Detailed characterization and morphological studies of these and other related vesicles are now in progress. Our interests are also directed to vesicle formation by copolymers with dialkyl amphiphilic monomers, thereby enabling one to control the thermal stability of vesicles.

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(18) ^{1}H NMR ($CDCl_3$): δ 6.12 (m, 1 H, vinyl), 5.63 (m, 1 H, vinyl), 5.19 (m, 1 H, $CH_2CH{=}C$), 4.96 (s, 2 H, $OCOCH_2{}^+N$), 4.63 (t, 2 H, OCH_2), 4.46 (t, 2 H, $CH_2{}^+N$), 4.7–4.3 (br m, 1 H, OCH), 3.76 (s, 6 H, $(CH_3)_2{}^+N$), 1.95 (s, 3 H, CH_3C), 2.5–0.65 (br m, 43 H, cholesterol).
(19) Du Pont Model 910 differential scanning calorimeter: concentration, 2% in water; heating rate, 5 °C/min.
(20) Beckman Model LS-3133T scintillation spectrometer: cocktail solution, 10 mL.

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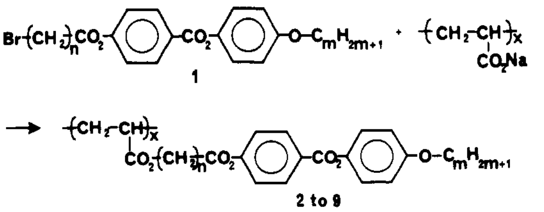
Synthesis of Liquid Crystalline Side-Chain Polyacrylates via Phase-Transfer Catalysis

Thermotropic liquid crystalline polymers, which have been the subject of intensive scientific and technological research,[1-6] are classified in two categories: "main-chain" and "side-chain" polymers. In the first, the liquid crystalline character is a property of the chain backbone; i.e., the mesogenic groups are linked to form the macromolecular chain. In the side-chain liquid crystalline polymers, with which this work deals, low molar mass mesogenic groups are linked to the polymeric chain as side chain directly or via flexible spacers.

Scheme I



Liquid crystalline side-chain polymers can be prepared by two general processes.[6] The most conventional method is to introduce into a mesogenic molecule a reactive group capable of undergoing addition polymerization. Generally, the polymerizable group is a methacrylate[7,8] or an acrylate[8], which form a flexible vinyl backbone after radical polymerization. The second possibility starts with "reactive polymers" which can be modified to mesogenic side-chain polymers by using suitable reactive mesogenic monomers. An example is the addition of vinyl-substituted mesogenic monomers to poly(hydrogenmethylsiloxane) to form mesogenic polysiloxane.[9,10] This synthetic method has some advantages, one being that known polymers are used as starting materials for liquid crystalline polymer synthesis. This could permit unambiguous studies on the effect of the chemical structure of the mesogenic moiety on the liquid crystalline properties of the polymers. However, analogous reactions involving polymers other than polysiloxanes, have not been extensively investigated.[11,12]

We describe here a new synthesis of mesomorphic polyacrylates resulting from the reaction of sodium polyacrylates on mesogenic ω-bromoalkyl esters (1) under phase-transfer conditions.

Results and Discussion. The synthesis of mesomorphic polyacrylates (Scheme I) is achieved by displacement of bromide ion from ω-bromoalkyl esters 1 with sodium polyacrylates under phase-transfer conditions. Formally, this substitution reaction is similar to the well-known displacement of bromide ion by acetate anion[13] (or methacrylate–acrylate anions[14]) under phase-transfer conditions.

The required ω-bromoalkyl esters 1 are prepared by direct esterification of (alkyloxy)phenyl 4-hydroxybenzoates[15] with ω-bromoalkanoic acids using the convenient procedure of Hassner and Alexanian.[16]

The sodium polyacrylate solutions are obtained by neutralization with sodium hydroxide of poly(acrylic acid) samples of commercial sources, with two different average molecular weights ($\overline{MW}$ = 2000; $\overline{MW}$ = 5000) (see experimental part).

The ω-bromoalkyl esters 1 are heated under reflux in water–chloroform solvent with sodium polyacrylates and tetrabutylammonium bromide as phase-transfer reagent. Mesomorphic polyacrylates are isolated from chloroform solutions by precipitation with diethyl ether and methanol as nonsolvents (see experimental part).

The melting and transition points for the prepared ω-bromoalkyl esters (1) and the mesomorphic polyacrylates (2–9) are listed in Tables I–III. Identification of the mesophases has been done by examination of the textures exhibited by thin samples sandwiched between two glass slides.

From the data given in Tables II and III, it can be seen that the mesomorphism of the polyacrylates is strongly influenced by the structure of the mesogenic side chain. Polymers with mesogenic groups bearing a short terminal chain (m = 1; polymers **2**, **3**, **6**, and **7**) exhibit only a nematic phase whatever the molecular weight of the poly-

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Table I
Mesomorphic Properties of ω-Bromoalkyl Esters 1

product no.	*n*	*m*	phase transitions[a]
1a	4	1	K 66 N 78 I
1b	5	1	K 84 (N 82.5) I
1c	4	4	K 64 N 87 I
1d	5	4	K 47 N 85 I

[a] Transition temperatures in °C; K = crystal, N = nematic, I = isotropic; transitions in parentheses are monotropics.

Table II
Transition Temperatures for Mesomorphic Polyacrylates 2–5 Prepared with Poly(acrylic acid) of $\overline{MW}$ = 2000[a]

polymer no.	*n*	*m*	phase transitions
2a[b]	4	1	g 115–125 N 168–178 I
2b	4	1	g 120–130 N 210–220 I
3a	5	1	g 70–80 N 190–210 I
4a	4	4	g 65–72 N 110–120 I
4b	4	4	g 100–110 S 138–142 N 180–190 I
5a	5	4	g 40–50 S 90–110 N 130–145 I
5b	5	4	g 80–90 S 149–152 N 190–205 I

[a] Transition temperatures in °C; g = glass, S = smectic, N = nematic, I = isotropic. [b] **a**, precipitated by methanol; **b**, precipitated by diethyl ether.

Table III
Transition Temperatures for Mesomorphic Polyacrylates 6–9 Prepared with Poly(acrylic acid) of $\overline{MW}$ = 5000[a]

polymer no.	*n*	*m*	phase transitions
6a[b]	4	1	g 115–125 N 160–170 I
6b	4	1	g 130–140 N 180–190 I
7a	5	1	g 108–113 N 235–245 I
8a	4	4	g 50–60 S 95–105 N 140–160 I
8b	4	4	g 100–105 S 138–143 N 165–172 I
9a	5	4	g 85–90 S 127–131 N 195–200 I
9b	5	4	g 95–105 S 152–154 N 192–202 I

[a] Transition temperatures in °C; g = glass, S = smectic, N = nematic, I = isotropic. [b] **a**, precipitated by methanol; **b**, precipitated by diethyl ether.

(acrylic acid) used as starting material. For polymers with mesogenic group terminated with longer end chain (*m* = 4; polymers **4**, **5**, **8**, and **9**), the nematic phase is almost systematically preceded by a smectic phase. (This behavior is commonly found in other thermotropic liquid crystalline side-chain polymer series.[6])

The average molecular weight of the poly(acrylic acid) used as starting material has little effect on the mesomorphism, at least in the limited investigation realized here (compare Tables II and III). The fractional precipitations made on the mesomorphic polyacrylates (see experimental part) give fractions of polymers with the same mesomorphism but with different transition temperatures: polyacrylates resulting from precipitation with diethyl ether have higher transition temperatures than fractions precipitated with methanol (compare polymers **5a** and **5b**; Table II).[17] Clearly, further work has to be done in order to characterize much more thoroughly the mesomorphic polyacrylates prepared here (dosage of remaining carboxylic groups,[18] measurement of the molecular weights of the polymers, identification of the mesophases by X-ray diffraction, etc.).

Finally, the procedure described here for the preparation of mesomorphic polyacrylates could be applied for the synthesis of other mesomorphic side-chain polymers such as polymethacrylates or copolymers of polyethylene with polymethacrylates. Work is in progress and results will be forthcoming.

Experimental Section. Transition temperatures were measured by optical microscopy using a polarizing microscope (Leitz) fitted with a Mettler FP82 hot stage and an FP80 control unit. They were checked by differential thermal analysis (DTA2000, Mettler). Structural checks were carried out with a Shimadzu IR-408 instrument for infrared spectra.

Materials. The two kinds of poly(acrylic acid) used in the preparation of mesomorphic polyacrylates were purchased commercially (Aldrich) and had the following characteristics: poly(acrylic acid), 50% in water, $\overline{MW}$ = 5000; poly(acrylic acid), 65% in water, $\overline{MW}$ = 2000. They have been used as received. Other compounds and solvents were of commercial sources.

4-(Butyloxy)phenyl 4-((5-Bromopentanoyl)oxy)benzoate (**1c**). Typical Procedure (after ref 16). A solution of 5-bromopentanoic acid (1.81 g, 0.01 mol), 4′-(butyloxy)phenyl 4-hydroxybenzoate[15] (3.14 g, 0.011 mol), *N*,*N*-dicyclohexylcarbodiimide (2.26 g, 0.011 mol), and 4-pyrrolidinopyridine (0.148 g, 0.001 mol) in dichloromethane (50 mL) was stirred for 24 h at room temperature. The *N*,*N*-dicyclohexylurea was filtered and the filtrate washed with water (3 × 100 mL), 5% acetic acid (4 × 100 mL), and again with water (2 × 100 mL) and dried over sodium sulfate. The solvent was evaporated to give the ester, which was recrystallized from ethanol until constant transition temperatures (K 64 N 87 I) (3.2 g, 71%).

Sodium Polyacrylate Solution ($\overline{MW}$ = 2000). Typical Procedure. Poly(acrylic acid) ($\overline{MW}$ = 2000) (65% solution in water) (1 g, 9.02×10^{-3} mol) in a measuring flask (10 mL) was neutralized by 1 N sodium hydroxide solution (9.02 mL) and the volume adjusted to 10 mL with distilled water. This stock solution of sodium polyacrylate contained 9.02×10^{-4} mol of carboxylate equivalent by milliliter.

Mesomorphic Polyacrylate (Polymer 5). Typical Procedure. A mixture of 4-(butyloxy)phenyl 4-((6-bromohexanoyl)oxy)benzoate (**1d**) (0.5 g, 1.08×10^{-3} mol), tetrabutylammonium bromide (0.058 g, 1.8×10^{-4} mol) in 6 mL of chloroform, and 1 mL (9.02×10^{-4} mol) of sodium polyacrylate solution ($\overline{MW}$ = 2000) was refluxed in an oil bath for 96 h. The mixture was diluted with 50 mL of chloroform, washed with water (2 × 40 mL), and dried over sodium sulfate. The solvent was evaporated and the solid dissolved in the minimum of chloroform (5 mL). Addition of a large excess of diethyl ether (100 mL) gave a precipitate, which was filtered (*m* = 0.03 g; polymer **5b**).[17] The filtrate was evaporated to dryness and the residue dissolved again in chloroform (5 mL). Addition of methanol (100 mL) produced a precipitate, which was filtered off (*m* = 0.11 g; polymer **5a**)[17].

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(17) Diethyl ether and methanol are both solvents for 4′-(butyloxy)phenyl 4-((6-bromohexanoyl)oxy)benzoate.
(18) IR spectra of the polymers present only ester carbonyl absorptions at 1748 and 1775 cm^{-1}, whereas peaks attributed to unreacted COOH are not present.
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Ring Strain Is Not an Important Factor Contributing to the Rate of Olefin Metathesis Polymerization

It has been widely asserted that the rate of polymerization of cyclic olefins by metathesis catalysis is a function of ring strain in the monomer.[1-3] Strained olefins such as cyclobutene and norbornene have been used to test sluggish catalysts for activity.[4] This communication questions these assertions and offers another interpretation of the kinetic data, namely that reactivity differences between different cyclic olefins can be attributed to the relative reactivity of the propagating carbenes. The geometry of the growing polymer chain about the catalyst site determines the reactivity.

Whether ring strain should increase or decrease the rate of metathesis polymerization is, a priori, not obvious. Scheme I depicts the generally accepted mechanism for the propagation step in cyclic olefin metathesis polymerization. Whether the coordination step is association–dissociation or dissociation–association, whether or not the penultimate or other chain double bond is coordinated, and whether or not a cocatalyst is involved are not considered and are extraneous to this argument. If k_1 or k_3 is the overall rate-determining step, a strained cyclic olefin could be expected to react faster than one with less strain: the coordination of a strained olefin or the opening of fused strained rings would lower the free energy of the transition state. If, however, k_2 is rate limiting, ring strain could impede the reaction: formation of fused strained rings would raise the free energy of the transition state. It has been pointed out[3] that differences in energy between **1**, **2**, and **3** must be small to explain the observed rates and activation parameters. Experiments detailed below suggest that ring strain in the cyclic olefin does little to affect the polymerization rate and that the rate is principally a function of the structure of **1**.

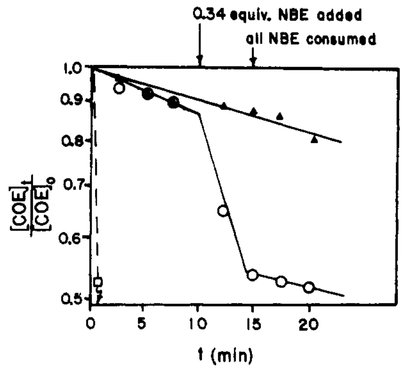


Figure 1. Homopolymerizations of NBE (□) and COE (△) and polymerization of COE to which 0.34 equiv of NBE was added at t = 10 min (○). $[\mathrm{NBE}]_0$(homopolymerization) = 0.13 M, $[\mathrm{COE}]_0$ = 0.37 M, T = 25 °C.

Scheme I
Propagation Step in Cyclic Olefin Metathesis Polymerization

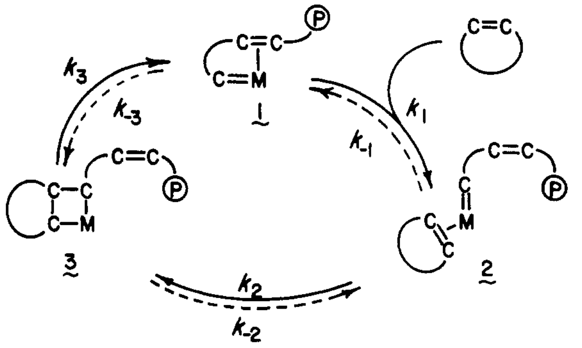
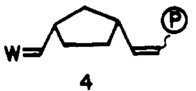
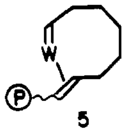


Figure 1 displays first-order plots for three polymerization reactions: norbornene (NBE) and cyclooctene (COE) homopolymerizations and a COE polymerization to which 0.34 equiv of NBE was added at t = 10 min (90% of the COE was unreacted at this point). Tungsten hexachloride/tetramethyltin was the catalyst; the solvent was chlorobenzene. The initial monomer/catalyst ratio was 11/1/1 COE/W/Sn and the initial monomer concentration was 0.37 M. NBE homopolymerizes at an unmeasurably large rate under these conditions and has the effect of increasing the rate of COE polymerization: upon NBE addition (at 10 min) the rate of COE consumption increases by ~6-fold and after the NBE is depleted, the rate returns to its initial value. Accurate rate constants cannot be determined from the plots in Figure 1, but qualitatively we can say that NBE homopolymerizes >100 times as fast as COE (separate polymerizations), but in a competitive experiment (NBE and COE in same polymerization) NBE reacts only 2–3 times as fast as COE.

We interpret this result in terms of the relative reactivity of NBE- and COE-derived carbenes (**4** and **5**, respectively).



4



5

The olefin in **4** cannot coordinate with the carbene tungsten as in **5**, making **4** the more reactive carbene. When present with both COE and NBE, **4** is not very selective, and COE competes effectively. Ring strain in NBE, therefore, cannot be the reason for its greater (than COE) reactivity.

The same type of experiments have been performed with NBE and 1,5-cyclooctadiene (COD). Similar results were obtained (Figure 2) and we interpret them identically.

In an attempt to determine the relative stabilities of COE-derived carbene **5** and COD-derived carbene **6**, the experiments detailed in Figure 3 were performed. In

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