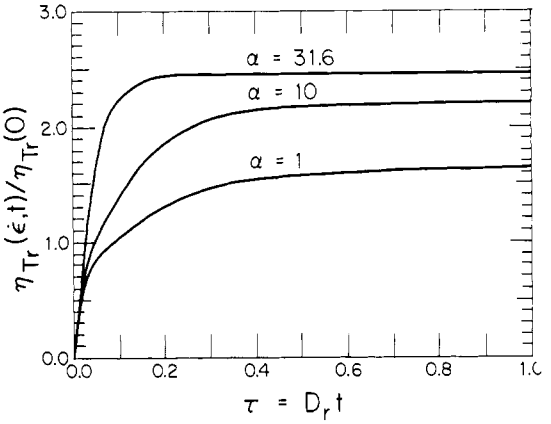

Figure 7. Time dependence of the Trouton viscosity, in units of its steady-state value for a zero rate of extension. The flow begins at time $t = 0$ and proceeds thereafter with a constant rate of extension.

discarding the convective, quartic contribution to $Y_{Ex}(\alpha)$. The third curve in Figure 6 has been labled JC because it is related to our general formula (24) in the same way that Jain and Cohen's shear viscosity increment $\delta\eta$ is related to our formula (14). Thus, the JC curve of Figure 6 was computed from (24) by setting the hydrodynamic screening factor F equal to unity. The noteworthy feature is the immense importance to the Trouton viscosity of the convective driving force that was neglected by Kuzuu and Doi. It is this alone which is responsible for the enormous difference between the JC and KD curves of Figure 6, a difference which is directly comparable to that between the curves JC and DE of Figure 1.

Kuzuu and Doi presented plots of the time-dependent Trouton viscosity $\eta_{Tr}(\dot{\epsilon},t)$ for the three values 1, 10, and 31.6 of the dimensionless rate of extension $\alpha = 3\dot{\epsilon}/2D_r$. From the KD curves of Figure 6 we see that the values of $\mathcal{R}_{KD}(\alpha) \equiv [\eta_{Tr}(\dot{\epsilon})/\eta_{Tr}(0)]_{KD}$ which correspond to these three homogeneous rates of extension are ordered as follows: $\mathcal{R}_{KD}(1) > \mathcal{R}_{KD}(10) > \mathcal{R}_{KD}(31.6)$. However, according to the JC approximation this ordering is reversed, viz., $\mathcal{R}_{JC}(1) < \mathcal{R}_{JC}(10) < \mathcal{R}_{JC}(31.6)$. It is this which accounts for the totally different arrangement of the three (JC) curves in our Figure 7 and those appearing in the comparable Figure 2 of Kuzuu and Doi's paper.

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Notes

Synthesis of Methacrylate and Acrylate Monomers of Cholesteric Esters via Phase-Transfer Catalysis

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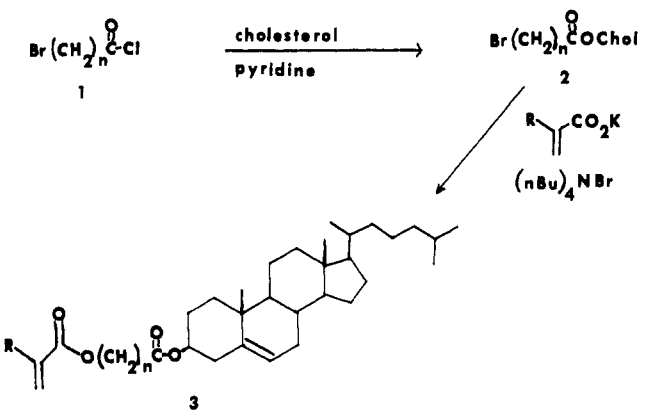
We have been interested in the synthesis and properties of polymeric liquid crystals that have liquid crystalline moieties connected to the main polymer chain by flexible spacer groups as originally described by Ringsdorf et al.[1] The synthesis of polymethacrylates and polyacrylates of this type requires the formation of monomers such as **3** (Scheme I), which have a mesogen (in this case, the cholesteric ester) connected to the methacrylate moiety by a flexible methylene chain. Although monomers containing such functionality have been synthesized,[2-5] the acylation methods used in their preparation require chromatographic purification of the products and give only modest yields of the desired monomers. We describe here a new two-step approach to methacrylate and acrylate monomers of type **3**, which involves no chromatography and gives high overall yields (Scheme I).[6]

Results and Discussion

The efficient synthesis of monomers **3** relies upon insertion of the polymerizable moiety in the last step by displacement of bromide ion from ω-bromo esters **2** with potassium methacrylate or potassium acrylate. The substitution reaction can be performed in dimethylformamide solvent or by use of appropriate phase-transfer conditions. Although displacement of bromide ion by acetate anion under phase-transfer conditions is well-known,[7,8] the use of methacrylate or acrylate salts for such reactions has not received much attention.[9]

Scheme I



The requisite cholesteryl ω-bromoalkyl esters **2** are conveniently prepared by acylation of cholesterol in ethanol-free chloroform or ether–dichloromethane (4:1) with ω-bromoalkyl acid chlorides. The cholesteric esters **2** are heated to reflux in water–chloroform solvent with an excess of acrylate or methacrylate potassium salt, a catalytic amount of tetra-*n*-butylammonium bromide phase-transfer reagent, and ionol, a radical inhibitor. Alternatively, dimethylformamide can be used in place of the biphasic solution and phase-transfer reagent. Our experience indicates that although dimethylformamide provides a higher rate of reaction, the phase-transfer conditions result in a higher yield in product. In either case the monomers can be readily purified by recrystallization. Yields, phase transitions, and spectroscopic data for the monomers and ω-bromoalkyl esters we have prepared are listed in Table I.

It should be noted that several of these monomers have

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Table I
Physical and Spectroscopic Data of Esters 2 and 3[a]

product no.	n	R	yield, %	phase transitions,[b,c] °C	IR ($CHCl_3$), cm^{-1}	^1H NMR ($CDCl_3/Me_4Si$) δ
2a	10		89	k 99-100 i	1715	2.1-0.65 (m, 57 H), 2.27 (m, 4 H), 3.38 (t, 2 H), 4.60 (m, 1 H), 5.36 (m, 1 H)
2b	5		86	k 120-121 i	1715	2.1-0.65 (m, 47 H), 2.30 (m, 4 H), 3.39 (t, 2 H), 4.60 (m, 1 H), 5.38 (m, 1 H)
2c	4		86	k 98.5-100 i (90.5 c)	1715	2.10-0.65 (m, 45 H), 2.3 (m, 4 H), 3.40 (t, 2 H), 4.6 (m, 1 H), 5.36 (m, 1 H)
2d	3		86	k 87 c 90 i	1715	2.55-0.65 (m, 47 H), 3.45 (t, 2 H), 4.60 (m, 1 H), 5.36 (m, 1 H)
3a	10	CH_3	88	k 58.7 c 64.1 i (55.3 s)	1715 1640	2.1-0.65 (m, 60 H), 2.28 (m, 4 H), 4.12 (t, 2 H), 4.62 (m, 1 H), 5.38 (m, 1 H), 5.53 (bs, 1 H), 6.08 (bs, 1 H)
3b	5	CH_3	90	k 48.2 c 57.3 i (25.0 s)	1720 1640	2.1-0.65 (m, 50 H), 2.30 (m, 4 H), 4.13 (t, 2 H), 4.60 (m, 1 H), 5.37 (m, 1 H), 5.54 (bs, 1 H), 6.08 (bs, 1 H)
3c	4	CH_3	74	k 58.6 c 68.5 i (28.7 s)	1710 1635	2.1-0.65 (m, 48 H), 2.30 (m, 4 H), 4.15 (t, 2 H), 4.55 (m, 1 H), 5.35 (m, 1 H), 5.53 (m, 1 H), 6.10 (m, 1 H)
3d	3	CH_3	75	k 73-74 i (56.0 c)	1710 1635	2.1-0.65 (m, 46 H), 2.34 (m, 4 H), 4.18 (t, 2 H), 4.6 (m, 1 H), 5.35 (m, 1 H), 5.55 (m, 1 H), 6.10 (m, 1 H)
3e	10	H	83	k 56.0 s 57.6 c 71.9 i	1715 1635 1615	2.1-0.65 (m, 57 H), 2.27 (m, 4 H), 4.12 (t, 2 H), 4.62 (m, 1 H), 5.36 (m, 1 H), 6.5-5.7 (m, 3 H)
3f	5	H	87	k 46.0 c 68.5 i (31.0 s)	1715 1635 1615	2.1-0.65 (m, 47 H), 2.30 (m, 4 H), 4.15 (t, 2 H), 4.62 (m, 1 H), 5.38 (m, 1 H), 6.5-5.7 (m, 3 H)
3g	4	H	83	k 86-87 i (82.0 c)	1720 1635 1615	2.1-0.65 (m, 45 H), 2.30 (m, 4 H), 4.15 (t, 2 H), 4.6 (m, 1 H), 5.38 (m, 1 H), 6.55-5.7 (m, 3 H)
3h	3	H	83	k 68.5-70.5 i (67.5 c)	1720 1635 1615	2.5-0.65 (m, 47 H), 4.2 (t, 2 H), 4.6 (m, 1 H), 5.38 (m, 1 H), 6.55-5.7 (m, 3 H)

[a] All compounds gave satisfactory C and H analysis. [b] Transition temperatures: k = crystal; c = cholesteric; n = nematic; s = smectic, i = isotropic; transitions in parentheses are monotropic. [c] See ref 10.

relatively low melting points and broad cholesteric mesophases. We have found that mixtures of two or more of these monomers exhibit broad-range cholesteric properties extending well below room temperature. As a result, we have been able to successfully "freeze-in" the structure of the cholesteric mesophases derived from these monomers by photopolymerization. These results will be forthcoming.

Experimental Section

Materials. Ethanol-free chloroform was prepared by eluting chloroform through a column of 80–200-mesh alumina (200 g/400 mL of chloroform). Potassium methacrylate and acrylate were prepared by neutralization of the respective acids with an equivalent of potassium hydroxide in methanol followed by precipitation of the salts with ether. The acid chlorides were prepared from commercial samples of the corresponding acids and were distilled before use.

Cholesteryl 11-Bromoundecanoate (2a). Typical Procedure. To a solution of cholesterol (38.6 g, 0.10 mol) and pyridine (9.5 g, 012 mol) in ethanol-free chloroform (200 mL) was added a solution of 11-bromoundecanoyl chloride (35.0 g, 0.124 mol) in chloroform (50 mL) at 0 °C over 0.5 h. The mixture was stirred 2 h at 0 °C and 16 h at room temperature. The mixture was diluted with chloroform (300 mL), washed with 1 N hydrochloric acid (2 times 200 mL), washed with water, and dried over magnesium sulfate. Concentration gave a solid, which was recrystallized (ether–ethanol, 1:3) to give **2a**: 56.8 g (89%); mp 99–100 °C; IR ($CHCl_3$) 1715 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 2.1–0.65 (m, 57 H), 2.27 (m, 4 H), 3.38 (t, 2 H), 4.60 (m, 1 H), 5.36 (m, 1 H). Anal. Calcd for $C_{38}H_{65}BrO_2$: C, 72.01; H, 10.34. Found: C, 72.20; H, 10.50.

Methacrylate Monomer (3a). Typical Procedure. A solution of potassium methacrylate (18.6 g, 0.15 mol), cholesteryl 11-bromoundecanoate (31.7 g, 0.05 mol), tetra-*n*-butylammonium bromide (3.22 g, 0.010 mol), and 2,5-di-*tert*-butylcresol (0.75 g, 3.4 mmol) in water (30 mL) and chloroform (15 mL) was heated to 110–115 °C in an oil bath for 40 h. The mixture was diluted with ether–dichloromethane (500 mL, 4:1), washed twice with water, and dried over magnesium sulfate. Concentration gave a white solid, which was recrystallized (ether–ethanol, 1:1) to give **3a**: 28.2 g (88%); mp 58–64 °C (mesophase);[10] IR ($CHCl_3$) 1715, 1640 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$) δ 2.1–0.65 (m, 60 H), 2.28 (m, 4 H), 4.12 (t, 2 H), 4.62 (m, 1 H), 5.38 (m, 1 H), 5.53 (bs, 1 H), 6.08 (bs, 1 H). Anal. Calcd for $C_{42}H_{70}O_4$: C, 78.94; H, 11.04. Found: C, 79.08; H, 11.02.

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