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Synthesis and Characterization of Liquid Crystal Trimers Based on Laterally Attached Terphenyls

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Synthesis and Characterization of Liquid Crystal Trimers Based on Laterally Attached Terphenyls

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Liquid crystal trimers consisting of a laterally attached terphenyl in the center and two terminally attached mesogenic groups at both ends have been synthesized. The thermal and phase behavior of these trimers were studied using DSC and polarized light microscopy methods. It is shown that incorporating laterally attached terphenyl rods into these trimers does not eliminate liquid crystallinity although it destabilizes the mesophase to some extent. In addition, increasing the length of the terminally attached rods results in a more stable mesophase. It is concluded that in the nematic phase the laterally attached rods are forced to orient in the nematic field direction of the terminally attached rods.

Keywords: Synthesis; Characterization; Liquid crystals; Trimers; Laterally attached rods

INTRODUCTION

In accord with our intrinsic expectations, stretching of a polymeric material leads to a thinning in the direction normal to the extension. Such a material is said to have a positive Poisson ratio. Alternatively, a negative Poisson ratio polymer[1,2] would expand laterally when stretched. Polymer materials with a negative Poisson ratio have been proposed for many applications[3]. In a previous paper[4], we have proposed an approach to achieving negative Poisson ratio polymers using a liquid crystalline polymer consisting of a main chain having both laterally attached (l.a.) and terminally attached (t.a.) rods separated by flexible alkyl chains. The liquid crystallinity of the polymer leads to both the l.a. rods and t.a. rods being oriented along the polymer chain direction (nematic director). When streched, the extension of the flexible spacers will force the l.a. rods from being roughly parallel to the tensile axis to positions normal to it. This rod reorientation would push the

neighboring chains further apart and enable the polymer to exhibit negative Poisson ratio behavior. We[5] have earlier described this model and have used trimeric mesogens with t.a.-l.a.-t.a. attachment sequence to probe the ordering tendency of the central l.a. rod. Although in main chain LCPs the rod segment is typically attached to the flexible spacer at the ends of the rod (terminal attachment), there have been interesting reports of architectures in which the rod attachment is lateral[6,7] or a combination of terminal and lateral[8,9,10]. In this paper we report the synthesis and phase behavior of trimeric mesogens which are structurally analogous to our LCPs designed[4] for auxetic response. The critical issue examined is the effect on mesophase behavior of a central rod which is transversely connected in these trimer model compounds.

SYNTHESIS

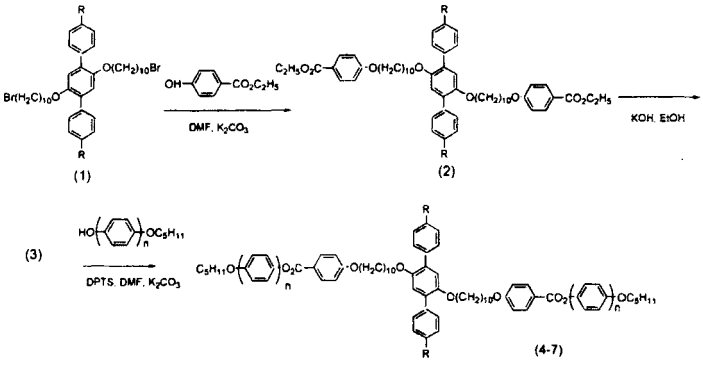
The synthetic scheme is shown in figure 1. Compounds 1 and 8 have been prepared in our laboratory and will be reported in a later paper[11].

Synthesis of diester (2) (R=C_3H_7): Compound (1) (R=C_3H_7) (7.84g, 10mmol), ethyl 4-hydroxybenzoate (3.49g, 21mmol) and potassium carbonate (4.0g, 28.9mmol) were placed in a 200ml Erlenmeyer flask and mixed with 50ml DMF. This mixture was heated to reflux with stirring for 6 hours. The reaction mixture was then cooled to room temperature and poured into 1000ml of water and filtered to obtain a white solid. This crude product was further purified by column chromatography (silica gel, chloroform) to yield a white solid (7.96g, 86.2%). Mp=88-89 °C; ^{1}H NMR ($CDCl_3$) δ: 0.98 (t, 6H, C$\underline{H_3}$), 1.35 (30H, C$\underline{H_2}$ & O=C-O-CH$_2$-C$\underline{H_3}$), 1.68 (12H, C$\underline{H_2}$-CH$_2$-O & Ar-CH$_2$-C$\underline{H_2}$), 2.63 (t, 4H, Ar-C$\underline{H_2}$), 3.90 (t, 4H, C$\underline{H_2}$-O), 4.00 (t, 4H, C$\underline{H_2}$-O), 4.34 (q, 4H, O=C-O-C$\underline{H_2}$-CH$_3$), 6.98 (s, 2H, Ar-$\underline{Ar}$-Ar), 7.37 (split d, 8H, $\underline{Ar}$-Ar-$\underline{Ar}$), 7.39 (split d, 8H, O-$\underline{Ar}$-C=O); ^{13}C NMR ($CDCl_3$) δ: aliphatic [13.9, 14.4, 24.6, 26.0, 29.2, 29.4, 37.8, 60.6, 68.2, 69.6]; aromatic [114.0, 116.3, 122.7, 128.0, 129.4, 130.5, 131.5, 135.8]; C=O [166.5]; FT-IR (polyethylene substrate, cm^{-1}): 2935.8, 1711.0, 1604.9, 1163.2, 1103.4.

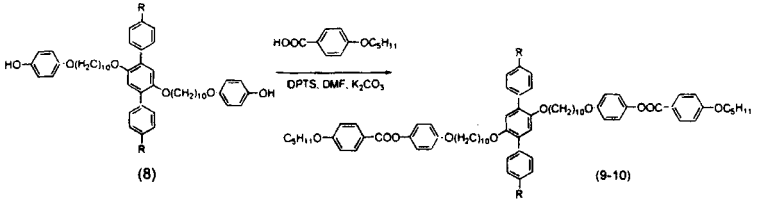
Synthesis of diester (2') (R=H) Quantities: Compound (1) (R=H) (7.00g, 10mmol), ethyl 4-hydroxybenzoate (3.49g, 21mmol), potassium carbonate (4.0g, 28.9mmol). The experimental procedure was as described for the preparation of compound (2). Yield: 8.15g, 82%. Mp=94-96 °C; ^{1}H NMR ($CDCl_3$) δ: 1.36 (m, 30H, C$\underline{H_2}$ & O=C-O-CH$_2$-C$\underline{H_3}$), 1.68 (m, 4H, C$\underline{H_2}$-CH$_2$-O), 1.77 (m, 4H, C$\underline{H_2}$-CH$_2$-O), 3.91 (t, 4H, C$\underline{H_2}$-O), 4.00 (t, 4H, C$\underline{H_2}$-O), 4.34 (q, 4H, O=C-O-C$\underline{H_2}$-CH$_3$), 6.99 (s, 2H, Ar-$\underline{Ar}$-Ar), 7.44 (10H, $\underline{Ar}$-Ar-$\underline{Ar}$), 7.51 (split d, 8H, O-$\underline{Ar}$-C=O); ^{13}C NMR ($CDCl_3$): δ aliphatic [14.4, 26.0, 29.4, 60.6, 68.2, 69.6], aromatic [116.4, 122.7, 126.9, 130.9, 138.4, 150.3, 162.9], C=O [166.5]; FT-IR (polyethylene substrate, cm^{-1}): 2941.6, 1711.0, 1606.8, 1512.3, 1390.8, 1167.0.

Synthesis of diacid (3) (R=C_3H_7):Compound (2) (9.24g, 10mmol) was dissolved in 150ml 10% KOH-ethanol solution in a 500ml Erlenmeyer and was heated to reflux with stirring. After 4 hours, the mixture was cooled to

room temperature and then poured into 2000ml of water. The white precipitate was filtered, dried under vacuum and recrystallized from acetone to give a white solid (7.63g, 84%). Mp= 152-154 ^{O}C; ^{1}H NMR ($CDCl_3$): δ 0.98 (t, 6H, C<u>H</u>$_3$), 1.28 (24H, C<u>H</u>$_2$), 1.68 (m, 8H, C<u>H</u>$_2$-CH$_2$-O), 2.63 (t, 4H, Ar-C<u>H</u>$_2$), 3.90 (t, 4H, C<u>H</u>$_2$-O), 4.02 (t, 4H, C<u>H</u>$_2$-O), 6.98 (s, 2H, Ar-<u>Ar</u>-Ar), 7.38 (split d, 8H, <u>Ar</u>-Ar-<u>Ar</u>), 7.49 (split d, 8H, O-<u>Ar</u>-C=O); ^{13}C NMR ($CDCl_3$): δ aliphatic [14.0, 24.6, 26.0, 29.4, 37.8, 68.3, 69.6], aromatic [114.2, 116.3, 121.4, 128.0, 129.4, 130.6, 132.3, 135.8, 141.3, 150.3, 163.7]; C=O [171.7]; FT-IR (polyethylene substrate, cm^{-1}): 2939.7, 1680.1, 1603.0, 1423.6, 1167.0.



Compound 4: R=H, n=2; Compound 5: R=H, n=1; Compound 6: R=C_3H_7, n=2; Compound 7, R=C_3H_7, n=1



Compound 9: R=C_3H_7; Compound 10: R=H

FIGURE 1: Synthesis Scheme

Synthesis of diacid (3') (R=H) Quantities: Compound (2') (9.96g, 10mmol). The experimental procedure was as described for the preparation of compound (3). Yield: 8.15g, 87%. Mp=184-185 ^{O}C; ^{1}H NMR (DMSO, d-6): δ 1.23 (24H, C<u>H</u>$_2$), 1.59 (m, 8H, C<u>H</u>$_2$-CH$_2$-O), 3.94 (8H, C<u>H</u>$_2$-O), 7.01 (s, 2H, Ar-<u>Ar</u>-Ar), 7.45 (10H, <u>Ar</u>-Ar-<u>Ar</u>),

7.48 (split d, 8H, O-Ar-C=O); ^{13}C NMR (DMSO, d-6): δ aliphatic [25.5, 28.9, 67.8, 68.7], aromatic [114.2, 115.7, 122.8, 126.9, 127.9, 129.3, 129.9, 131.3, 137.9, 149.7, 162.3], C=O [167.0]; FT-IR (polyethylene substrate, cm^{-1}): 2922.3, 1683.96, 1604.9

Synthesis of diester (4): Under the flow of nitrogen, 4-hydroxy-4'-pentyloxy-biphenyl (512mg, 2mmol), diacid (3') (814mg, 1mmol) and Stupp regent DPTS (4-(dimethylamino) pyridine toluenesulfonic acid salt) (646mg, 2.2mmol) were dissolved in 10ml of dry DMF. This mixture was stirred for 20 minutes then 1,3-diisopropyl carbodiimide (280mg, 2.2mmol) was added dropwise via syringe. This mixture was allowed to stir overnight and then poured into 200ml water. The white precipitate was filtered, washed thoroughly with water, and further purified by column chromatography (silica gel, chloroform) to give a white solid (1.10g, 85%). ^{1}H NMR ($CDCl_3$) δ: 0.96 (t, 6H, CH_3), 1.38 (32H, CH_2), 1.70 (m, 4H, O-CH_2-CH_2), 1.83 (m, 8H, O-CH_2-CH_2), 3.92 (t, 4H, O-CH_2), 4.03 (8H, O-CH_2), 7.01 (s, 2H, Ar-Ar-Ar), 7.44 (16H, Ar-Ar), 7.47 (10H, Ar-Ar-Ar), 7.58 (split d, 8H, O-Ar-C=O); ^{13}C NMR ($CDCl_3$) δ: aliphatic [14.1, 22.5, 26.0, 28.3, 29.1, 29.4, 29.5, 68.1, 68.3, 69.63], aromatic [114.3, 114.8, 116.4, 121.6, 122.0, 126.9, 127.6, 127.9, 128.1, 129.6, 130.9, 132.3, 132.8, 138.5, 138.6, 150.0, 150.3, 158.8, 163.6], O=C [165.1]; FT-IR (Polyethylene Substrate, cm^{-1}): 2931, 2850, 1728, 1604, 1508, 1213, 1168.

Synthesis of diester (5): Quantities: diacid (3') (814mg, 1mmol), 4-*pentyloxyphenol* (360mg, 2mmol), DPTS (646mg, 2.2mmol), 1,3-diisopropyl carbodiimide (280mg, 2.2mmol). The experimental procedure was as described for the preparation of compound (4). Yield: 854mg, 75%. ^{1}H NMR ($CDCl_3$) δ: 0.94 (t, 6H, CH_3), 1.28 (32H, CH_2), 1.68 (m, 4H, O-CH_2-CH_2), 1.79 (m, 8H, O-CH_2-CH_2), 3.96 (8H, O-CH_2), 4.03 (t, 4H, O-CH_2), 6.94 (s, 2H, Ar-Ar-Ar), 7.04 (10H, Ar-Ar-Ar), 7.50 (split d, 8H, Ar), 7.55 (split d, 8H, O-Ar-C=O); ^{13}C NMR ($CDCl_3$) δ: aliphatic [14.0, 22.5, 25.9, 26.1, 28.2, 29.0, 29.1, 29.2, 29.4, 29.5, 68.3, 68.4, 69.6], aromatic [116.4, 126.9, 127.9, 129.5, 130.9, 132.2, 138.4, 144.4, 150.3, 163.5], O=C [165.4]; FT-IR (Polyethylene Substrate, cm^{-1}): 2936, 2857, 1732, 1604, 1510, 1194, 1165, 1070.

Synthesis of diester (6): Quantities: diacid (3) (908mg, 1mmol) 4- hydroxy-4'-pentyloxy biphenyl (512mg, 2mmol), DPTS (646mg, 2.2mmol), 1,3-diisopropyl carbodiimide (280mg, 2.2mmol). The experimental procedure was as described for the preparation of compound (4). Yield: 1.12g, 85%. ^{1}H NMR ($CDCl_3$) δ: 0.97 (12H, CH_3), 1.45 (32H, CH_2), 1.74 (16H, O-CH_2-CH_2 & Ar-CH_2-CH_2), 2.63 (t, 4H, Ar-CH_2), 3.90 (t, 4H, O-CH_2), 4.02 (8H, O-CH_2), 6.98 (s, 2H, Ar-Ar-Ar), 7.38 (split d, 8H, Ar-Ar-Ar), 7.41 (16H, Ar-Ar), 7.56 (split d, 8H, O-Ar-C=O); ^{13}C NMR ($CDCl_3$) δ: aliphatic [14.1, 22.5, 24.6, 26.0, 28.2, 29.0, 29.1, 29.3, 29.4, 29.5, 68.1, 68.3, 69.6], aromatic [116.3, 121.6, 122.7, 127.7, 130.6, 132.8, 135.8, 141.3, 150.0, 158.8, 163.6], O=C [165.1]; FT-IR (Polyethylene Substrate, cm^{-1}): 2912, 2850, 1728, 1604, 1494, 1213, 1158.

Synthesis of diester (7): Quantities: diacid (3) (908mg, 1mmol), 4-pentyloxyphenol (360mg, 2mmol), DPTS (646mg, 2.2mmol), 1,3-diisopropyl carbodiimide (280 mg, 2.2mmol). The experimental procedure was as described for the preparation of

compound (4). Yield: 989mg, 78%. ^{1}H NMR ($CDCl_3$) δ: 0.98 (12H, $C\underline{H}_3$), 1.36 (32H, $C\underline{H}_2$), 1.75 (16H, O-CH_2-$C\underline{H}_2$ & Ar-CH_2-$C\underline{H}_2$), 2.64 (t, 4H, Ar-$C\underline{H}_2$), 3.95 (12H, O-$C\underline{H}_2$), 6.99 (s, 2H, Ar-Ar-Ar), 7.01 (split d, 8H, Ar-Ar-Ar), 7.38 (split d, 8H, Ar), 7.54 (split d, 8H, O-Ar-C=O); ^{13}C NMR ($CDCl_3$) δ: aliphatic [14.1, 22.5, 24.6, 26.0, 26.1, 28.2, 29.0, 29.1, 29.3, 29.4, 29.5, 29.5, 37.9, 68.3, 68.4, 69.6], aromatic [114.3, 115.1, 116.3, 121.7, 128.0, 129.4, 130.6, 130.6, 132.2, 135.8, 141.3, 144.4, 150.3, 163.5], O=C [165.4]; FT-IR (Polyethylene Substrate, cm^{-1}): 2931, 2856, 1730, 1606, 1510, 1197, 1076.

Synthesis of diester (9): Quantities: diphenol (8) (R=C_3H_7) (842mg, 1mmol), 4-pentyloxybenzoic acid (416mg, 2mmol), DPTS (646mg, 2.2mmol), 1,3-diisopropyl carbodiimide (280mg, 2.2mmol). The experimental procedure was as described for the preparation of compound (4). Yield: 978mg, 80%. ^{1}H NMR ($CDCl_3$) δ: 0.98 (12H, $C\underline{H}_3$), 1.38 (32H, $C\underline{H}_2$), 1.75 (16H, O-CH_2-$C\underline{H}_2$ & Ar-CH_2-$C\underline{H}_2$), 2.64 (t, 4H, Ar-$C\underline{H}_2$) 3.96 (12H, O-$C\underline{H}_2$), 6.94 (s, 2H, Ar-Ar-Ar), 7.04 (split d, 8H, Ar-Ar-Ar), 7.40 (split d, 8H, Ar), 7.52 (split d, 8H, O-Ar-C=O); ^{13}C NMR ($CDCl_3$) δ: aliphatic [14.1, 22.5, 26.0, 26.1, 28.2, 29.0, 29.1, 29.2, 29.4, 29.5, 29.5, 68.3, 68.5, 69.6], aromatic [115.1, 116.4, 121.7, 122.5, 126.9, 127.9, 129.6, 130.9, 138.5, 144.4, 150.3, 156.8, 163.5], O=C [165.4]; FT-IR (Polyethylene Substrate, cm^{-1}): 2908, 2849, 1732, 1604, 1510, 1388, 1194, 1165, 1070.

Synthesis of diester (10): Quantities: diphenol (8') (R=H) (758mg, 1mmol), 4-pentyloxybenzoic acid (416mg, 2mmol), DPTS (646mg, 2.2mmol), 1,3-diisopropyl carbodiimide (280mg, 2.2mmol). The experimental procedure was as described for the preparation of compound (5). Yield: 921mg, 81%. ^{1}H NMR ($CDCl_3$) δ: 0.96 (t, 6H, $C\underline{H}_3$), 1.38 (32H, $C\underline{H}_2$), 1.70 (m, 4H, O-CH_2-$C\underline{H}_2$), 1.80 (8H, O-CH_2-$C\underline{H}_2$), 3.96 (8H, O-$C\underline{H}_2$), 4.05 (t, 4H, O-$C\underline{H}_2$), 6.95 (s, 2H, Ar-Ar-Ar), 7.06 (10H, Ar-Ar-Ar), 7.52 (split d, 8H, O-Ar-O), 7.54 (split d, 8H, O-Ar-C=O); ^{13}C NMR ($CDCl_3$) δ: aliphatic [14.1, 22.5, 26.1, 28.2, 28.8, 29.4, 68.4, 69.6], aromatic [114.3, 115.1, 116.4, 121.7, 122.5, 126.9, 127.9, 129.6, 130.9, 132.2, 138.5, 144.4, 150.3, 156.8, 163.5], O=C [165.4]; FT-IR (Polyethylene Substrate, cm^{-1}): 2935, 2862, 1726, 1606, 1510, 1390, 1203, 1170.

CHARACTERIZATION

Infrared (IR) spectra were recorded using a Mattson Instruments Polaris FT-IR; NMR, using a Bruker AC-300. Proton chemical shifts reflect the center of splitting patterns or envelopes. DSC data was obtained using a TA Instruments DSC 2920. Heating rates were 10 °C/min. All optical data was obtained using a Leica optical microscope (laborlux 12 POL S) with a Mettler Toledo PP82HT heating stage.

RESULTS AND DISCUSSION

Table 1 lists phase transition temperatures for the model compounds in this study. All the model compounds exhibit a nematic phase, the majority being monotropic. In

addition, a smectic phase (S_c by miscibility) was observed in compound 4. On cooling crystallization was greatly retarded. In our system, the model compounds are trimers which consist of one laterally attached (l.a.) rod in the center and two terminally attached (t.a.) rods at the ends as structural mimics to the rod arrangements in our polyesters[4]. These rods are linked through flexible alkyl chains, $(CH_2)_{10}$, as shown in figure 2. Considering this unusual chemical structure, the mesophase observed should be the result of the interaction of the terminally and laterally attached rods.

TABLE 1: Phase transition temperatures of trimers

Compound	R	n	Phase transition temperature (°C)
Compound 4	H	2	K165I; I159.7N122.7Sc
Compound 5	H	1	K113.7I; I60.6N
Compound 6	C_3H_7	2	K137.9N154.6I; I149.2N
Compound 7	C_3H_7	1	K106I; I56.8N
Compound 9	C_3H_7	1	K110.6I; I55.3N
Compound 10	H	1	K120.1I; I64.2N

K: crystalline solid; N: nematic; Sc: smectic C; I: isotropic

The influence of the l.a. rods on the molecular packing structure and mesophase behavior are twofold. Firstly, the l.a. side rods destabilize the mesophase. This is because in order to form a nematic phase, both the l.a. rods and t.a. rods should be oriented roughly along the same director (nematic field). The orientation of l.a. rods will result in a 'carbuncle' at the center of the molecules as shown in figure 2, which does not favor efficient parallel packing of adjacent molecules.

FIGURE 2: Illustration of orientation of laterally-attached rods in the nematic phase

There are two types of laterally attached rods in this study, terphenyl with hydrogen at the ends and terphenyl with propyl groups at the ends. This study shows that the model compounds with propyl groups have lower phase transition temperatures ($T_{I\text{-}N}$) than their hydrogen counterparts. For example, model compound 4 has a $T_{I\text{-}N}$ of 159.7 °C, while its counterpart model compound 6, which has propyl groups on the terphenyl side rods, has a $T_{I\text{-}N}$ of 149 °C. Although compound 4 has a monotropic nematic phase, its clearing temperature is higher than that of compound 6, therefore it has the more stable nematic phase. The other two pairs of compounds, i.e. compound 5/compound 7 and compound 10/compound 9, also show a similar trend. The difference in the phase transition temperatures between model compounds with and without propyl groups is in the range of about 10 °C (shown in the table 1). Grafting of propyl groups onto the ends of terphenyl effectively increases the length

of the side rods. Destabilization of the nematic phase by propyl ends is expected if the l.a. rod is not fully oriented along the local nematic director. However, the relatively small destabilization (~10 °C) is consistent with a greater lateral protrusion by propyl but is not nearly as great as one would anticipate if the propyl group were fully extended in the perpendicular direction. As anticipated for these trimers, and consistent with a previous report of analogous polymers[8], in the nematic phase l.a. rods are oriented in a direction parallel to that of t.a. rods. As a result, any increase in length of the l.a. rod should not cause a large disruption to the parallel packing structure as long as the flexible alkyl linkage is sufficiently long to allow for the parallel orientation of the l.a. rods. This is important in our approach to negative Poisson ratio polymers. Our previous study[4] showed that the length of terphenyl l.a. rod is at the minimum length required for a polymer to exhibit negative Poisson ratio behavior. In order to achieve negative Poisson ratio behavior, the l.a. rod must be longer than terphenyl, and four-phenyl or five-phenyl rods may be useful in this regard. Since longer laterally-attached rods do not effect the liquid crystallinity of the polymer to any great extent, we can likely use main chain liquid crystalline polymers consisting of longer l.a. rods to achieve negative Poisson ratio behavior in polymers.

The intrinsic mesogenicity of the trimers orients all rods along a common direction. If the l.a. rods were to lie normal or about 60 degrees to the t.a. rods, the increase in the length of the l.a. rods by incorporating propyl groups should have a more profound negative effect on the nematic stability of the model compounds. The difference in the $T_{I\text{-}N}$ temperatures induced by increase in the l.a. rod length was, however, only about 10 degrees. This provides indirect evidence that the l.a. rods are indeed oriented roughly in the same direction as the mesogenic groups. In addition, orientational susceptibility and elastic constant measurements of compound 6 near its nematic-isotropic phase transition indicated that the l.a. rod and t.a. rod are oriented in a common direction[12]. Further confirmation for the likelihood of common orientation comes from the study by Li and Yu[10] who investigated polymers consisting of alternating l.a. and t.a. rods which are separated by flexible alkyl linkages. They showed that polymers exhibited liquid crystallinity if the flexible linkage was long, C_6H_{12}. If the flexible linkage is short, only a single CH_2, the polymer lost its liquid crystallinity. This is because longer alkyl chains facilitate the orientation of the l.a. side rods while the short alkyl chain linkage prevents such orientation. This indicates that flexible spacers play an important role in orientating the l.a. side rods and in influencing the liquid crystallinity of the resulting structures.

Increasing the length of the t.a. rods by adding a third (n=2) para-substituted phenyl group leads to a significant increase in $T_{I\text{-}N}$ of model compounds. For example, trimer 4 has longer t.a. rods than trimer 5. The $T_{I\text{-}N}$ for trimer 4 is about 100 degrees higher than that of trimer 5. Moreover, trimer 4 has an additional smectic phase which implies an increased ordering tendency. Another example is the comparison between trimers 6 and 7. Increasing the length of the mesogenic groups in the terminally-attached rods surely results in a greater degree of

structural anisotropy and thereby leads to a more stable mesophase.

In summary, introducing an l.a. rod as the central unit in a trimeric rod molecule does not eliminate the liquid crystallinity of the resulting trimers. The l.a. rod is likely oriented in the direction of the local nematic field as the t.a. rods and the flexible alkyl linkage play important roles in orienting the l.a. rod. In addition, the l.a. rods destabilize the mesophase of the compounds. This is due mainly to the orientation of l.a. rods which results in a 'carbuncle' structure rather than simply being due to the length of l.a. rods. The results of this study provide us with a structural design basis for our approach to negative Poisson ratio polymers using main chain liquid crystalline polymers consisting of l.a. and t.a. rods.

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