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Synthesis and Properties of Main Chain Discotic Liquid Crystalline Polyethers Based on Rufigallol

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ABSTRACT: Two series of thermotropic main chain discotic liquid crystalline polyethers, PR4*m*-*n*, based on rufigallol were prepared starting from the symmetric tetraethers of rufigallol, R4*m*; *m* and *n* represent the number of carbon atoms in the side chain and spacer segment, respectively. The symmetric tetraethers were in turn readily prepared by selective alkylation of rufigallol under controlled phase-transfer conditions. GPC analysis of the polymers suggested that they were all of moderate molecular weights, with M_n varying between 5400 and 17 000. The length of the spacer segment *n* in these polyethers was systematically varied, and its effect on the phase transition temperatures and the mesophase structure was examined using DSC, polarized light microscopy, and X-ray diffraction. It is noticed that when the spacer lengths are relatively long ($n \geq 2m$), the isotropization temperature (T_{D-i}) decreases as the spacer length *n* increases, an observation that is in accordance with those previously made. However, when the spacer lengths are relatively small ($n < 2m$), the dependence of T_{D-i} is quite the opposite; T_{D-i} actually increases with an increase in spacer length. Furthermore, X-ray diffraction studies indicate that, in the discotic columnar mesophases that are formed, the columns pack in a hexagonal manner when $n \geq 2m$, while they do so in a rectangular lattice when $n < 2m$, leading to the formation of Dh and Dr mesophases, respectively. Finally, comparison of the discotic polyethers with their low molar mass analogues confirms the role of polymerization in stabilizing the mesophase; while all the polymers exhibit columnar mesophases, some of their low molar mass analogues are not liquid crystalline.

Introduction

The field of liquid crystalline polymers with rodlike (calamitic) units in the main and side chain has been investigated extensively, and their industrial relevance has been well established.[1] Till recently, however, polymers based on discotic mesogenic units have been relatively less explored. Discotic liquid crystalline phases are exhibited by disklike molecules. A typical discotic molecule has an aromatic core to which are attached, via ester or ether links, six to eight alkyl chains of the same length.[2] Such discotic molecules have been shown to form both nematic and columnar mesophases. In a typical columnar mesophase the molecules stack to form columns that in turn form a 2-D array, leading to various types of columnar mesophases, namely, hexagonal (Dh), rectangular (Dr), and oblique (Dob). In polymeric discotic liquid crystals, such disk-shaped mesogenic moieties form either an integral part of the polymer main chain[3−6] or are attached to the polymer backbone as pendant side groups.[7,8] Recently, there have also been reports of discotic polymer networks[9−11] and elastomers.[12]

Most discotic main chain liquid crystalline polymers, reported thus far, are either inseparable mixtures of isomers[3] and/or cases where the discotic cores have two types of linking groups—one type linking them to the alkyl side chains and the other linking them to the flexible polymer backbone, for instance, as in the case of polyesters prepared from dimethyl 2,3,6,7-tetrakis(pentyloxy)triphenylene-10,11-dicarboxylate and various α,ω-dihydroxyalkanes.[4] The effect of a few ester linkages, in otherwise ether-linkage-containing discotic systems (monomers, dimers, and polymers), has been shown to be significant, in that it causes an increase in their isotropization tempratures (T_{D-i}).[5,13] Thus, the development of new efficient synthetic strategies for the production of discotic monomers and polymers will be a major step, both in terms of advancement of our fundamental understanding and also for the possible development of newer applications of discotic liquid crystalline polymers. Recently, this problem has been addressed by Boden et al., who reported a general regiospecific synthesis of various partially alkylated triphenylenes[14] and further exploited this method for the synthesis of main chain liquid crystalline polyethers.[6]

The two most important structural features in main chain discotic liquid crystalline polymers are (a) the length of the side chains and (b) the length of the spacer segment that links the discotic units together to form the polymer backbone. While Boden et al.,[6] demonstrated the elegance of their synthetic methodology to prepare single-isomer homogeneous polymers, no attempt was made to study the effect of variation of the length, of either the spacer or the side chains, on the mesomorphic behavior of the resulting polymers. The role of these structural parameters in triphenylene-based main chain discotic polyesters, where the triphenylene cores are linked to the alkyl side chains via ether groups and to the polymer backbone via ester groups, has been reported.[5] As previously noted, the study of phase behavior of such polymers with variation in side chain and spacer length is complicated by the existence of specific interactions between ester groups of neighboring discotic molecules, which have been postulated to play a significant role in raising their clearing transition temperatures.[5] With the objective of gaining a better understanding of the role of both the

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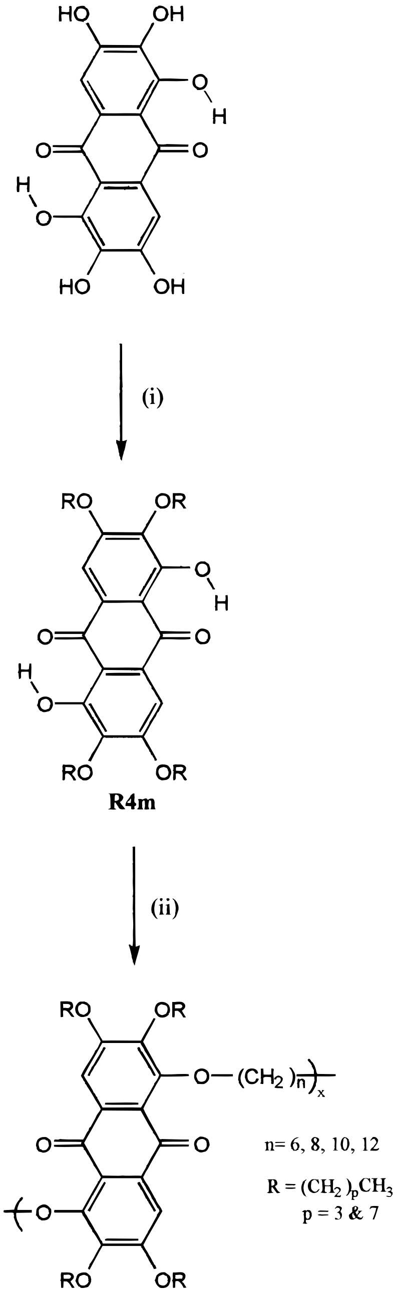
Scheme 1. General Scheme for the Preparation of the Monomers and Polymers[a]



PR4m-n

[a] (i) RBr, TBAB, NaOH, DMSO, 80 °C, 24 h; (ii) $Br(CH_2)_nBr$, *o*-dichlorobenzene−aqueous K_2CO_3 (5 M), TBAB.

spacer length and the side chain length, we report in this study the synthesis of two series of single-isomer homogeneous main chain discotic polyethers (PR4*m*-*n*) based on rufigallol, specifically PR44-*n* and PR48-*n* (Scheme 1), where both the spacer and side chains are linked via ether groups. The variation of the phase transition temperatures and transition entropies with a systematic increase in alkyl spacer length in these polymers has been investigated by DSC. The effect of variation of spacer length on the structure of the mesophases formed in these polymers has been studied by X-ray diffraction and polarized light microscopy.

Experimental Section

Table 1

sample	% yield	M_n	PD	DP
PR44-6	78	6800	2.8	11
PR44-8	76	17000	1.5	27
PR44-10	88	6400	2.8	10
PR44-12	60	5400	2.5	8
PR48-6	35	7400	2.6	9
PR48-8	74	14500	1.5	17
PR48-10	73	8800	2.7	10
PR48-12	67	7600	2.7	8

^1H NMR spectra were recorded on a Bruker ACF-200 MHz spectrometer, using TMS as the internal reference and $CDCl_3$ as the solvent. Molecular weights were determined by gel permeation chromatography (GPC) using a Waters GPC-150C instrument, Waters Ultrastyragel columns (10^3, 500, and 100 Å columns in series), and THF as the solvent (1 mL/min, 30 °C). Polystyrene standards were used for generating the GPC calibration curve. Polarized light microscopic studies were carried out using a Leitz Ortholux II Pol-BK microscope equipped with a Mettler FP82HT hot stage. DSC studies were done using a Rheometric Scientific DSC Plus instrument. The thermograms were recorded, both during the heating and cooling runs, using a heating/cooling rate of 10 deg/min. A slow purge of nitrogen gas (5 mL/min) was maintained to prevent any possible oxidative degradation. The reproducibility of the thermograms was confirmed by recording the second and third heating runs. Additionally, the cooling runs of PR44-8 and PR48-8 were recorded using a cooling rate of 2 deg/min in order to observe phase transitions that occur very slowly. The enthalpies (ΔH) of the phase transitions were determined from the areas under the corresponding peaks (normalized per mole of the repeat unit) and the entropies (ΔS) were taken as the ratio $\Delta H/T$, where T is the peak transition temperature. For determining the T_g's, the polymer samples were quenched from the melt by bringing the DSC pans, containing the sample, in contact with a precooled metal block (cooled in liquid nitrogen). The DSC's of these quenched samples were then recorded in the usual manner using a heating rate of 10 deg/min. The X-ray diffraction patterns of the liquid crystalline phases were recorded using an image plate (Marresearch, Germany), using Cu Kα radiation.

General Procedures. Rufigallol was prepared from gallic acid using a previously reported procedure.[16] It was then purified by hydrolysis of the recrystallized hexaacetate derivative. The two monomers, 1,5-dihydroxy-2,3,6,7-tetrabutoxy-9,10-anthraquinone **(R44)** and 1,5-hydroxy-2,3,6,7-tetrakis-(octyloxy)-9,10-anthraquinone **(R48)** were synthesized according to the procedure previously reported by us.[15] The dialkyl bromides were distilled prior to use.

Typical Procedure for PR4*m*-*n*. PR44-6. R44 (1.013 g, 1.92 mmol), 0.467 g (1.92 mmol) of 1,6-dibromohexane, and 1.299 g (4.03 mmol) of tetrabutylammonium bromide (TBAB) were dissolved in 10 mL of *o*-dichlorobenzene, and 5 mL of aqueous K_2CO_3 (5 M) was added to it. The reaction mixture was stirred at 90 °C for 2 weeks under a nitrogen atmosphere. It was then cooled, and 30 mL of chloroform was added to it. The organic layer was separated, washed with water, and dried using anhydrous Na_2SO_4. The solvent was removed under reduced pressure to yield the crude polymer. It was further purified by two reprecipitations, once from $CHCl_3$/MeOH and then from THF/MeOH. It was then dried in a vacuum oven at 50 °C. The yield of the polymer was 78%.

^1H NMR ($CDCl_3$), δ (in ppm): 7.61 (s, 2H, aromatic), 4−4.2 (m, 12H, Ar−O−CH_2), 1.1−2 (m, 24H, alkyl protons), 0.9−1.1 (m, 12H, terminal CH_3). $M_n = 6820$; PD = 2.8.

All other members of both the PR44-*n* series and the PR48-*n* series were synthesized using essentially the same procedure to give the required polymers in yields ranging from 35 to 88%. The ^1H NMR spectra of all the polymers exhibited essentially the same features with a single aromatic signal (at ca. 7.6 ppm), the only difference being the relative intensities of the aromatic and aliphatic proton signals, which were found to match with the expected values. The molecular weights of the polymers were determined using GPC (calibrated against polystyrene standards) and are listed in Table 1.

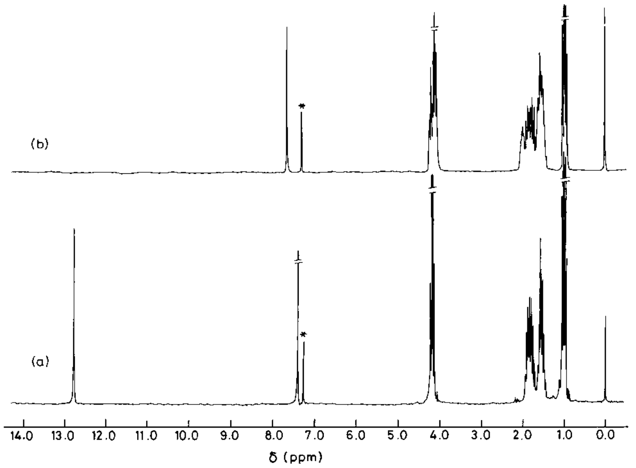


Figure 1. ^{1}H NMR spectra of the monomer R44 (a) and the polymer PR44-*n* (b). The peak marked by an asterisk is due to $CHCl_3$.

Results and Discussion

The rufigallol core presents the advantage of unequal reactivity of the six phenolic groups. This permits the selective alkylation of four of the phenolic groups, leaving behind the two intramolecularly hydrogen-bonded ones. Utlilizing this strategy, the synthesis of the symmetric tetraethers, 1,5-dihydroxy-2,3,6,7-tetrabutoxy-9,10-anthraquinone **(R44)** and 1,5-hydroxy-2,3,6,7-tetrakis(octyloxy)-9,10-anthraquinone **(R48)**, was reported by us recently.[15] The tetraethers crystallize out of the reaction mixture in essentially pure form and are further easily purified by recrystallization. Thus, these monomers were readily accessible in multigram quantitites, without the need for any tedious chromatographic separations, making them ideally suited for the synthesis of polymers. Two series of polymers, namely PR44-*n* and PR48-*n*, were prepared using a modified two-phase polyetherification procedure, in the presence of a phase-transfer catalyst.[17] Thus, the polyetherification of R44 and R48 with equimolar quantities of various α,ω-dialkyl bromides was carried out under a nitrogen atmosphere at 90 °C in *o*-dichlorobenzene−aqueous K_2CO_3, in the presence of tetrabutylammonium bromide, to yield the respective polymers (Scheme 1). The base used for the polymerizations was aqueous K_2CO_3, instead of aqueous NaOH as done previously,[17] since the latter was shown to cause degradation of the rufigallol core. The polymers were further purified by two reprecipitations, once from $CHCl_3$/MeOH and then from THF/MeOH to give the product in good yields (Table 1). The ^{1}H NMR spectra of all the polymers suggested that the alkylation was essentially complete. A typical NMR spectrum of the polymer (Figure 1b) exhibited a single aromatic peak at ca. 7.6 ppm, which is characteristic of hexaethers of rufigallol because of the presence of a C_2 axis of symmetry. The peak at 12.8 ppm, corresponding to phenolic protons present in the monomer (Figure 1a), is reduced to background level intensity in all the polymers, suggesting that this end group concentration in these polymers is fairly low. Furthermore, the peak due to the other possible end group, namely, the bromomethyl group, $-\mathbf{CH_2}Br$ (expected around 3.42 ppm), was also not visible, confirming that the polymers formed are indeed of reasonable molecular weight. The molecular weights of the polymers were determined by GPC using polystyrene as standards and the values obtained are listed in Table 1. The degree of polymerization (DP) of all the polymers fall in the same range (8−11), except for PR44-8 and PR48-8, which have much higher DP values of 27 and 17, respectively. It was shown earlier[5] that, in addition to other factors that affect the mesophase stability such as side chain and spacer alkyl chain lengths, the clearing transition temperature increases with an increase in DP. However, this effect was shown to level off after a DP of about 10, in the triphenylene-based main chain polymers.[5] Thus, in the current series of discotic liquid crystalline polyethers, most of the polymers have a DP in a range where it may be reasonable to assume that their thermal properties would be invariant with molecular weight. The comparative analysis of their thermal behavior with variation of other molecular structural parameters, specifically that of spacer length, is made by assuming such an invariance. The polymers are represented by the general formula PR4*m*-*n*, where *m* and *n* represent the number of carbon atoms in the side chain and spacer segment, respectively.

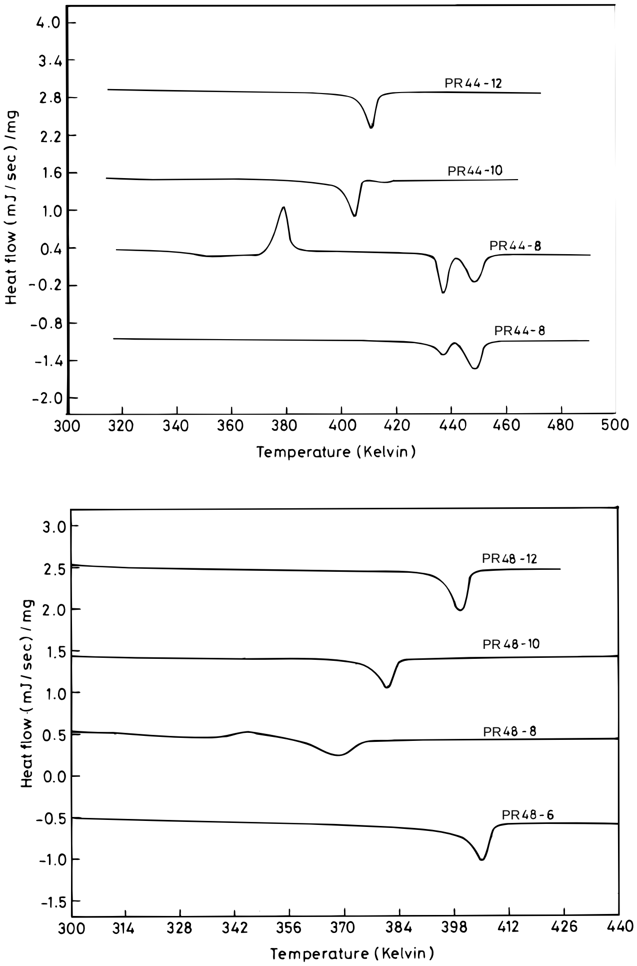


Figure 2. DSC traces of PR44-*n* series (a, top) and PR48-*n* series (b, bottom); recorder at a heating rate of 10 deg/min.

Thermal Properties

The DSC thermograms of the discotic polymers, belonging to the PR44-*n* and PR48-*n* series, are shown in Figure 2a,b, respectively. In general, it is noticed that all the polymers do not exhibit a melting transition, but instead they go directly from a glassy state to the mesophase and further isotropize at higher tempera-

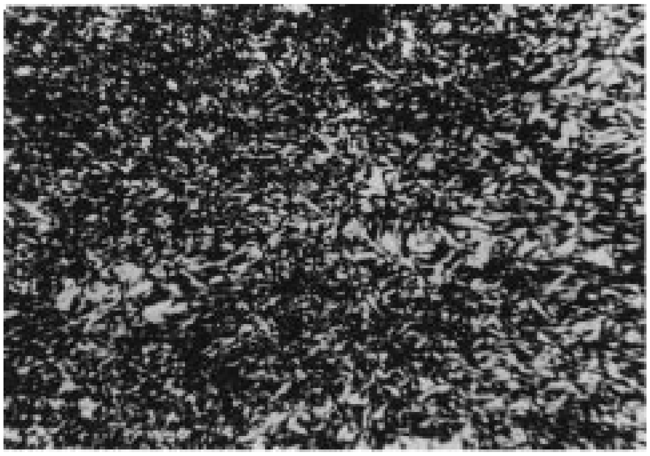


Figure 3. Typical columnar mesophasic texture of PR44-8 viewed under crossed polarizers; under a magnification of 250×. Reduced to 80% for reproduction.

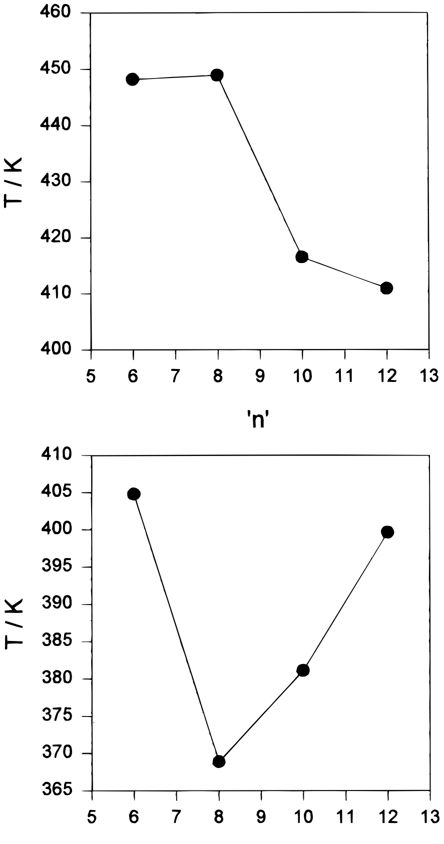


Figure 4. Plot of T_{D-i} versus the spacer length (*n*) for the PR44-*n* series (a, top) and for the PR48-*n* series (b, bottom).

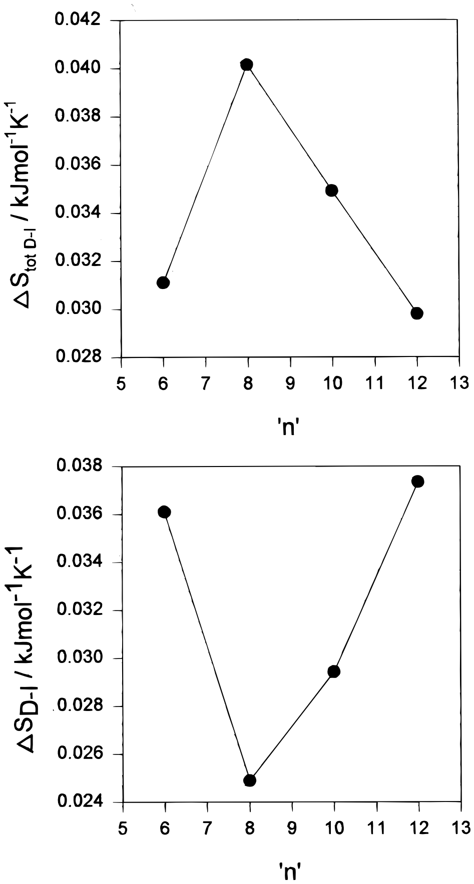


Figure 5. Plot of ΔS_{D-i} versus spacer length (*n*) for the PR44-*n* series (a, top) and for the PR48-*n* series (b, bottom).

tures. In the DSC traces where only a single endotherm is visible, this corresponds to the isotropization temperature (T_{D-i}), while in cases where two distinct endotherms are observed (as in PR44-6, PR44-8, and PR44-10), these correspond to the presence of two types of columnar mesophases. In the case of PR44-10, the second endotherm corresponding to T_{D-i} is rather weak and barely visible. The presence of two types of mesophases was confirmed by polarized light microscopic observations. In most cases the T_g's could not be observed by DSC, except in the cases of PR44-8 & PR48-8 for which they appear as very weak transitions. Under the microscope these polymers exhibit viscous birefringent mesophases; the texture of a typical columnar mesophase, that of PR44-8, is shown in Figure 3. At room temperature the mesophasic textures of all the polymers are frozen and they exhibit no flow. The thermal data for the two series of polymers, PR44-*n* and PR48-*n*, are presented along with data for their model compounds in Table 2ab, respectively. The monomeric model discotics for these main chain polymers (PR4*m*-*n*) are those that have the same four alkyl side chains (*m*) and two other alkyl groups (*x*) with half the number of carbon atoms as present in the spacer segment of the corresponding polymer; i.e., they have a general formula R4*m*-2*x*, where $x = n/2$. Thus, the model compound for the polymer PR44-12 will be R44-26, both of which have the same number of total alkyl chain carbon atoms. A systematic study of asymmetric discotic liquid crystals of the type, R4*m*-2*x*, was reported by us earlier.[15] A plot of the isotropization temperatures (T_{D-i}) versus spacer length (*n*) for the PR44-*n* series is shown in Figure 4a. It is seen that T_{D-i} first increases marginally and then falls sharply with an increase in the spacer length. However, in the PR48-*n* series (Figure 4b), the behavior is very different. In this case, T_{D-i} first falls and then increases with spacer length. A similar behavior is also observed in the variation of their isotropization entropies (ΔS_i) versus *n*. In the PR48-*n* series, the variation of ΔS_i versus *n* (Figure 5b), parallels that observed in the case of T_{D-i}. However, in the case of the PR44-*n* series, the presence of more than one type of discotic mesophase in some of the polymers makes such a direct comparison less straightforward. It was noticed that plotting the isotropization entropy directly versus *n*, gave no discernible trend (see Table 2a for values of ΔS corresponding to various transisitons). However, if the

Table 2

Part a

sample	T_g/K	$T_{\mathrm{D1-D2}}$/K	$T_{\mathrm{D2-i}}$/K	$\Delta S_{\mathrm{D1-D2}}$/ kJ mol^{-1} K^{-1}	$\Delta S_{\mathrm{D2-i}}$/ kJ mol^{-1} K^{-1}	$\Delta S_{\mathrm{totD-i}}$ kJ mol^{-1} K^{-1}	model compd	$T_{\mathrm{D-i}}$/K	$\Delta S_{\mathrm{D-i}}$/ kJ mol^{-1} K^{-1}
PR44-6	344.9	436.6	448.2	0.0102	0.0209	0.0311	R4423	406.4[a]	
PR44-8	344.6	437.4	448.9	0.02	0.0201	0.0402	R4424	404.0[a]	
PR44-10		405.5	416.5	0.0334	0.0016	0.0349	R4425	396.2	0.0357
PR44-12			410.9		0.0298	0.0298	R4426	391.7	0.0350

Part b

sample	T_g/K	$T_{\mathrm{D-i}}$/K	$\Delta S_{\mathrm{D-i}}$/ kJ mol^{-1} K^{-1}	model compd	$T_{\mathrm{D-i}}$/K	$\Delta S_{\mathrm{D-i}}$/ kJ mol^{-1} K^{-1}
PR48-6		404.8	0.03061	R4823	353.2[a]	
PR48-8	327.2	368.9	0.0249	R4824	353.7[a]	
PR48-10		381.1	0.0294	R4825	346.9	0.019
PR48-12		399.6	0.0373	R4826	359.5	0.029

[a] Crystal to isotropic transition temperature.

sum total of the transistion entropies on going from D_1 to the isotropic phase (in cases where more than one mesophase is observed) is plotted versus n (Figure 5a), a similar trend, as was seen in the case of $T_{\mathrm{D-i}}$, is observed.

This difference in the behavior between the two series of polymers can be rationalized on the basis of the relative sizes of the alkyl side chain (m) and alkyl spacer segments (n). In most main chain discotic liquid crystalline polymers, reported thus far, the length of the spacer segment is at least twice that of the alkyl side chains, i.e., $n \geq 2m$. This is probably because of a tacit assumption that there would be severe steric hinderance to the formation of columnar mesophases in polymeric systems where the spacer segment does not meet the above stated criterion. Thus, in general, it has been observed in most such main chain discotic polymeric systems (where $n \geq 2m$) that increasing the length of the spacer segment leads to a fall in the isotropization temperatures.[3-5] In the PR44-n series, this trend is generally followed, except in the case of R44-6 where in $n < 2m$. Remarkably, in the PR48-n series, where all the polymers have spacer lengths that are smaller than twice the side chain length, i.e., $n < 2m$, it is generally observed that $T_{\mathrm{D-i}}$ increases with n, with the exception of PR48-6. These trends are reminiscent of those seen in asymmetric discotic liqiud crystals (R4m-2x),[15] where it was observed that the most symmetric discotic molecule (where $x = m$) exhibits the highest isotropization temperature. These observations, when viewed in the context of others reported in the literature[3-5] and also those of asymmetric discotic liquid crystals,[15] appear to suggest that the behavior of main chain discotic polymers may be rationalized, in a more generalized sense, as follows: the most symmetric polymer (where $n = 2m$) will have the highest isotropization temperatures, and when the spacer segments are either shorter or longer, $T_{\mathrm{D-i}}$ will decrease. Although this rationalization is based on a limited number of data points, it explains the behavior of all but one of the members of both the series, the exception being PR48-6. While in the PR44-n series, the spacer length variations span both sides of the symmetric case, in the PR48-n series, n is always $<2m$. As will be seen later, the odd behavior of PR48-6 is also reflected in its substantially smaller area/column value, suggesting the formation of a highly compact mesophase. Furthermore, when pairs of polymers having the same spacer segment from the two series, for instance PR44-8 and PR48-8, are compared, it is seen that increasing the length of the side chain decreases $T_{\mathrm{D-i}}$. This observation is true for all pairs of polymers (see Table 2a,b); i.e., in general, increasing the length of the side chain causes a decrease of $T_{\mathrm{D-i}}$, which is contrary to the observations made in the triphenylene-based polymers.[5] Here again, the different behavior exhibited by our system is probably because the relative sizes of the spacer and the side chain in the two series are different; in most PR44-n polymers, $n \geq 2m$, while in PR48-n, $n < 2m$.

As mentioned earlier, the glass transition temperatures of only three samples, PR44-6, PR44-8, and PR48-8, could be determined by DSC and they are listed in Table 2a,b. In other samples, even quenching the samples from the melt by bringing the DSC pans, containing the sample, directly in contact with a precooled metal block (cooled in liquid nitrogen) proved futile, since crystallization and mesophase formation in these cases occur very rapidly. PR44-8 and PR48-8 do not exhibit any exotherm during the controlled cooling (10 deg/min) run, but during the subsequent heating run they exhibit an exotherm (see Figure 2a,b) at a temperature above their T_g, which is reminiscent of the typical cold crystallization process observed in, for example, PET. However, in this case, the exotherm corresponds to the formation of a columnar discotic mesophase rather than a crystalline phase as in the case of PET. On the other hand, if PR44-8 and PR48-8 are cooled from the isotropic melt at 2 deg/min a weak exotherm corresponding to the formation of the mesophase is indeed observable. Polarized light microscopic observations confirm the above conjecture. On cooling the samples from the isotropic melt at 10 deg/min, they do not become birefringent even at room temperature. But, on cooling at a much slower rate of 2 deg/min, they become birefringent at a temperature corresponding to the exotherms observed in their DSC's, recorded at the same cooling rates. This rather unique behavior of the polymers PR44-8 and PR48-8 may be rationalized on the basis of their relatively higher molecular weights and hence higher melt viscosities. This in turn slows down the process of crystallization and presumably also mesophase formation.

Comparison of the behavior of the polymers with those of the model compounds also brings out some marked differences. While all the polymers exhibited discotic columnar mesophases, some of the corresponding model compounds, such as R4423, R4823, and R4824, are not liquid crystalline. Furthermore, the symmetric tetraether R64 was monotropic with a very narrow mesophase of 1 deg. This demonstrates the stabilization of the discotic mesophases by polymer fixation, concurrent with the conclusions drawn from other main chain discotic polymers based on benzene[3] and also other main chain calamitic liquid crystalline polymers.[18]

X-ray Diffraction

The X-ray diffraction experiments were carried out using unoriented samples taken in glass capillaries. In their mesophases, all the polymers, except PR44-6 and PR44-8, exhibit two diffuse diffraction peaks in the wide-angle region. These correspond to spacings of about 3.8 and 4.4 Å, which are typical of a discotic columnar mesophase.[19] The 3.8 Å reflection corresponds to the interdisk spacing within a column, and the one at 4.4 Å arises from the disordered alkyl chains. These spacings correspond well to those observed in low molecular weight hexaethers of rufigallol.[15,20] In PR48-8, there is a very broad diffuse peak centered around 4.1 Å; its large width most probably is due to the overlap of two diffuse peaks similar to the ones seen in the other compounds. In PR44-6 and PR44-8, the reflections in the wide-angle region are rather sharp, in both the mesophases (D_1 and D_2) exhibited by these polymers. Though both these mesophases appear to be columnar in nature (see the discussion below), the distinction between the two is presently not clear and is under investigation.

In the small-angle region, all the members of the PR48-*n* series show two strong diffraction peaks. This is generally characteristic of a rectangular columnar phase.[21] A typical diffraction pattern of the Dr mesophase, that of PR48-12, is shown in Figure 6b. On the other hand, most members of the PR44-*n* series show only a single strong diffraction peak in the small-angle region, except PR44-6, which shows two peaks. Generally, the presence of a single strong small-angle peak along with two diffuse peaks in the wide-angle region is characteristic of a hexagonal columnar phase. This is clearly the case for PR44-10 and PR44-12. A typical diffraction pattern of the Dh mesophase, that of PR44-12, is shown in Figure 6a. In the case of PR44-8, an additional weak reflection in the small-angle region is also seen; the two spacings are in the ratio $1:\sqrt{3}$, which again is consistent with a hexagonal lattice. In the case of PR44-6, however, the presence of two small-angle reflections, suggests the formation of a rectangular unit cell. We can, therefore, conclude that most members of the PR44-*n* series display a hexagonal columnar discotic mesophase, with the exception of PR44-6, which exhibits a rectangular columnar mesophase. Furthermore, as mentioned earlier, DSC and optical microscopic studies show that the three lower members of this series, PR44-6, PR44-8, and PR44-10, exhibit two types of mesophases. However, the diffraction patterns of these polymers do not change significantly across this phase transition. Work is currently underway in order to determine the structure of the mesophases in PR44-6 and PR44-8 and that of the high-temperature mesophase in PR44-10. Another interesting feature is the observation of a rather sharp, but weak, reflection in PR44-6 at 7.2 Å. The fact that this peak in PR44-6 could not be indexed on any two-dimensional lattice along with the other peaks suggests that it may be due to some degree of ordering along the column direction.

The X-ray diffraction data for the two series of polymers are presented in Table 3. From these data it is clear that the structure of the columnar mesophase in these polymers is significantly influenced by the relative alkyl chain lengths of the spacer and the side chains. Thus, a Dh phase is obtained if the length of the spacer is greater than or equal to that of the side chains, i.e., $n \geq 2m$, while a Dr mesophase results when $n < 2m$. It may be added here that, while our classification of the columnar mesophases as hexagonal and rectangular is unambiguous, the absence of a sufficient number of reflections, despite exposure times of over 4 h, makes it impossible to determine the lattice parameters of the Dr mesophase from the present data alone; the few observed reflections could be indexed by using more than one two-dimensional unit cell. We index the two strong small angle peaks as the (2 0) and (1 1) reflections from a centered rectangular lattice. The parameters, presented in Table 3 for the Dr phase, are for the unit cell that gives an area per column closer to that of its corresponding model compound. In the absence of any other supplementary information, we

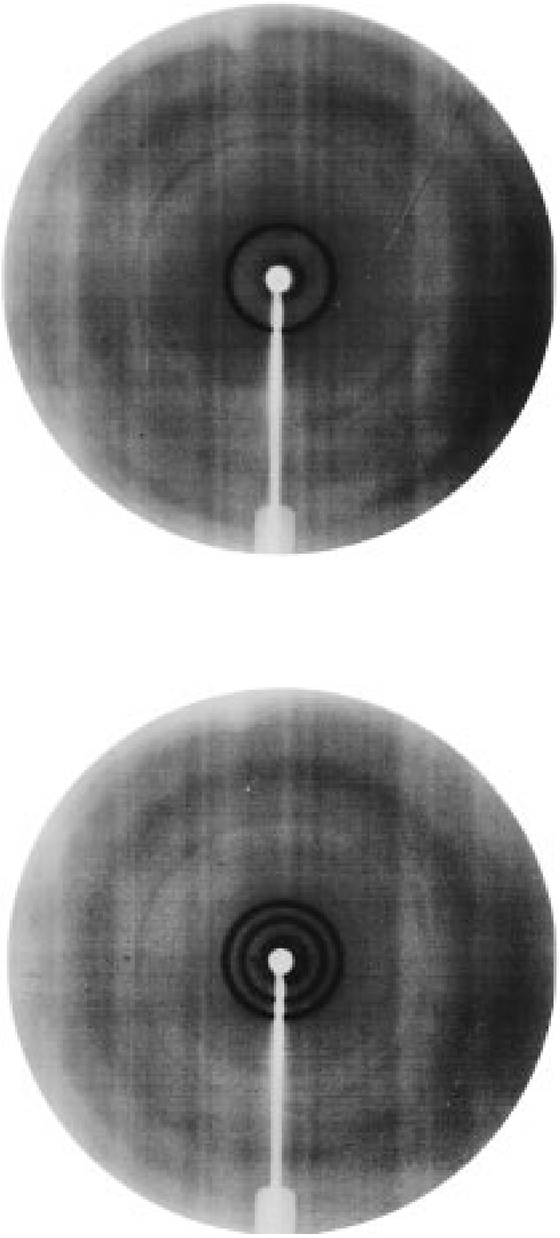


Figure 6. X-ray diffraction patterns of a typical Dh mesophase, that of PR44-12 at 120 °C (a, top), and a Dr mesophase, that of of PR48-12 at 112 °C (b, bottom).

Table 3

sample	lattice type	small-angle spacings (Å) (Miller indices)	wide-angle spacing (Å)	lattice params[a] (Å)	area/column (Å^2)
		R44-*n* Series			
PR44-6	Dr	15.6 (11), $(\bar{1}_a1)$; 12.5 (20); 10.4 (21); 7.2 (31)	4.7, 4.2, 3.8	$a = 24.98$, $b = 18.06$	451.1
PR44-8	Dh	13.8 (10), (01), $(\bar{1}1)$; 7.9 (11)	4.6, 4.0, 3.8	$a = 27.46$	437.9
PR44-10	Dh	15.5 (10), (01), $(\bar{1}1)$	4.4, 3.6	$a = 31.0$	556.6
PR44-12	Dh	16.2 (10), (01), $(\bar{1}1)$	4.5, 3.7	$a = 32.3$	602.4
		R48-*n* Series			
PR48-6	Dr	22.6 (20); 13.2 (11), $(\bar{1}1)$		$a = 45.14$, $b = 13.80$	622.9
PR48-8	Dr	21.1 (20), 17.6 (11), $(\bar{1}1)$		$a = 42.14$, $b = 19.34$	815
PR48-10	Dr	20.1 (11), $(\bar{1}1)$; 16.2 (20); 8.8 (13)	4.6, 3.8	$a = 32.3$, $b = 25.76$	832
PR48-12	Dr	21.1 (11), $(\bar{1}1)$; 14.7 (20); 10.5 (22), (22)	4.6, 3.9	$a = 30.2$, $b = 29.5$	890.9

[a] In the case of rectangular lattice, the number of columns per unit cell was determined by using the area of the corresponding monomeric models.

assume this to be a reasonable criterion to arrive at the correct unit cell. This criterion would be exact if the two systems have the same density and the same average separation of the disks along the columns. While we have not measured the densities of these materials, the X-ray data indicate that the latter condition is satisfied. The area per column of the liquid crystalline model compounds can be represented by the expression, area $= 73.54 + 7.54C_n$, where C_n is the total number of alkyl chain carbon atoms in a molecule, as was described by us previously.[15] In the absence of a better alternative, we have used the same expression to calculate the area per column for a few of the nonmesomorphic model compounds also. Further, on the basis of the lattice parameters, the area per column, i.e., the area occupied by a single repeat unit, was calculated, and these are also listed in Table 3. From these data two interesting observations emerge. First, PR48-6 appears to have a significantly smaller value for this area when compared to the other members of this series.[22] The remarkably higher mesophase stability for this polymer, as reflected by its higher isotropization temperature when compared to others in the series, may, thus, be due to the more compact packing present in its mesophase. In the PR44-*n* series, on the other hand, the area/column value first decreases slightly and then increases with *n*, the symmetric polymer PR44-8 having the smallest value. In this series, however, the lowest member is in a Dr type mesophase while the others form a Dh mesophase, which makes any kind of generalization regarding this behavior difficult.

In conclusion, we have synthesized two series of single-isomer homogeneous main chain discotic liquid crystalline polyethers based on the rufigallol core, PR44-*n* and PR48-*n*, with four alkyl chains of one length (butyl and octyl, respectively) and a connecting alkyl spacer segment having *n* carbon atoms. The monomers, tetraethers of rufigallol, R44 and R48, were readily synthesized in multigram quantities directly from rufigallol. The effect of spacer segment length on the mesophase structure and stability was examined in both series. First, it is shown that columnar discotic mesophases can indeed be formed even in polymers where the spacer segment length is less than twice the length of the side chains, a fact that had hitherto been largely unexamined. Most main chain discotic polymers examined thus far appear to suggest that the isotropization temperature decreases with an increase in spacer length.[3-5] The present study suggests that this may be true only in cases where the spacer lengths are fairly long (i.e., $n \geq 2m$); when a more complete variation of spacer lengths is considered, it appears that the relative size of the alkyl side chain and alkyl spacer segments is of greater importance. Thus, in general, it may be appropriate to rationalize the behavior of such discotic polymers in terms of the asymmetry; in other words, the isotropization temprature is highest for the most symmetric (with respect to the relative sizes of the spacer segment and alkyl side chains) cases, i.e., when $n = 2m$, and lower when the spacer segments are both longer and shorter. This hypothesis is concurrent with most of the observed results in the literature, as most of them suggest a decrease of T_{D-i} with an increase in spacer length (but only for cases where $n \geq 2m$). Furthermore, in our system, the effect of side chain length on the isotropization temperatures is contrary to that observed in the literature,[5] and we ascribe this again to the relative sizes of the alkyl side chain and alkyl spacer segments. Another interesting aspect that emerges from this investigation is that the X-ray analysis of the mesophases suggests that in cases where $n < 2m$, rectangular columnar mesophases are formed, but in cases where $n \geq 2m$, they are hexagonally packed. The latter is concurrent with the observations made thus far in similar systems. The remarkable stability of the mesophase in the case of PR48-6 and also its unusually small column area appear to suggest the formation of a rather compact mesophase in this case. Finally, comparison of the discotic polyethers with their low molar mass analogues confirms the role of polymerization in stabilizing the mesophase; while all the polymers exhibit columnar mesophases, some of their low molar mass analogues are not liquid crystalline.

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