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Effects of stereochemistry, mesogenic core and spacer length on crystallization from nematic and isotropic melts of cyclohexane-based glass-forming liquid crystals

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The crystallization velocity of a series of glass-forming, nematic liquid crystals derived from cyclohexane was determined as a function of temperature between T_g and T_m via the observation of linear spherulitic growth from a nematic as well as an isotropic melt using a polarizing optical microscope. The results suggest that stereochemistry plays a predominant role in maximum crystallization velocity (CV), which was found to occur at $(0{\cdot}93 \pm 0{\cdot}01)T_m$ for all glass-forming liquid crystals presently investigated. Specifically, the observed maximum CV values follow the order: all-axial > all-equatorial > axial-equatorial mixed modes. Furthermore, the axial-equatorial mixed modes exhibited maximum CV values comparable to that of a typical 'slowly crystallizing' polymer, for example, isotactic polystyrene. In addition, it was found that a stronger nematogenic core with a higher T_m and T_c and a broader T_m to T_c range tends to depress morphological stability of the resultant GLMLC system by showing a greater maximum CV value. However, the flexible spacer length was found to play a negligible role in affecting the maximum CV value, although both T_g and T_m were found to be depressed whereas T_c significantly elevated with a longer spacer.

1. Introduction

Liquid crystals (LCs) have found numerous potential applications to optics and optoelectronics both as active and passive elements. The relatively mature liquid crystal display, LCD, technology that has evolved since the early 1970s is largely based on the field-induced orientation of LC molecules [1] with a response time ranging from micro- to millisecond. Another class of active device applications is based on electronic or photonic stimuli [2] with a much shorter response time in the pico- to femtosecond range, where the dynamics of molecular orientation is not involved. In the area of passive device applications, response time is not an issue, and the modulation of light or laser beam is accomplished by optical anisotropy arising from spontaneous alignment of LC molecules [3]. Except for applications where field-induced molecular orientation is critical, as in LCD displays, it is preferable that the desired mesophase be frozen in a glassy matrix to offer long-term stability of LC mesomorphism and environmental robustness. Although LC polymers serve to accomplish this specific aim, their relatively high viscosity values present a potential hurdle to practical applications in which processing into uniform thin films is required. As a consequence, we have been pursuing glass-forming low molar mass LCs, GLMLCs, with a glass transition temperature, T_g, above the ambient.

The majority of existing low molar mass LCs tend to crystallize upon cooling from the melt. The resultant polycrystallinity is detrimental to optical quality because of light scattering in the presence of grain boundaries. A number of GLMLCs have been reported in the literature [4–13], but many of these compounds were found to be semicrystalline or to show a distinct tendency to crystallize upon heating through T_g. In a recent series of papers [14, 15], we have established the feasibility of a novel molecular design concept in which mesogenic cores are attached to cyclohexane ring as an excluded-volume moiety. It is crucial that a subtle structural balance be reached between the two constituents by chemically combining them with an appropriate flexible spacer. It was demonstrated that capabilities for both vitrification and LC mesomorphism can be rendered without residual crystallinity or tendency toward crystallization upon heating through T_g, an indication of morphological stability over

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a relatively short term. Nevertheless, none of the GLMLCs have ever been investigated to date in terms of morphological stability against crystallization or any other potential thermally activated phase transformations.

In view of the fact that glass lies in a non-equilibrium state, one would suspect that thermally activated phase transformation (for example, crystallization) may occur given sufficient energy and time. This is particularly relevant to device manufacturing process in which thermal annealing is normally performed to maximize mesogenic ordering. In this process the desired mesophase may give into an energetically favoured one, which is not detectable by standard techniques for the characterization of thermotropic properties, such as differential scanning calorimetry (DSC) and hot stage polarized optical microscopy under finite scanning rates. In fact, crystallization from mesomorphic and isotropic melts of thermotropic LC polymers [16, 17] and from isotropic melts of non-mesogenic, low molar mass materials [18] has been observed and its kinetics intensively investigated in recent years.

Hence, the main objective of this study is to offer a definitive basis for assessing morphological stability of glass-forming liquid crystals as a novel class of advanced organic materials. Model compounds will be synthesized, their stereochemical characteristics determined by proton NMR spectroscopy, and morphological stability evaluated via the measurement of crystallization velocity, CV, defined as the linear spherulitic growth rate, as a function of temperature between T_g and T_m, the crystalline melting point. A comparison of morphological stability will then be made between GLMLC model systems presently studied, and a further assessment will be made by comparing to polymeric materials in terms of maximum CV to furnish new insight into the role played by stereochemistry and other structural factors.

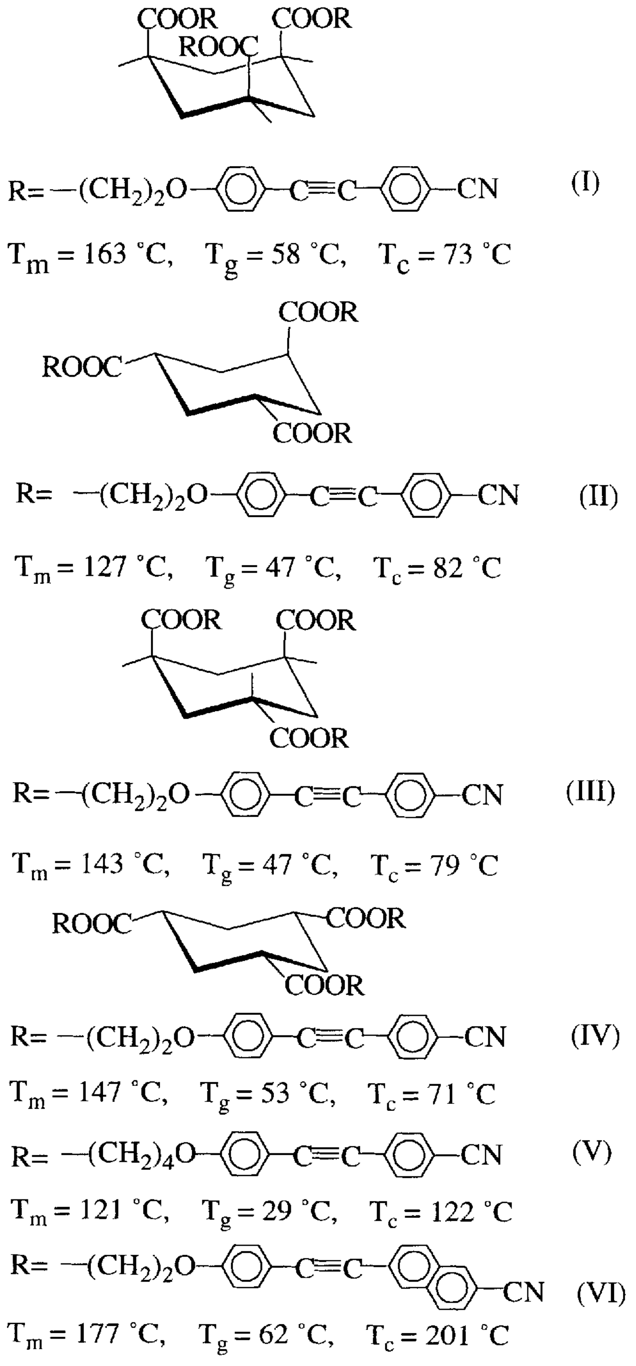

Figure 1. Chemical structures and thermal transition data for the model GLMLCs synthesized and characterized for the present study of thermally induced crystallization; note that all six compounds show nematic threaded textures between T_g and T_c under polarizing optical microscopy.

2. Experimental

2.1. *Synthesis of glass-forming low molar mass liquid crystals*

Six GLMLC model compounds shown in figure 1 were synthesized for the present study based on the Mitsunobu reaction, as sketched in figure 2, using a triacid (**VII**) and a mesogenic precursor (**VIII**) following the experimental procedures presented in [14, 15] where the synthesis of mesogenic precursors employed here was also described in detail. Stereoisomers *cis*-1,3,5-cyclohexanetricarboxylic acid (95 per cent), (1α, 3α, 5β)- and *cis*-1,3,5-trimethylcyclohexane1,3,5-tricarboxylic acids (99 and 99 per cent, respectively) as received from Aldrich Chemical Company. Steitz's procedures [19] were followed to convert *cis*-1,3,5-cyclohexanetricarboxylic acid into a *trans-isomer*, which was unavailable from commercial

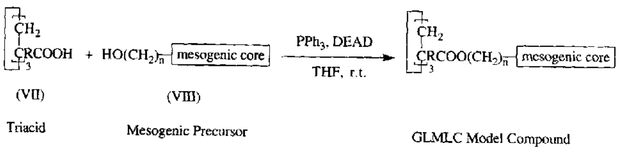

Figure 2. Reaction scheme (i.e. the Mitsunobu reaction) for the synthesis of model GLMLCs in which $R = \mathrm{H}$ or CH_3.

sources. To obtain pristine crystalline samples for the determination of T_m. Compound (**V**) was recrystallized from ethyl acetate/*n*-hexane (10:90), and the rest of the GLMLCs were recrystallized from acetone/methanol (10:90).

2.2. *Characterization techniques*

A Hitachi high performance liquid chromatography, HPLC, system comprising an L-2000 metering pump and an L-4200 UV–vis absorbance detector equipped with an LiChrosorb® column (RP-18, 10 μm) was employed to determine the number of components and purity of the products. The purity levels of all final products were found to be better than 99 per cent based on HPLC analysis with chemical structures elucidated by the FTIR (Nicolet 20 SXC) and proton NMR (QE-300, GE, typically 1 wt% in $CDCl_3$) spectroscopic techniques. Thermal transition temperatures were determined by differential scanning calorimetry, DSC (Perkin–Elmer DSC-7 at a nitrogen purge of 50 cc min^{-1}) with mesophase textures identified under a polarizing optical microscope (Leitz Orthoplan-Pol) equipped with a hot stage (FP82, Mettler) plus a central processor (FP80, Mettler).

2.3. *Determination of crystallization velocity*

A glassy thin films of a GLMLC sample was prepared on a single glass substrate and between a pair of substrates with a thickness of 5 and 12·5 μm as defined by Kapton® or Mylar® films (DuPont). Upon annealing at 0·90 T_m on a programmable hot plate, the film was transferred to a programmable hot stage, which had been thermally equilibrated, for observation of crystallization under a polarizing opical microscope. Conceptually, crystallization from a nematic or an isotropic melt consists of two steps, nucleation and growth. Depending on the substrate surface characteristics and system cleanliness, nucleation rate may vary a great deal from one experiment to another. To eliminate this experimental uncertainty, we focused on growth rate upon the appearance of nuclei. In situations where nucleation was difficult to induce, crystallites obtained by grinding pristine crystalline samples were added to a melt film to facilitate the observation of spherulitic growth under hot stage polarizing optical microscopy. The thermal transition data compiled in figure 1 suggest that the added crystallites are capable of serving as sites for growth from the melt because of the broad T_g to T_m range over which the melt may be nematic and/or isotropic depending on T_c relative to T_m. Growth processes are illustrated in figure 3: radial growth of compound (**I**)

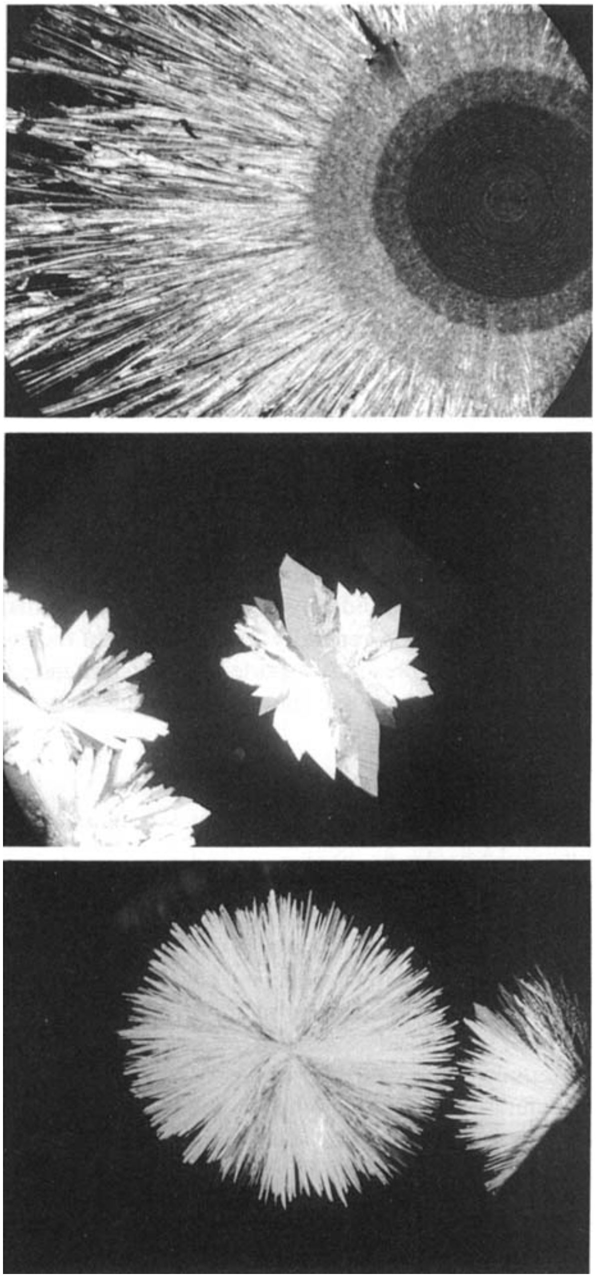

Figure 3. Optical micrographs for the measurement of crystallization velocity, CV: (*a*) compound (**I**), growth observed (20 ×) at selected temperatures in the 90 to 150°C range as revealed by concentric regions; (*b*) compound (**II**), growth observed (50 ×) at 120°C with CV determined by half of the mean between long and short axes; (*c*) compound (**III**), growth observed (50 ×) at 100°C, showing typical spherulite.

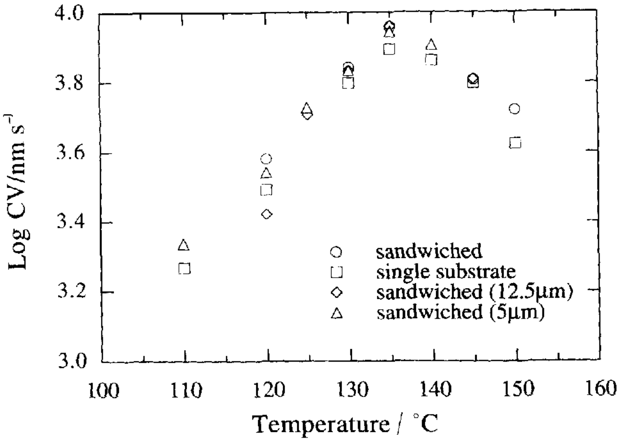

Figure 4. Experimentally observed crystallization velocity, CV, as a function of temperature for compound (**I**) to illustrate the independence of CV data on film thickness and the number of substrates, one or two.

at increasing temperatures is indicated by concentric regions in (*a*); growth of compound (**II**) shown in (*b*) was evaluated by half of the mean between the long and short axes; radial growth of compound (**III**) is shown in (*c*). Crystallization velocity was determined by the linear time dependence of spherulite radius or its equivalent. Figure 4 plotted for compound (**I**) shows that the experimental uncertainty on CV is generally ± 15 per cent of the mean within which the presently reported CV data are independent of film thickness and the number of substrates.

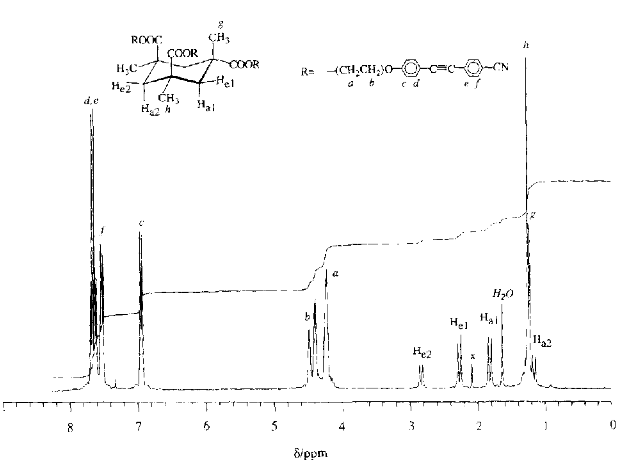

Figure 5. Proton NMR spectrum to validate the chemical structure of compound (**I**) with stereochemical features determined using signals in the 1 to 3 ppm range.

3. Results and discussion

The chemical structures of the six glass-forming nematic LCs are as depicted in figure 1. The DSC thermograms were collected to locate thermal transition temperatures, T_g and T_c (both from second heating scans of quenched nematic glass) and T_m (from first heating scan of pristine crystal), and the data are also included in figure 1. Typical proton NMR spectra are presented in figure 5 to 8. The proton NMR spectra in the $\delta = 1$ to 3 ppm region were employed to validate the stereochemical features of compounds (**I**) to (**IV**); the proton NMR spectra of compounds (**V**) and (**VI**) in the same region are similar to that of compound (**IV**). Note that the ubiquitous moisture peak at 1·65 ppm should be discounted in making use of peak integration. Stereochemistry was determined through peak assignments in the 1 to 3 ppm range for all the protons on the cyclohexane ring using the formerly established conformations [20, 21] of 1,3,5-cyclohexanetricarboxylic and 1,3,5-trimethylcyclohexane-1,3,5-tricarboxylic acids and their trimethyl esters. Specifically, the difference in the δ values of the equatorial and axial protons on the same carbon atom compiled in table 1 of reference [20] and the proton NMR spectra shown in figures 2 and 3 of reference [21] were the basis of our peak assignments. It should be pointed out that the relatively flat carboxyl groups in compound (**I**) seem to pack into the triaxial configuration better than the three methyl groups as previously suggested for the trimethyl ester derivative [20, 21]. Furthermore, the conformations in the solid state are expected to be the same as those shown for compounds (**I**), (**IV**), (**V**) and (**VI**) in figure 1, as determined in solution by proton NMR spectroscopy, based on a combination of *X*-ray crystallographic data and proton NMR spectra presented for similar compounds [21]. Note that the axial-equatorial mixed modes shown for compounds (**II**) or (**III**) in figure 1 cannot be converted to an all-axial or all-equatorial conformation, such as (**I**) or (**IV**), via rotation about single bonds.

Crystallization velocity (or radial spherulitic growth) as

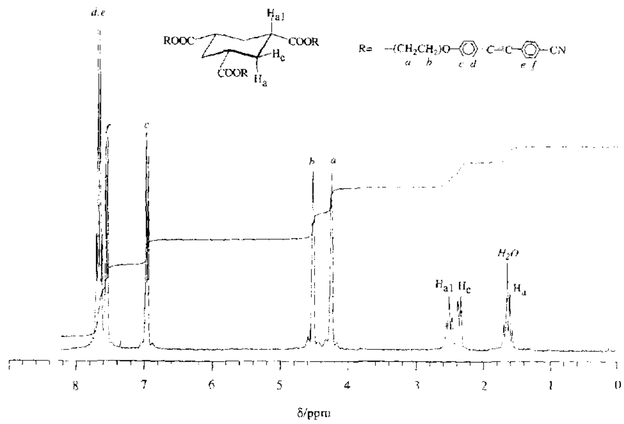

Figure 6. Proton NMR spectrum to validate the chemical structure of compound (**II**) with stereochemical features determined using signals in the 1 to 3 ppm range.

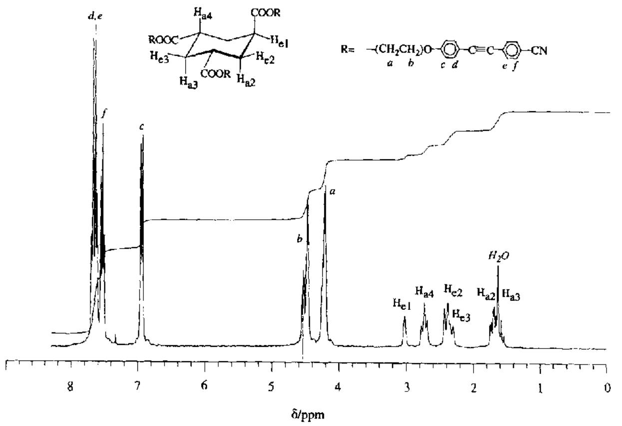

Figure 7. Proton NMR spectrum to validate the chemical structure of compound (**III**) with stereochemical features determined using signals in the 1 to 3 ppm range.

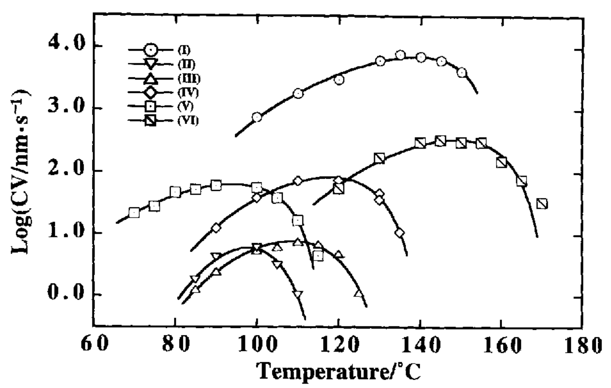

Figure 9. Crystallization velocity, CV, as a function of temperature for all six model GLMLCs to display the effects of stereochemistry, mesogenic core structure, and spacer length.

a function of temperature was experimentally determined for all model compounds with the results presented in figure 9. As previously reported for non-mesogenic, low molar mass [18] and polymeric [22, 23] materials, all the presently investigated GLMLCs show a CV curve going through a maximum as the temperature is lowered from T_m. Furthermore, the ratio of the temperature at which the maximum CV occurs to the crystalline melting point, T_{mcv}/T_m, was found to be 0·93 ± 0·01 for all GLMLCs, in agreement with what was reported for non-mesogenic glass formers, 0·92 ± 0·03 [18]. A scrutiny of the data plotted for compounds (**I**) and (**IV**) in figure 9 reveals that the cyanotolan group placed at the equatorial position depresses maximum CV by two orders of magnitude in comparison to axial substitution, a difference far beyond what can be accounted for by the presence of three additional methyl groups in the equatorial position that compound (**I**) possesses. A supportive evidence can be gathered by comparing the maximum CV values of compounds (**II**) and (**III**). It is demonstrated in figure 9 that compounds (**II**) and (**III**) carrying axial-equatorial mixed modes exhibit the best morphological stability of all with a comparable maximum CV of 6 nm s^{-1} a value close to that reported for isotactic polystyrene which was considered to be a typical 'slowly crystallizing' polymer [23]. The lower maximum CV values observed for compounds (**II**) and (**III**) than the rest of the GLMLCs are attributable to the increased overall structural irregularity with the presence of three additional methyl groups in compound (**III**) compared to compound (**II**) playing a negligible role in affecting the maximum CV value. From a comparison between the CV curves for compounds (**IV**) and (**V**), the morphological stability does not appear to be affected by lengthening the spacer from 2 to 4, which was intended to depress the tendency of the mesogenic core and/or the excluded-volume moiety to crystallize by furnishing some degree of coupling between the two. Nonetheless, the DSC data summarized in figure 1 reveal a depression in both T_g and T_m but a significant elevation in T_c with a longer spacer length. Compound (**VI**) containing 1-phenyl-2-(6-cyanonaphth-2-yl)ethyne, a stronger nematogen than cyanotolan in terms of a higher T_m and T_c and a broader nematic temperature range [24, 25] was found to have a maximum CV almost an order of magnitude greater than those of compounds (**IV**) and (**V**).

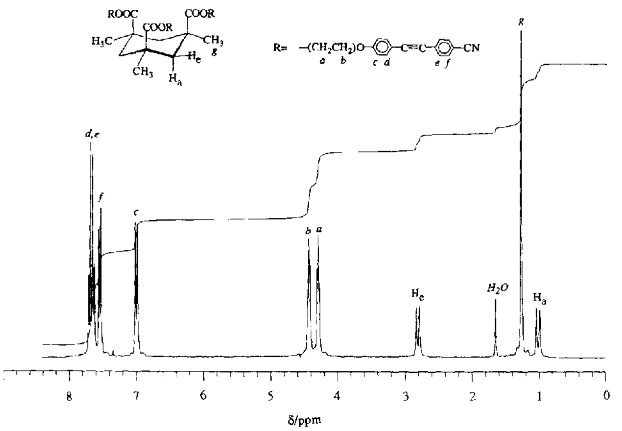

Figure 8. Proton NMR spectrum to validate the chemical structure of compound (**IV**) with stereochemical features determined using signals in the 1 to 3 ppm range.

4. Summary

Several GLMLC model compounds were synthesized by attaching nematogenic groups to cyclohexane rings with all possible stereochemical features to permit an investigation of morphological stability in relation to stereochemistry, spacer length, and mesogenic core structure. Radial spherulitic growth as a function of temperature was experimentally determined, and the maximum CV was adopted as a basis for assessing morphological stability against crystallization. The following main points emerge from the present study:

(i) All-equatorial configuration enhances morphological stability over all-axial configuration by two orders of magnitude with cyanotolan as the pendant mesogenic core.

(ii) The morphological stability is largely unaffected by the spacer length connecting the mesogenic core to the excluded-volume moiety, although both T_g and T_m are depressed whereas T_c is significantly elevated by a longer spacer.

(iii) As cyanotolan is replaced by 1-phenyl-2-(6-cyanonaphth-2-yl)ethyne as the mesogenic core, a stronger nematogen in terms of transition temperatures and mesophase temperature range, the morphological stability was found to diminish by almost an order of magnitude.

(iv) Equatorial–axial mixed modes increase morphological stability over all-equatorial and all-axial modes to such an extent that the morphological stability turns out to be comparable to a typical 'slowly crystallizing' polymer.

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