

in DMF, may be compared with experimental values of 26.6 and 22.7, respectively.^{10,11} However, the latter figure appears too high by 2-3 kcal/mol on the basis of correlations for a series of halide ion plus methyl halide reactions.¹¹ The simulation results show the correct trends in reactivity and that the rate retardation in solution is due to the expected preferential stabilization of the reactants over the more charge-delocalized transition state. Though the comparison with experiment is favorable, it should be emphasized that computational resources have not yet permitted us to include intramolecular vibrational effects or to explore the full multidimensional reaction surface in solution. However, the present results are consistent with the notion that the lowest energy reaction path in the gas phase may not be seriously perturbed in solution for the present case; certainly the stereochemistry is well-known to be the same.

The present results lead one to question the likelihood of concerted S_N2 reactions in nonaqueous media, i.e., proceeding without the presence of intermediates.¹² Analyses of Brønsted plots for S_N2 reactions in Me_2SO have also been recently interpreted in terms of a two-stage mechanism.¹³ Obvious challenges are to define the optimal systems and conditions for occurrence of the ion-dipole complex and to directly detect the species in solution.¹⁴

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Dimer vs. Polymer Liquid Crystals: Alkyl Chain Flexibility via Deuterium NMR

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Received February 11, 1985

Prolate, low molar mass mesogens—*monomeric liquid crystals* (MLCs)—can be readily functionalized and coupled to form oligomers of liquid crystals. In 1981 Griffin and Britt¹ showed that a flexible-center, "Siamese-twin" liquid crystal—a *dimer liquid crystal* (DLC) that is a precursor to *polymeric liquid crystals* (PLCs)—can be prepared by coupling two mesogenic cores with an aliphatic *spacer* chain. The textures and thermodynamic properties of several classes of DLCs have subsequently been reported.² Nematic melts of DLCs generally exhibit thermodynamic properties intermediate between those of MLCs and those of the corresponding PLCs. In particular, the oscillations in the nematic-isotropic transition temperature, T_{NI} , and the enthalpy and entropy of this transition with the number of me-

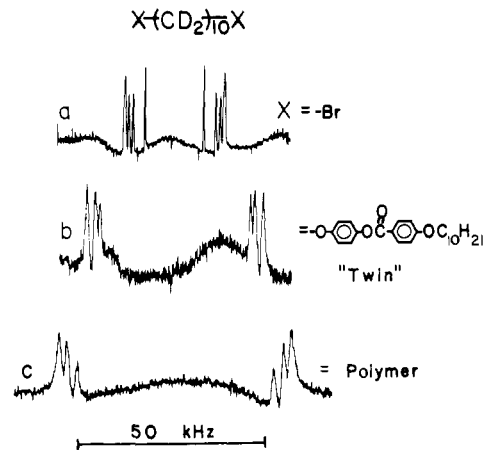
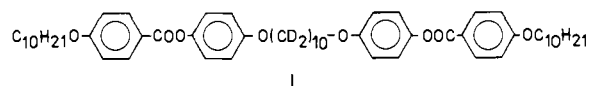


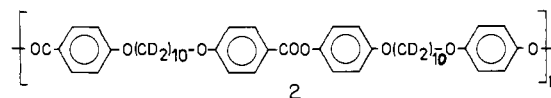
Figure 1. 2H NMR spectra of 1,10-disubstituted decane- d_{20} chains; (a) and (b) are spectra of labeled solutes (~ 2 wt % in Merck Phase 5 at 300 K). Spectrum (c) is the polymer eutectic (see text) just below the T_{NI} .

thylenes in the spacer chain—the *even-odd* effect—are more exaggerated than that reported for corresponding MLCs approaching behavior characteristic of PLCs.^{1,2c,d} In this paper we present a direct measurement of the spacer chain reorientation mobility in the nematic phases of a DLC and a PLC using deuterium NMR (2H NMR). The temperature dependence of the quadrupolar splitting pattern of the labeled spacer chain in the DLC is similar to that reported for MLCs³ while that exhibited by the PLC is fundamentally different. This observation implies that, despite the thermodynamic similarities of these two related classes of liquid crystals, in the DLC the conformational constraints on the spacer of the polymer precursor are considerably more relaxed than those operative in the polymer mesophase.

The DLC or "twin" mesogen **1** was prepared by reaction in



pyridine of 4-(*n*-decyloxy)benzoyl chloride with 4,4'-dihydroxy-1,10-diphenoxydecane- d_{20} in a 2:1 molar ratio of acid chloride/bis(phenol). The deuterated bis(phenol) above was prepared from 1,10-dibromodecane- d_{20} ⁴ by using a route previously described for the protonated analogue.⁵ The corresponding PLC **2** was



prepared by the interfacial polycondensation reaction of 4,4'-dihydroxy-1,10-diphenoxydecane- d_{20} and 4,4'-bis(chloroformyl)-1,10-diphenoxydecane- d_{20} by a method described earlier.⁵

As the $T_{NI} \approx 485$ K of the polymer is not accessible in the spectrometer, a eutectic mixture⁶ of the related nematogen, *p*-phenylenebis(4-methoxybenzoate), and the labeled PLC (weight ratio 3:1 PLC/nematogen; $T_{NI} \approx 455$ K) was studied. The 2H NMR spectra were recorded at 13.2 MHz after cooling the isotropic phases of the neat DLC **1** and the eutectic mixture containing the PLC **2** in the spectrometer. Macroscopically aligned uniaxial samples were rapidly produced (< 1 minute) just below T_{NI} for both mesophases.

In nematic phases the DMR spectrum of a multiply labeled molecule is a superposition of quadrupolar splittings $\Delta\nu_i$ the magnitudes of which reflect the efficacy of the molecular motion

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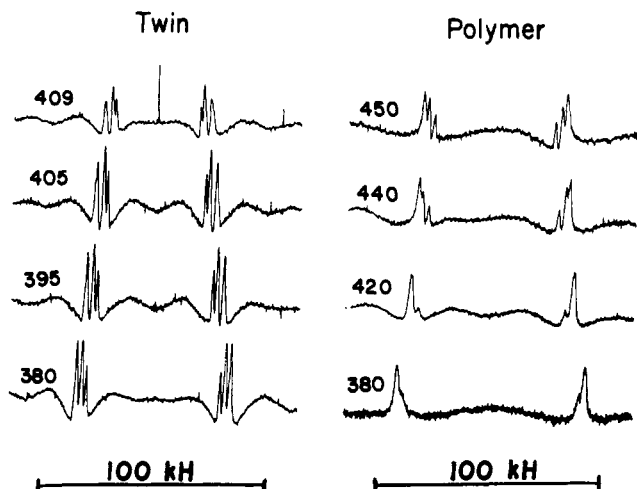


Figure 2. The temperature dependence of the quadrupolar splitting patterns of the neat dimer or "twin" (1) mesophase (left) and the analogous polymer (2) in the eutectic mixture (right).

(rigid body reorientation, libration and internal isomerization) for averaging the electric field gradient at the deuterons, i.e., averaging the orientation of the C-D bond vectors relative to the nematic director.⁷ For flexible alkyl chains the number of $\Delta\nu_i$ resolved in the quadrupolar splitting pattern reflects the degree of differential averaging of the electric field gradient at the various methylene segments and is determined by the facility of isomerization at the respective positions along the chain.^{8,9}

Figure 1 shows the evolution of the quadrupolar splitting pattern for 1,10-disubstituted decane-*d*₂₀ solutes in nematic solvents as a function of the substituent size. A comparison of the spectra of the disubstituted decanes with the corresponding *n*-alkane and molecular modeling suggest that the CD₂ segments closest to the chain ends are the most effectively averaged and exhibit the smallest $\Delta\nu_i$.^{9,10} Replacing the bromines with mesogenic cores (Figure 1b) increases the splittings as the larger and more orientationally restricted substituents impose additional constraints on the isomerization of the labeled spacer chain. Embedding an alkyl spacer into the backbone of a linear polymer (Figure 1c) further constrains the spacer chain.

Figure 2 shows the *T* dependence of the ²H NMR spectra of the neat dimer and the polymer eutectic liquid crystals. The behavior of the former is reminiscent of that exhibited by *n*-alkanes (dissolved in nematic solvents) and alkyl chains appended to conventional, low molar mass thermotropic mesogens: On lowering the temperature the nematic order increases yielding larger $\Delta\nu_i$. And, as reported here for the dimer, this increase in the $\Delta\nu_i$ always occurs with the relative $\Delta\nu_i$ diverging at low temperature.^{3,7} By contrast in the polymer eutectic, the width of the quadrupolar splitting pattern increases on lowering the temperature, but at comparable reduced temperatures, the $\Delta\nu_i$ converge to and coalesce at some limiting value $\Delta\nu_0 = 80$ kHz.

In one idealized limit of an all-trans chain perfectly aligned parallel to the director, the calculated quadrupolar splitting is $\Delta\nu_i = |3/2qS_{CD}| = 126$ kHz where the quadrupole coupling constant $q = 168$ kHz and the methylene C-D bond-order parameter $S_{CD} = -1/2$; i.e., the C-D bond vector is normal to the nematic director. Even at the lowest temperatures $\Delta\nu_0 \ll \Delta\nu_i$ implying that there is still considerable mobility of the C-D bond vector. The observed coalescence ($\Delta\nu_i \rightarrow \Delta\nu_0$) suggests that, concomitant with the increased nematic order, averaging of the C-D bond vector orientation becomes independent of the methylene segment's proximity to the mesogenic cores.

These marked differences in the ²H NMR data for the DLC

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and the PLC reflect the distinctly different abilities of the spacer chain to accommodate the increasing orientational constraints imposed on the mesogenic cores terminating the respective chains and raise additional questions about the relationship of the dimer mesophase to that of the polymer. The thermodynamic characteristics of oligomeric polymer precursors (amplified *even-odd* phenomena relative to that of low molar mass mesogens) asymptotically approach those of the corresponding PLC at rather low degrees of polymerization (≤ 10).^{2b} As the ²H NMR observations reported here clearly show averaged conformational differences between the dimer and the polymer, it would be interesting to ascertain the *critical degree of polymerization* above which the spacer dynamics of the oligomer cross over to behavior characteristic of the polymer.

Acknowledgment. We are grateful to Dr. Li-Ping Yu for help with the ²H NMR measurements. This research is supported in part by the National Science Foundation DMR 8115703 (A.C.G.) and by the NIH AM17497 (E.T.S.).

Punaglandins: Halogenated Antitumor Eicosanoids from the Octocoral *Telesto riisei*¹

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Marine prostaglandins, first discovered in a gorgonian,² have since been isolated from other invertebrates and from red algae.³ An algal metabolite, hybridalactone,⁴ and the octocoral-derived clavulones,⁵ claviridenones,⁶ feature C-12 oxygenation, which has led Corey⁷ to suggest a distinctive biosynthetic pathway for these marine eicosanoids. The punaglandins,⁸ which are described here, are also characterized by C-12 oxygen and unprecedented C-10 chlorine functions. One of the Δ^7 compounds, punaglandin 3 (3), inhibits L 1210 leukemia cell proliferation with an IC₅₀ value of 0.02 μ g/mL, which represents 15-fold greater activity than is shown by the corresponding clavulone.⁹

Telesto riisei, a source of the punaglandins, is an octocoral that lacks symbiotic algae.¹⁰ A 1976 collection from Enewetak furnished two pregnanes;¹¹ the punaglandins were isolated from collections of *T. riisei* at several Oahu sites.

Refluxing hexane extraction of the freeze-dried animal (760 g) yields a residue (9.5 g), of which 1.9 g partitions into 80% MeOH/H₂O, containing the punaglandins. Column chromatography on Biosil A (hexane/EtOAc, 7:3) monitored at 254 nm yields four fractions which are in order of elution, punaglandin 4 (4, 0.08% of freeze-dried animal), 3 (3, 0.1%), 2 (2, 0.2%), and 1 (1, 0.8%) as almost colorless oils, each further purified by HPLC (Lichrosorb Magnum RP-18, 80% MeOH/H₂O).¹²

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