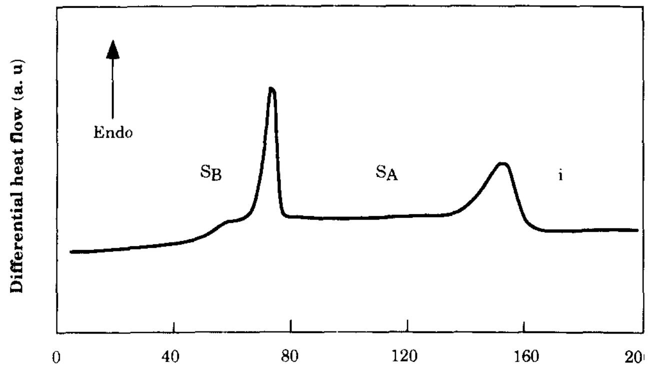


Figure 3 Heating thermogram of poly(**3**) 50/50 (*m*/*r*) obtained at 10°C min^{-1} scanning rate

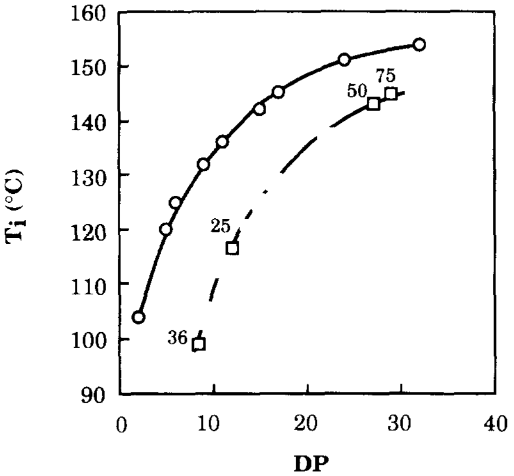


Figure 4 Isotropization temperature as a function of degree of polymerization (*DP*) for poly(**3**) (□, the molar *meso*-dyad contents are shown adjacent to each data point) and poly(9-(*p*-(cyanobiphenyl)-oxy) nonanyl vinyl ether) (○). Data for the latter polymer were taken from Gedde *et al.*[20]. Note that the *DP* data for poly(**3**) are based on s.e.c. polystyrene equivalents

that vinyltrimethylsilyl ether polymerized in methylene chloride and $SnCl_4$ at −78°C yielded predominantly syndiotactic polymer. There was no such result when butylvinyl ether was polymerized with $SnCl_4$ (*Table 1*). This may be due to the lesser bulkiness of the butylvinyl ether. Matsuzaki *et al.*[8,15] reported that there was no large difference between the behaviour of BF_3OEt_2 and $SnCl_4$ when methylvinyl ethers were polymerized.

With monomer **3** it was possible to obtain polymers with a broader tacticity range (*Table 1*). This is probably a consequence of the bulky side group present in this monomer. Monomer **2**, with a shorter pendant group, yielded polymers with less pronounced stereoregularity (*Table 1*).

Kunitake and Takarabe[9] showed that when *tert*-butylvinyl ether was polymerized with a series of triphenylmethyl salts, the isotacticity increased with decreasing polarity and decreased with increasing radius of the counterion. It was suggested that the front-side attack becomes favourable as the coulomb interaction between the ions is weakened. The tightness decreases with increasing anion size. Steric hindrance of bulky substituents of terminal and penultimate monomer units may be minimized, and the assumption of a planar carbo-cation attack of monomer on the same side as the counterion leads mainly to syndiotactic placements. When the bulkiness of the monomer side chain is reduced, the steric repulsion of the side chain and the counterion will not be significant. A larger counterion may then retard the front-side attack, giving more isotactic placement.

Poly(**3**) exhibited a single SAXS diffraction peak and at temperatures of 23°C and 100°C the layer thicknesses were 34.6 Å and 32.4 Å respectively (*Table 2*). Further analysis of the X-ray diffraction pattern, also including the wide-angle scattering (WAXS) peaks showed that this polymer exhibited smectic B and smectic A mesomorphisms at 23°C and 100°C respectively (see also *Table 3*). The assessment of the mesophases was also supported by polarized light microscopy showing the formation of batonettes from the melt, followed by the formation of a focal conic structure typical of smectic A mesomorphism. The data obtained for the smectic layer spacings indicated interdigitated smectic structures A_d and B_d, according to the conformational analysis of Sahlén *et al.*[19]. Most important, however, was the fact that the layer spacing was insensitive to variations in tacticity (*Table 2*). The sharp WAXS reflection recorded at room temperature, indicative of smectic B mesomorphism, was also unaffected by changes in tacticity (*Table 2*). This invariance of tacticity in intermesogenic group spacing was also evident in the case of the smectic A phase present at 100°C (*Table 2*). Further structural characterization of poly(**2**) was not performed because of the less pronounced variation of tacticity in these polymers (*Table 1*).

Poly(**3**) exhibited, according to d.s.c., two first order transitions during both heating and cooling, indicative of an enantiotropic behaviour of these polymers. Data for the transition temperatures and enthalpies are summarized in *Table 3*. A typical heating thermogram of poly(**3**) showing two prominent first order transitions (from smectic B to smectic A and from smectic A to isotropic melt) is presented in *Figure 3*. Two prominent first order transitions. The variation in the transition temperatures is significant but it related mostly to the difference in molar mass of the different polymers and essentially not to the variation in tacticity (*Table 3*). The isotropization temperature data reported in this paper are compared in *Figure 4* with corresponding data for an atactic poly(vinyl ether) reported in reference 20. Both series of polymers exhibited essentially the same molar mass dependence, and the effect of tacticity on the isotropization temperature seems negligible.

CONCLUSIONS

Polymers based on butylvinyl ether (**1**), 4-ethoxyphenyl 4-[4-(vinyloxy)butyloxy]benzoate (**2**) and 4-ethoxyphenyl 4-[11-(vinyloxy)undecyloxy]benzoate (**3**) with different tacticities were synthesized, although there was a problem in achieving predominantly syndiotactic polymers with sufficiently high molar mass. X-ray diffraction of poly(**3**) indicated the formation of identical interdigitated smectic layers in polymers with different tacticities. The variation in transition temperatures recorded for different poly(**3**) seems to be related more to molar mass than to tacticity.

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