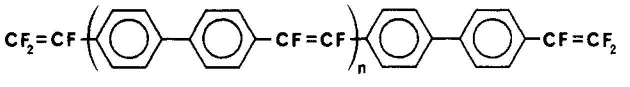
Macromolecules **1987**, *20*, 462–464

Table I
Elemental Analysis of 1

	% C	% H	% F
found	76.55	4.04	18.99
calcd for n = 10	76.28	3.61	20.11
calcd for n = 20	77.31	3.68	19.00

afford poly(4,4′-biphenyldiyl-1,2-difluoroethenyl), 1 (90%, based on the repeat unit).



1

Characterization of 1 by infrared spectroscopy, CP-MAS ^{13}C NMR spectroscopy, and elemental analysis was consistent with the assigned structure. Infrared spectroscopy (KBr pellet) showed aromatic absorptions at 3040, 1605, 1500, and 820 (para substitution) cm^{-1} and absorptions associated with fluorine substitution at 1755 (CF_2=CF— end groups), 1680 (—CF=CF—), and 1275 and 1105 (s, C—F) cm^{-1}. For NMR analysis, solid-state techniques were employed due to the intractable nature of 1. ^{1}H–^{13}C cross polarization magic angle spinning (CP-MAS) NMR spectroscopy at 62.9 MHz showed carbon-13 chemical shifts for the biphenyl moiety at 128 and 139 ppm (relative to Me$_4$Si).[14] Good agreement between elemental analysis and the proposed structure of 1 was obtained (Table I). The degree of polymerization was estimated to be 10–20, assuming that all chains were terminated with trifluorovinyl end groups (a slight excess of tetrafluoroethylene was used in the polymerization reaction).

Differential scanning calorimetry (DSC) of 1 revealed no T_g or T_m over the temperature range 40–500 °C. While the polymer was stable at room temperature for several months, heating in air resulted in oxidation of the trifluorovinyl end groups (DSC exotherm at 225 °C). Infrared spectroscopy after heating in air showed the absence of the trifluorovinyl absorption at 1755 cm^{-1} and the appearance of a new absorption at 1810 cm^{-1}. Oxidation apparently resulted in conversion of the trifluorovinyl end groups to acid fluorides. This was consonant with a previous observation[15] that oxidation of trifluorostyrene in moist air afforded the corresponding carboxylic acid, probably by hydrolysis of the acid fluoride intermediate.

The electrical conductivity of a pressed powder pellet of 1 was 5 × 10^{-9} (Ω cm)$^{-1}$. The conductivity increased to 1.7 × 10^{-4} (Ω cm)$^{-1}$ by exposing the powder to 250 Torr of AsF$_5$ for 1 h prior to pressing (unoptimized single-point determination). Further conductivity evaluation and the preparation of other poly(arylenedifluorovinylenes) will be examined in an effort to elucidate the structure–conductivity relationships of these fluorinated polymers.

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Registry No. 1 (SRU), 106213-30-3; (copolymer), 106213-31-4; AsF$_5$, 7784-36-3.

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Synthesis of Liquid Crystalline Side-Chain Polyacrylates by Solid-Liquid Phase-Transfer Catalysis without Added Solvent

During the last decade, the chemical and physical properties and potential applications of liquid crystalline side-chain polymers have been widely investigated.[1,2] A variety of synthetic approaches have been utilized to prepare these mesomorphic side-chain polymers. These include free-radical polymerization of mesogenic methacrylates,[3] acrylates,[4] and chloroacrylates;[5] anionic[6] and group-transfer[7] polymerizations of methacrylates; ring-opening polymerizations of glycidyl esters to side-chain poly(ethylene oxides);[8] polycondensations to give side-chain polyesters;[9] and transformation of "reactive polymers" by reaction with terminally functionalized mesogens to give mesomorphic polysiloxanes,[1,10-13] polyacrylates,[14] polymethacrylates,[15] poly(methyl vinyl ether comaleates),[16] and polyitaconates.[17]

The last of these methods has the advantage that known polymers are used to prepare the liquid crystalline polymers. It also permits the preparation of such nonclassical mesomorphic polymers as poly(methyl vinyl ether comaleates)[16] and polyitaconates,[17] which are not easily accessible by other routes. We have used this procedure to devise a simple synthesis of mesomorphic polyacrylates by reaction of sodium polyacrylates with ω-bromoalkyl esters

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Table I
Mesomorphic Properties of ω-Bromoalkyl Esters (1, 2)

product no.	n	m	X	phase transitions[a]
1a	6	1	$-CO_2-$	K 78 (N 75.5) I
1b	6	3	$-CO_2-$	K 71.5 (SA 55) N 81 I
1c	6	4	$-CO_2-$	K 71 (SA 56) N 80.5 I
1d	6	5	$-CO_2-$	K 55 SA 70 N 82.5 I
2a	6	1	$-O_2C-$	K 62 N 69.5 I
2b	6	4	$-O_2C-$	K 61 N 85 I
2c	8	4	$-O_2C-$	K 65 N 77 I
2d	11	4	$-O_2C-$	K 61 N 76 I

[a] Transition temperatures in °C; K = crystal, SA = smectic A, N = nematic, and I = isotropic.

(**1**, **2**) under conditions of solid–liquid phase-transfer catalysis without added solvent.

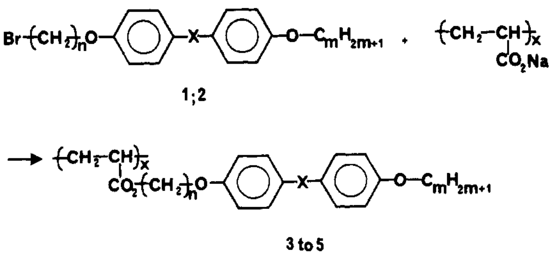
Results and Discussion. We recently described a new synthesis of mesomorphic polyacrylates by reaction of sodium polyacrylates with mesogenic ω-bromoalkyl esters under liquid–liquid phase-transfer conditions.[14] This reaction is similar to the well-known alkylation of carboxylate anions by alkyl halides to give carboxylic esters under liquid–liquid phase-transfer conditions.[18] Barry et al. have shown that powdered potassium acetate or benzoate can be converted into esters by reaction with alkyl halides without added solvent in the presence of catalytic amounts of a tetraalkylammonium salt.[19,20] This solid–liquid phase-transfer alkylation is easier than alkylation under classical phase-transfer conditions, and the yields are nearly quantitative.

We have now applied this procedure to the preparation of mesomorphic polyacrylates. The synthesis (Scheme I) involves the displacement of bromide ion from ω-bromoalkyl esters **1** and **2** with sodium polyacrylates using phase-transfer catalysis. Esters **1** and **2**, in their isotropic states, were heated with powdered sodium polyacrylate at 100 °C for 96 h in the presence of a catalytic amount of tetrabutylammonium bromide. The mesomorphic polyacrylates were isolated by extraction of the cooled solid mass with chloroform and precipitated from the chloroform solution by addition of methanol. The melting and transition temperatures of the ω-bromoalkyl esters are given in Table I, while Table II lists the polymer yields, inherent viscosities, and transition temperatures.

All of the polyacrylates so prepared exhibit liquid crystalline behavior and have transition temperatures in reasonable agreement with those reported for the same polymers synthesized by free-radical polymerization (see, e.g., ref 4 for **3a**). Our procedure also provided a route to new polymers **5a–d**, which would be rather difficult to prepare by conventional methods.

Further work is in progress to optimize polymer yields by studies of the phase-transfer catalyst and the molar ratio of alkyl halide to polyacrylate.

Scheme I



1;2

3 to 5

Experimental Section. Thermal properties of the compounds were studied by optical microscopy using a polarizing microscope (Leitz Ortholux II Pol BK) fitted with a Mettler FP 82 heating stage and FP 80 control unit. They were checked by DSC (Mettler FP 85 TA cell and FP 80 control unit). Inherent viscosities of the polymers were determined at 25 °C using 0.5 g·dL^{-1} solutions in chloroform. KPG Ubbelohde microviscometers were used with an AVS 300 automatic viscometer assembly (Schot-Geräte). Infrared spectra were determined with a Shimadzu IR-408 instrument.

Materials. The sodium polyacrylates ($\overline{MW}$ = 6000 and $\overline{MW}$ = 2100) used in the preparation of mesomorphic polymers were purchased commercially (Polysciences Inc.) and were used as received. Other compounds and solvents were from commercial sources.

4′-Butoxyphenyl 4-((6-Bromohexyl)oxy)benzoate (**1c**). Typical Procedure: 4′-(Butoxyphenyl 4-hydroxybenzoate (2.86 g, 0.01 mol), 1,6-dibromohexane (24.4 g, 0.1 mol), potassium carbonate (10 g, 0.072 mol), and potassium iodide (0.1 g, 6 × 10^{-4} mol) in acetone (40 mL) were refluxed for 24 h. After cooling to room temperature, the reaction mixture was filtered to remove the inorganic salts. Acetone was eliminated from the filtrate by distillation. The waxy residue was diluted with hexane (100 mL), and the resulting solution was cooled to −18 °C for a few hours. The precipitate was filtered off, washed with cold hexane, and recrystallized from hexane to a constant transition temperature (K 71 (SA 56) N 80.5 I) (2.8 g, 62%).

Mesomorphic Polyacrylate (Polymer **3a**). Typical Procedure: The powdered sodium polyacrylate (0.085 g, 9 × 10^{-4} mol), 4′-methoxyphenyl 4-((6-bromohexyl)oxy)benzoate (0.49 g, 1.2 × 10^{-3} mol), and tetrabutylammonium bromide (0.05 g, 1.5 × 10^{-4} mol) were placed in a 20-mL round-bottomed flask, and the flask was plunged in an oil bath preheated to 100 °C. After the alkylating agent melted, the mixture was slowly stirred and heated for 96 h, keeping the temperature at 100 °C. After cooling to room temperature, the solid mass was triturated with chloroform (20 mL) to dissolve the organic compounds. After filtration through filter paper to remove the insoluble inorganic salts, the chloroform solution was concentrated

Table II
Yields, Inherent Viscosities, and Transition Temperatures of Mesomorphic Polyacrylates (3–5)

polymer no.	n	m	X	yield, %	η_{inh},[a] dL·g^{-1}	phase transitions,[b] °C
3a	6	1	$-CO_2-$	20	0.086	g 35–40 S 97–98 N 115–120 I
3b	6	3	$-CO_2-$	23	0.12	g 35–40 S 90–92 N 113–116 I
3c	6	4	$-CO_2-$	23	0.078	g 25–30 S 65–70 N 105–115 I
3d	6	5	$-CO_2-$	29	0.05	g 30–35 S 58–60 N 105–110 I
4a[c]	6	1	$-CO_2-$	33	0.048	g 25–30 S 80–85 N 108–113 I
4b[c]	6	4	$-CO_2-$	35	0.048	g 30–35 S 55–58 N 95–105 I
5a	6	1	$-O_2C-$	23	0.054	g 45–50 S 99–100 N 103–106 I
5b	6	4	$-O_2C-$	30	0.06	g 35–40 S 80–85 N 109–112 I
5c	8	4	$-O_2C-$	33	0.05	g 40–45 S 58–62 N 97–105 I
5d	11	4	$-O_2C-$	50	0.04	g 35–40 S 59–62 N 88–96 I

[a] Determined in $CHCl_3$ at 25 °C. [b] g = glass, S = smectic, N = nematic, and I = isotropic [c] Polymer prepared with sodium polyacrylate of $\overline{MW}$ = 2100.

under vacuum to ~5 mL. Addition of a large excess of methanol (100 mL) gave a precipitate, which was filtered (0.07 g, 20%).

Registry No. 1a, 99542-62-8; **1b**, 105971-08-2; **1c**, 99542-63-9; **1d**, 105971-09-3; **2a**, 105971-10-6; **2b**, 105971-11-7; **2c**, 105971-12-8; **2d**, 105971-13-9; 4,4'-$HOC_6H_4CO_2C_6H_4O(CH_2)_3CH_3$, 70568-44-4; $Br(CH_2)_6Br$, 629-03-8.

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Stereoselective Copolymerization of Chiral α-Olefins by High-Activity Ziegler–Natta Catalysts

The intrinsically asymmetric structure of the active sites in Ziegler–Natta catalysts makes them able to chirally discriminate between the enantiomers of α-olefins bearing one stereogenic center in the α and β position to the double bond.[1] As a consequence each macromolecule is built up predominantly from a single enantiomer (stereoselective polymerization) as shown for both conventional[2] and supported high-activity[3] catalytic systems.

One application of stereoselectivity, carried out with conventional $TiCl_3/AlR_3$ catalyst, was based on the copolymerization of a racemic α-olefin, (*RS*)-3,7-dimethyl-1-octene [(*RS*)-DMO], with optically active (*S*)-3-methyl-1-pentene [(*S*)-3MP], also having the asymmetric carbon atom α to the double bond. As the active sites discriminate on the basis of chirality rather than chemical structure, a random copolymer of (*S*)-DMO with (*S*)-3MP was obtained together with the homopolymer of (*R*)-DMO[4] (Scheme Ia). This was demonstrated by fractionating the polymer by solvent extraction and measuring optical rotation ($[\alpha]^{25}{}_D$) and IR absorption (D_{763}/D_{732}) of the fractions. It resulted that the more soluble polymer fractions consisted, as expected, of copolymer of *S* monomers, whereas the last fraction was based on poly[(*R*)-DMO] (Table I). The same approach has now been extended to a high-activity Ziegler–Natta catalyst,[5] schematically indicated as $MgCl_2/EtB/PC/AlEt_3/TiCl_4$, where the internal base EtB is ethyl benzoate and PC is *p*-cresol. Experimental conditions are briefly indicated in footnote *a* of Table I.

Scheme I[a]

(a) Simultaneous Addition
$S' + S + R \rightarrow -SSS'SSSS'SSSS'SSSSS'- +$
$-RRRRRRRRRRRRRRR-$
(b) Two-Step Addition
Step 1
$S' \rightarrow -S'S'S'S'S'S'S'S'-$
Step 2
$-S'S'S'S'S'S'S'S'- + S' + S + R \rightarrow$
$-S'S'S'S'S'S'S'S'SSS'SSSS'SSSSSS- +$
$-RRRRRRRRRRRRRRR- + -SS'SSS'SSSS'-$

[a] *S'* = (*S*)-3-methyl-1-pentene, *R* = (*R*)-3,7-dimethyl-1-octene, and *S* = (*S*)-3,7-dimethyl-1-octene.

The copolymerization of racemic DMO with (*S*)-3MP in 3.8/1 molar ratio, slightly higher than that used with the conventional catalyst, in the presence of the above high-activity system activated by $Al(i\text{-}Bu)_3$ and *p*-methyl toluate (MT) as external base gave results very similar to the previous ones.[4] This indicates that the chiral recognition of active centers capable of polymerizing these sterically hindered branched olefins remains substantially the same even in the presence of the support ($MgCl_2$) and of the Lewis base.

The practically identical behavior of the two systems is confirmed by the fact that the recovered nonpolymerized DMO was optically active in both cases with the same prevalence of the *R* antipode, indicating that the DMO enantiomer having the same absolute configuration as the optically active comonomer is polymerized at a slightly higher rate[6] (Table II).

A second copolymerization experiment was then performed in two steps, starting with pure (*S*)-3MP and adding, after formation of some homochains, racemic DMO in an amount double of the initial (*S*)-3MP to compensate for the partial homopolymerization of the latter and realize, during the second step, a DMO/3MP ratio similar to that of the previous experiment. Solvent extraction gave, however, very different results. These results cannot be entirely accounted for by the possible higher amount of (*S*)-3MP present during the second step. Indeed, no fraction with negative optical rotation was isolated, indicating either that the stereoselectivity of the centers has been substantially modified by the preliminary interactions with pure (*S*)-3MP or that the extraction is now less efficient due to the presence of less soluble (less random) (*S*)-DMO/(*S*)-3MP copolymer. Taking into account the tendency of the catalyst to give a rather narrow molecular weight distribution,[7] we can explain this result also by assuming that when DMO is added, some (*S*)-3MP chains are still living. Indeed, this would finally lead to the formation on the *S* monomer polymerizing sites of a (*S*)-3MP/(*S*)-DMO copolymer consisting of a long block

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