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Modification of DOBOB mesogen

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Abstract

As part of our attempt to prepare a molecular spinning machine, we synthesized a new discotic liquid crystal polymethacrylate based on taper-shaped monoesters of triethylene glycol with 3,4,5-tris(*p*-dodecyloxybenzyloxy-*m*-methoxybenzyloxy)benzoic acid (DOVOB acid). In advance of this effort, we embarked on the modification of the DOBOB mesogen to provide segmental units with the requisite mobility to produce a nanorotor. The induction of a glass transition for the taper-shaped columnar discotic mesogen 3,4,5-tris(*p*-dodecyloxybenzyloxy) benzoic (DOBOB) acid was achieved by attaching a methoxy group to the benzyl unit resulting in 3,4,5-tris(*p*-dodecyloxy-*m*-methoxybenzyloxy) benzoic (DOVOB) acid, using the Adam–Gibbs configurational entropy theory as the guideline. Solid state deuterium NMR techniques have been used to study the rotation dynamics of both mesogens.

Keywords: Discotic liquid crystal; Glass transition modification; Molecular spinning machines

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1. Introduction

Nanorotors and molecular spinning machines are conceptual developments of nanotechnology. Although synthesizing molecules for these functions is technically challenging, nanorotors are the essential components of molecular spinning machines, and one way to make a nanorotor is by using the self assembled columnar structure of discotic liquid crystal molecules provided that correlated rotation of the disc-like molecules in the columns about the columnar axis (the axial rotation) is possible. Thus a glass transition temperature is required for these discotic molecules since the crystalline-melt transformation for the columnar structure is unsuitable for using them as nanorotors. Our work is focused on the DOBOB mesogen based macromolecule poly(2-(2-(2-methacryloyloxyethoxy) ethoxy)ethyl 3,4,5-tris(*p*-dodecyloxybenzyloxy)benzoate) (Table 1), or PMB which is highly crystalline and does not form a glassy viscoelastic state. Induction of the glassy state for the columnar structure of DOBOB based mesogen is the major objective of this work.

Percec and coworkers reported that the taper-shaped monoesters of mono, di, tri, and tetra-ethylene glycol with 3,4,5-tris(*p*-dodecyloxybenzyloxy)benzoic (DOBOB) acid and their corresponding polymethacrylates self-assembled into tubular supramolecular architectures comprising a columnar hexagonal mesophase with diameters of 5.02, 5.41, 5.98, and 6.00 nm, respectively, at 25 °C (I–IV in Table 1) [1]. X-ray structure analyses of poly(2-(2-(2-(2-methacryloyloxyethoxy)ethoxy)ethoxy)ethyl 3,4,5-tris(*p*-dodecyloxybenzyloxy)benzoate (IV in Table 1) and its precursor suggested that the taper-shaped mesogen DOBOB self-assembled into a ‘pine-tree’ type columnar structure (with a tilt angle 40–50° to the backbone) like a self-assembled stacking bowl [2–5]. The precursor, 2-(2-(2-hydroxyethoxy) ethoxy)ethyl 3,4,5-tris(*p*-octadecyloxybenzyloxy)benzoate (V in Table 1), [6] also self assembles like a stacking bowl. The model system chosen for this work is the DOBOB mesogen based macromolecule poly(2-(2-(2-methacryloyloxyethoxy)ethoxy)ethyl 3,4,5-tris(*p*-dodecyloxybenzyloxy)benzoate) (III in Table 1), or PMB. Unlike poly(2-(2-methacryloyloxyethoxy)ethyl 3,4,5-tris(*p*-dodecyloxybenzyloxy)benzoate) (II in Table 1) which exhibited a glass transition at 36 °C (although very weak from the DSC trace), PMB is highly crystalline and does not form the glassy viscoelastic state [1]. The glass transition of this material depends on the free volume inside the mesogen. By reducing the free volume inside the mesogen, the conformational freedom of the mesogen group is decreased resulting in loss of rotation of the benzyl group thereby

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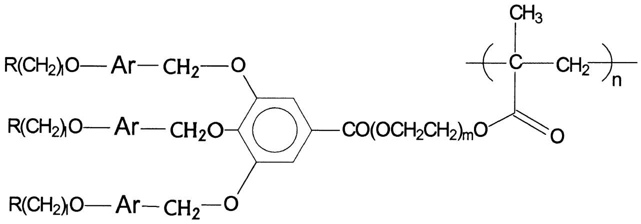
Table 1
Self-assembled columnar LCPs with taper-shaped side groups



No.	Ref	R	I	Ar	*m*	*d* (nm)	M_n (× 1000)	DSC (°C, kcal/mol, cal/mol/K)
I	1	H	12	1,4-C_6H_4	1	5.02	27.7	col127(0.36/0.9)iso
II	1	H	12	1,4-C_6H_4	2	5.41	24.6	g36col116(0.41/1.1)iso
III	1	H	12	1,4-C_6H_4	3	5.98	44.7	k48(3.32)col113(0.43/1.1)iso
IV	1	H	12	1,4-C_6H_4	4	6	69.1	k48(3.75)col103(0.50/1.3)iso
V	6	H	18	1,4-C_6H_4	3	5.7	1.3781	k65col75iso (precursor)
VI	14	F	10	1,4-C_6H_4	4	5.79	16.9	g3col66(0.24/0.71)iso
VII	14	$F(CF_2)_6$	4	1,4-C_6H_4	4	6.43	22.8	g14col200(0.34/0.72)iso
VIII	15	H	10	2,6-$C_{10}H_6$	4	6.19	78.3	g28col139(0.45/1.1)iso
IX	15	H	12	2,6-$C_{10}H_6$	4	6.51	32.5	g32col149(0.45/1.1)iso

inducing rotation about the axis of the molecule and resulting in the introduction of a glass transition temperature. Attaching a methoxy group to the benzyl unit results in the introduction of a glass transition temperature for DOOB due to the reduction of free volume associated with the mesogen.

Theoretically, the glass transition phenomenon can be described by the WLF equation with the free volume concept [7]

$$\log a_T = \log \frac{\tau_c(T)}{\tau_c(T_g)} = -\frac{C_1(T - T_g)}{C_2 + (T - T_g)}$$

$$\approx \log \frac{\eta(T)}{\eta(T_g)} \propto \left[\frac{1}{f(T)} - \frac{1}{f(T_g)} \right],$$

$$f(T) = f(T_g) + \alpha_f (T - T_g)$$

where $f(T) = V_f/(Vo + V_f)$ is the fractional free volume at a temperature T, α_f has the dimension of a thermal expansion coefficient, V_o and V_f are the occupied volume and the free volume. From the Adam–Gibbs configurational entropy theory [8]

$$\tau_c = \frac{K}{W} = A \exp\left(-\frac{s^* \Delta\mu}{TS_c} \right) = A \exp\left(\frac{C}{TS_c} \right)$$

where K is a constant of proportionality, $\Delta\mu$ is the hindrance-free energy barrier per particle to cooperative rearrangements, S_c is the excess configurational entropy, W is the average transition probability which is inversely related to the relaxation time τ_c, and s^* is the critical configurational entropy. Thus, the transition probability depends on the configurational entropy of glass forming liquid and the transition mechanism and mode can be controlled by limiting free volume associated with specific configurations of the molecule.

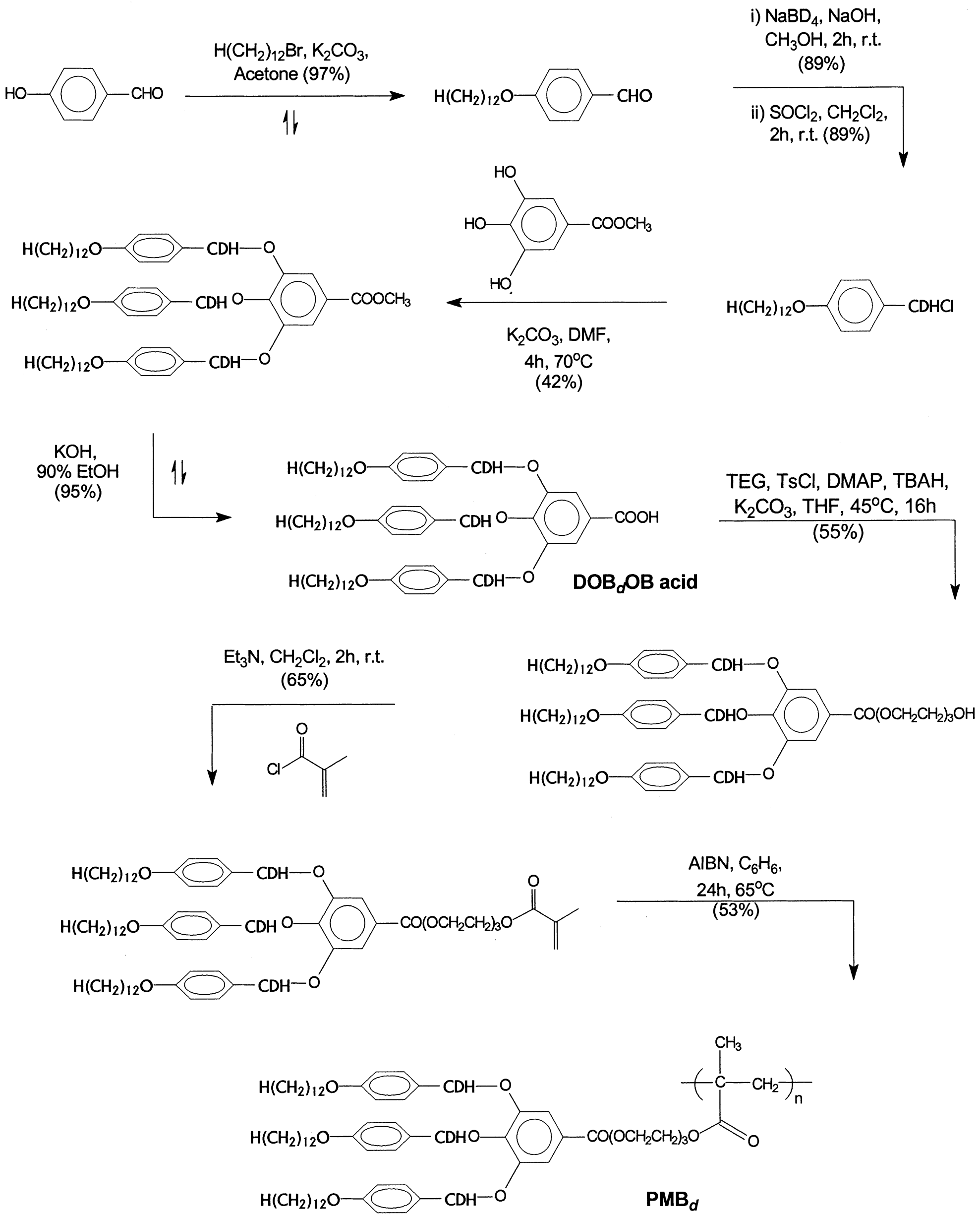
Since the crystalline state was inappropriate for the columnar structures we proposed for the molecular design of a nanorotor, we sought to induce a glass transition. Both free volume theory [7] and Adam–Gibbs configurational entropy theory [8] suggest that the induction of the glass transition temperature requires reducing the free volume inside the mesogen, thus decreasing the conformational freedom of the mesogen group.

The ^2H NMR study of the deuterated DOBOB mesogen containing compound suggested that there is enough free volume inside the mesogen for the rotation of the Ar–CH_2O bond [9]. The outer benzyl groups have enough space to undergo ring flips [10]. Therefore, ^2H NMR studies of the benzyl-d_3 deuterated polymethacrylate (PMB_d) would show whether the fast isotropic Ar–CDHO bond also rotates in the mesophase. As described in Section 3, ^2H NMR studies confirmed the presence of fast bond rotations within the mesogen resulting from the existence of free volume inside the mesogen. In the following section we describe in detail the synthesis work resulting in a new discotic system with diminished free volume in the mesogen to prevent the fast bond rotation and to induce rotation about the columnar axis thereby inducing a glass transition for the system.

2. Experimental

Deuterated DOBOB and deuterated PMB were synthesized for facilitating NMR studies. Scheme 1 outlines the synthesis of the selectively deuterated DOB_dOB containing polymethacrylate to obtain PMB_d. The preparation of PMB_d followed the literature-published procedure [1,11] with a slight change for the PMB_d preparation whereas $NaBH_4$ was replaced by $NaBD_4$.

In consideration of the ease of the chemical synthesis and the availability of the starting materials, one methoxy group



Scheme 1. Preparation of deuterated Percec model system PMB$_d$.

was introduced to the 3′-position of each phenyl ring of the taper-shaped DOBOB mesogen; thus, the syntheses could be carried out by a variation of literature procedures by using vanillyl alcohol as the starting material instead of *p*-hydroxybenzaldehyde. The modification of the mesogen was expected to stabilize the columnar mesophase and induce a glass transition of the corresponding polymethacrylate.

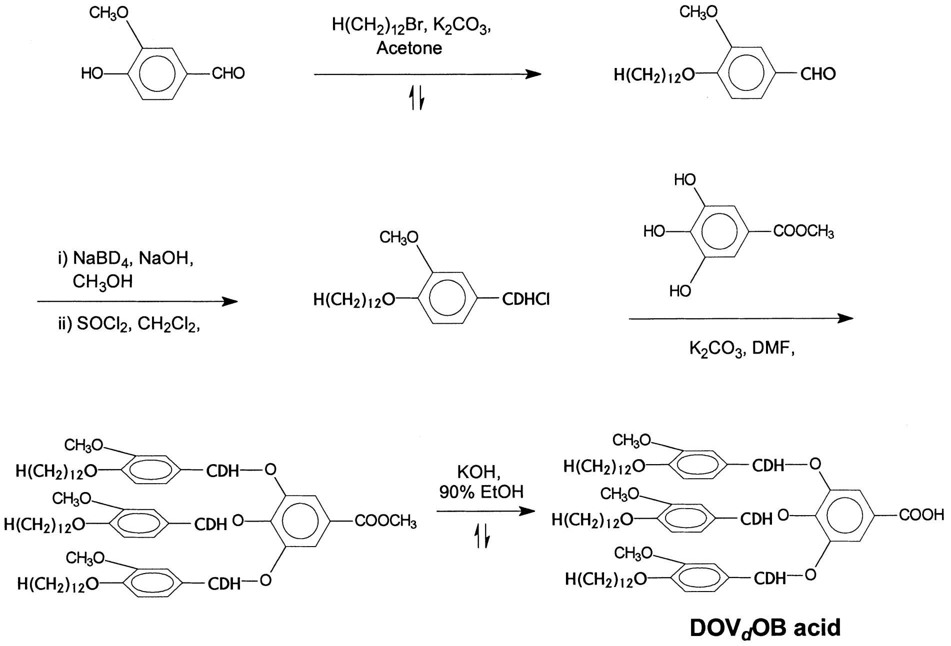
Scheme 2 outlined the synthesis of DOV$_d$OB acid, which is similar to that of DOB$_d$OB acid with vanillin as the starting compound and the use of $NaBD_4$ in the reduction step instead of $NaBH_4$.

2.1. Preparation of p-(n-dodecyloxy)benzaldehyde (DBa)

To 250 ml of acetone were added *p*-hydroxybenzaldehyde (82 mmol, 10.0 g), anhydrous K_2CO_3 (86 mmol, 11.87 g), and 1-bromododecane (86 mmol, 21.2 ml). The mixture was refluxed for 24 h. After removing acetone by rotary evaporation, the residue was added to chloroform (200 ml) followed by filtration. The solution was then dried over anhydrous $MgSO_4$, filtered and evaporated to give a yellow viscous liquid (21.5 g, 91%). ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.86 (t, 9H, CH_3, $J = 6.9$ Hz), 1.26 [m, 54H, $(CH_2)]_9$, 1.78 (m, 6H, CH_2CH_2OAr), 4.00 (t, 2H, RCH_2OAr, $J = 6.6$ Hz), 6.88 (d, 2H, C_6H_4CHD *o*-H, $J = 9.0$ Hz), 7.27 (d, 4H, C_6H_4CHD, *m*-H, $J = 8.7$ Hz).

2.2. Preparation of p-(n-dodecyloxy)benzyl-d alcohol (DBdA)

To a methanol solution (250 ml) of DBa (37.2 mmol,



Scheme 2. Synthesis of modified mesogen with selective deuteration.

10.8 g) was added an aqueous NaOH solution containing H_2O (30 ml), NaOH (9.7 mmol, 0.386 g) and $NaBD_4$ (38.6 mmol, 1.617 g). The mixture was stirred for 1 h at room temperature, then diluted with H_2O and acidified with aqueous HCl. After filtration, the resulting precipitate was recrystallized three times from hexane to yield 8.35 g (77%) of white crystals. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, CH_3, $J = 6.9$ Hz), 1.26 [m, 54H, $(CH_2)9$], 1.78 (m, 6H, CH_2CH_2OAr), 3.94 (t, 2H, RCH_2OAr, $J = 6.6$ Hz), 4.58 (s, 1H, CHDOH), 6.96 (d, 2H, C_6H_4CHD *o*-H, $J = 9.0$ Hz), 7.79 (d, 4H, C_6H_4CHD, *m*-H, $J = 9.3$ Hz), 9.84 (s, 1H, CHO).

2.3. Preparation of p-(n-dodecyloxy) benzyl-d chloride (DB_dC)

To a methylene chloride solution (CH_2Cl_2, 80 ml) of DB*d*A (27.3 mmol, 8.01 g) was added fresh thionyl chloride ($SOCl_2$, 3.0 ml) dropwise. The mixture was stirred for 2 h at room temperature, followed by washing with water, 2% aqueous $NaHCO_3$, and H_2O. After drying over anhydrous $MgSO_4$, the mixture was filtered, and the solvent was removed by rotary evaporation to give 7.23 g (85%) of a greenish solid. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, CH3, $J = 6.9$ Hz), 1.26 [m, 54H, $(CH_2)_9$], 1.78 (m, 6H, CH_2CH_2OAr), 3.94 (t, 2H, RCH_2OAr, $J = 6.6$ Hz), 4.53 (s, 1H, CHDCl), 6.84 (d, 2H, C_6H_4CHD *o*-H, $J = 6.6$ Hz), 7.28 (d, 4H, C_6H_4CHD, *m*-H, $J = 6.6$ Hz).

2.4. Preparation of methyl 3,4,5-tris[p-(n-dodecyloxy) benzyl-d-oxy] benzoate ($MDOB_dOB$)

To a DMF (110 ml) and K_2CO_3 (67.3 mmol, 9.30 g) mixture, purged with nitrogen for 3 h, was added methyl-3,4,5-trihydroxybenzoate (7.48 mmol, 1.38 g) followed by heating up to 70 °C and adding a DMF (10 ml) solution of DB_dC (22.4 mmol, 6.99 g) rapidly. The resulting mixture was kept for 4 h with stirring, and then poured into H_2O, acidified with aqueous HCl. The precipitate was filtered and recrystallized from acetone to give a white solid (3.54 g, 47%). ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, CH_3, $J = 6.9$ Hz), 1.26 [m, 54H, $(CH_2)_9$], 1.78 (m, 6H, CH_2CH_2OAr), 3.88 (s, 3H, OCH_3), 3.96 (tt, 6H, RCH_2OAr, $J = 6.6$ Hz), 4.98 (s, 1H, 4-CHDO–Ar–), 5.02 (s, 2H, 3 and 5-CHDO–Ar), 6.74 (d, 2H, C_6H_4, *o*′-H, $J = 8.4$ Hz), 6.90 (d, 4H, C_6H_4, *o*-H, $J = 8.7$ Hz), 7.24 (d, 2H, C_6H_4, *m*′-H, $J = 9.0$ Hz), 7.33 (d, 4H, C_6H_4, *m*-H, $J = 8.7$ Hz), 7.35 (s, 2H, C_6H_2).

2.5. Preparation of 3,4,5-tris[p-(n-dodecyloxy)benzyl-d-oxy] benzoic acid (DOB_dOB acid)

A mixture of MDOB*d*OB (4.95 mmol, 5.0 g) and 1N KOH in 90% ethanol solution (30 ml) was refluxed for 1 h, then poured into H_2O, and acidified with dilute HCl. After filtration, the precipitate was dissolved in chloroform (50 ml) containing 5% MeOH and acidified again with dilute HCl. The organic layer was obtained after adding more H_2O (40 ml), and then washing with H_2O, and drying over anhydrous $MgSO_4$ to give a white solid (4.93 g, 95%) after rotary evaporation. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, CH_3, $J = 6.9$ Hz), 1.27 [m, 54H, $(CH_2)_9$], 1.79 (m, 6H, CH_2CH_2OAr), 3.94 (tt, 6H, RCH_2OAr, $J = 6.6$ Hz), 5.01 (s, 1H, 4-CHDO–Ar), 5.04 (s, 2H, 3 and 5-CHDO–Ar–), 6.76 (d, 2H, C_6H_4, *o*′-H, $J = 9.0$ Hz), 6.90 (d, 4H, C_6H_4, *o*-H, $J = 6.9$ Hz), 7.26 (d, 2H, C_6H_4, *m*′-H, $J = 8.4$ Hz), 7.34 (d, 4H, C_6H_4, *m*-H, $J = 8.7$ Hz), 7.43 (s, 2H, C_6H_2).

2.6. Preparation of 2-[2-(2-hydroxyethoxy)ethoxy]ethyl 3,4,5-tris[p-(n-dodecyloxybenzyl-d-oxy) benzoate (HE$_3$DOB$_d$OB)

A mixture of THF (26 ml), DOB$_d$OB acid (4.50 g, 4.52 mmol), TEG (2.40 ml, 18.0 mmol), TsCl (0.86 g, 4.51 mmol), DMAP (0.18 g, 1.47 mmol), TBAH (0.18 g, 0.53 mmol), and K_2CO_3 (2.50 g, 18.1 mmol) was heated at 45 °C for 16 h, and then cooled to room temperature. The solution mixture was poured into H_2O, acidified to pH 1 slowly, and extracted with CH_2Cl_2. The organic phase was washed with H_2O, dried over anhydrous $MgSO_4$ and recrystallized from acetone to give a yellow viscous solid (4.00 g, 78%) ^{1}H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, CH_3, $J = 6.6$ Hz), 1.27 [m, 54H, $(CH_2)_9$], 1.79 (m, 6H, CH_2CH_2OAr), 2.41 (s, 1H, OH), 3.58 (t, 2H, CH_2CH_2OH, $J = 5.4$ Hz), 3.68 (s, 6H, $OCH_2CH_2OCH_2$), 3.81 (t, 2H, $COOCH_2CH_2O$, $J = 4.5$), 3.94 (tt, 6H, RCH_2OAr, $J = 6.6$ Hz), 4.44 (t, 2H, $COOCH_2CH_2O$, $J = 4.5$ Hz), 4.98 (s, 1H, 4-CHDO–Ar), 5.01 (s, 2H, 3 and 5-CHDO–Ar), 6.74 (d, 2H, C_6H_4, o'-H, $J = 9.0$ Hz), 6.88 (d, 4H, C_6H_4, o'-H, $J = 8.4$ Hz), 7.26 (d, 2H, C_6H_4, m'-H, $J = 8.4$ Hz), 7.36 (d, 4H, C_6H_4, m'-H, $J = 8.4$ Hz), 7.39 (s, 2H, C_6H_2).

2.7. Preparation of 2-[2-(2-methacryloyloxyethoxy) ethoxy]ethyl 3,4,5-tris[p-(n-dodecyloxybenzyl-d-oxy)] benzoate (ME$_3$DOB$_d$OB)

To the solution of CH_2Cl_2 (35 ml), HE$_3$DOB$_d$OB (4.00 g, 3.54 mmol), and methacryloyl chloride (1.4 ml, 14.3 mmol) was added dry Et_3N (2.8 ml, 20.1 mmol) dropwise. The mixture was stirred at room temperature for 1 h, then poured into H_2O, and extracted with CH_2Cl_2. The organic layer was washed with 5% HCl and H_2O, and dried over anhydrous $MgSO_4$. After filtration, the crude product was recrystallized from acetone to give a white solid (2.80 g, 66%). ^{1}H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, CH_3, $J = 6.6$ Hz), 1.26 [m, 54H, (CH_2)9], 1.79 (m, 6H, CH_2H_2OAr), 1.92 (s, 3H, CH_3), 3.68 (s, 6H, $OCH_2CH_2OCH_2$), 3.74 (t, 2H, $COOCH_2CH_2$0, $J = 4.8$ Hz), 3.82 (t, 2H, $J = 4.8$ Hz), 3.95 (tt, 6H, RCH_2OAr, $J = 6.6$ Hz), 4.28 (t, 2H, CH_2OCO, $J = 4.8$ Hz), 4.44 (t, 2H, $COOCH_2CH_2O$, $J = 4.8$ Hz), 4.98 (s, 1H, 4-CHDO–Ar), 5.01 (s, 2H, 3 and 5-CHDO–Ar), 5.54 (s, 1H, C=CH_2, *trans* to C=O), 6.11 (s, 1H, C=CH_2, *cis* to C=O), 6.74 (d, 2H, C_6H_4 o'-H, $J = 8.4$ Hz), 6.88 (d, 4H, C_6H_4, o'-H, $J = 8.4$ Hz), 7.28 (d, 2H, C_6H_4, m'-H, $J = 8.4$ Hz),7.32 (d, 4H, C_6H_4, m-H, $J = 8.7$ Hz), 7.39 (s, 2H, C_6H_2).

2.8. Preparation of poly(2-[2-(2-methacryloyloxyethoxy) ethoxy]ethyl 3,4,5-tris[p-(n-dodecyloxybenzyl-d-oxy)] benzoate (PMB$_d$)

A solution of benzene (15 ml), ME$_3$DOB$_d$OB (2.16 g, 1.80 mmol), and AIBN (0.0069 g, 0.043 mmol) was stirred at 65 °C for 24 h after five freeze–pump–thaw cycles. The product was dissolved in $CHCl_3$ and precipitated in CH_3OH for three times to give a white powder (1.6 g, 74%). $M_n = 81{,}244$, PDI = 1.78. Anal Calc. for $\{M_o + 3\,MeOH\}_n$: C, 71.68; H, 9.69. Found: C, 71. 32; H, 9.38.

2.9. Preparation of p-(n-dodecyloxy)-m-methoxybenzaldehyde (DVa)

A mixture of acetone (240 ml), vanillin (16.0 g, 100 mmol), K_2CO_3 (14.5 g, 105 mmol) and 1-bromododecane (20 ml, 95.0 mmol) was refluxed in a 500 ml round bottom flask for 24 h followed by removing acetone by rotary evaporation. The residue was redissolved in $CHCl_3$ (100 ml), filtered, dried over anhydrous $MgSO_4$ and after collection by rotary evaporation, recrystallized three times from hexane to give DVa (17.4 g, 68%) as a yellow solid. ^{1}H NMR, δ ($CDCl_3$, TMS, ppm): 0.84 (t, 3H, CH_3, $J = 6.7$ Hz), 1.22 [m, 18H, $(CH_2)_9$], 1.82 (m, 2H, CH_2CH_2OAr), 3.84 (s, 3H, CH_3O), 4.02 (t, 2H, CH_2OAr, $J = 6.9$ Hz), 6.88–7.36 (overlapped m, 3H, C_6H_3), 9.76 (s, 1H, ArCHO). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 13.8 (CH_3), 22.3 (CH_3CH_2), 25.6–29.3 [$(CH_2)_8$], 31.6 ($CH_2CH_2CH_3$), 55.5 (CH_3O), 68.7 (CH_2CH_2OAr), 108.8 (*ortho* to CHO, 2 position), 110.9 (*meta* to CHO, 5 position), 126.3 (*ortho* to CHO, 6 position), 129.5 (*ipso* to CHO), 149.4 (*meta* to CHO, 3 position), 153.8 (*para* to CHO), 190.2 (ArCHO).

2.10. Preparation of p-(n-dodecyloxy)-m-methoxybenyl-d alcohol (DV$_d$a)

Into a 250 ml CH_3OH solution of Dva (24.0 g, 75 mmol) was added an aqueous NaOH solution containing H_2O (60 ml), NaOH (18.8 mmol, 0.75 g), and $NaBD_4$ (3.32 g, 79.3 mmol) dropwise through an addition funnel. The mixture was stirred with a Teflon-coated magnetic stirrer for 4 h at room temperature, then diluted with H_2O (750 ml), and acidified with 5% HCl. After filtration, the resulting precipitate was washed with H_2O to yield DV$_d$a (21.5 g, 89%) as a white solid. ^{1}H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 3H, CH_3, $J = 6.7$ Hz), 1.26 [m, 18H, $(CH_2)_9$], 1.84 (m, 2H, CH_2CH_2OAr), 3.87 (s, 3H, CH_3O), 4.00 (t, 2H, CH_2OAr, $J = 6.9$ Hz), 4.59 (s, 1H, CHDOH), 6.85–6.92 (overlapped m, 3H, C_6H_3).

2.11. Preparation of p-(n-dodecyloxy)-m-methoxybenzyl-d chloride (DV$_d$C)

To a 100 ml round-bottom flask containing a Teflon-coated magnetic stirring bar and dry CH_2Cl_2 (100 ml) solution of DV$_d$A (10.0 g, 30.9 mmol) was added freshly distilled $SOCl_2$ (3.0 ml, 41 mmol) dropwise through an addition funnel. After stirring for 2 h at room temperature, the mixture was washed with H_2O, 5% NaOH, H_2O, and dried over anhydrous $MgSO_4$ resulting in the isolation of DV$_d$C (8.2 g, 77%) as a white solid after rotary evaporation. ^{1}H NMR, δ ($CDCl_3$, TMS, ppm): 0.87 (t, 3H, CH_3, $J = 6.7$ Hz), 1.27 [m, 18H, $(CH_2)_9$], 1.83 (m, 2H, CH_2CH_2OAr), 3.87 (s, 3H, CH_3O), 4.00 (t, 2H, CH_2OAr, $J = 6.9$ Hz), 4.54 (s, 1H, CHDCl), 6.80–6.91 (overlapped m, 3H, C_6H_3).

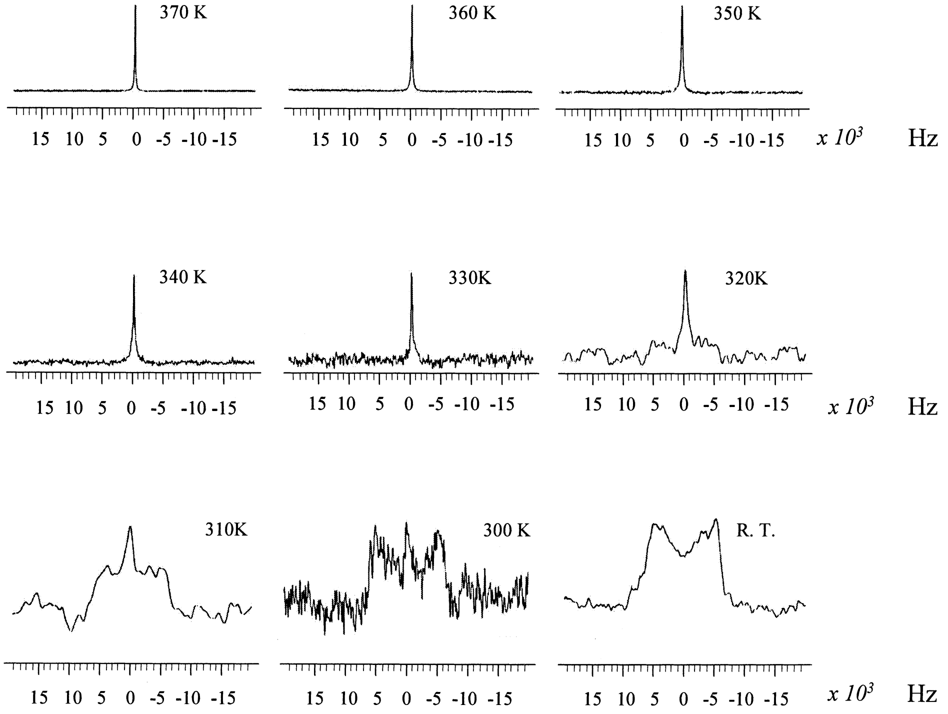


Fig. 1. ^2H NMR study of deuterated Percec model system (PMB$_d$).

2.12. *Preparation of 3,4,5-tris[p-(n-dodecyloxy)-m-methoxybenyl-d-oxy]benzoic acid (DOV$_d$OB acid)*

A mixture of DMF (45 ml) and K_2CO_3 (9.8 g, 71 mmol) in a 100 ml three-neck round-bottom flask containing a Teflon-coated magnetic stirring bar was purged with N_2 for 3 h at room temperature. After adding methyl-3,4,5-trihydroxybenzoate (1.3 g, 7.1 mmol) the temperature was raised to 70 °C, followed by addition of a DMF (15 ml) solution of DV$_d$C (7.3 g, 21.3 mmol) through an addition funnel. The mixture was kept at 70 °C for an additional 4 h, and then poured into H_2O, acidified with 5% HCl. After filtration, the residue was recrystallized from EtOH and then refluxed for 1 h in a 100 ml round-bottom flask with 1N KOH in 90% ethanol–water solution (30 ml). The reaction mixture was poured into H_2O (50 ml), acidified with 5% HCl. The resulting precipitate was redissolved in a $CHCl_3/CH_3OH$ mixture (95:5 ml) with acidification (5% HCl), and washed with H_2O followed by drying over anhydrous $MgSO_4$ and rotary evaporation to give DOV$_d$OB acid (4.6 g, 59%) as a yellow solid. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, CH_3, $J = 6.9$ Hz), 1.27 [m, 54H, $(CH_2)_9$], 1.84 (m, 6H, CH_2CH_2OAr, $J = 6.9$ Hz), 3.61 and 3.81 (ss, 3H + 6H, CH_3O), 4.00 (tt, 6H, RCH_2OAr, $J = 6.9$ Hz), 5.02–5.04 (ss, 6H, $ArCH_2OAr$), 6.71–7.00 (overlapped m, 9H, C_6H_3), 7.47 (s, 2H, C_6H_2). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 14.0 (CH_3), 22.6 (CH_3CH_2), 25.9–29.6 [$(CH_2)_8$], 31.8 ($CH_2CH_2CH_3$), 55.6 (CH_3O), 69.0 (CH_2CH_2OAr), 71.0–76.6 ($ArCH_2OAr$), 109.8 (*ortho* to CO_2H), 111.5 (*ortho* to CH_2OAr, 2′ position), 112.2 (*meta* to CH_2OAr, 5′ position), 120.6 (*ortho* to CH_2OAr, 6′ position), 124.3 (*ipso* to CO_2H), 129.3 (*ipso* to CH_2OAr), 143.1 (*para* to CO_2H), 148.4 (*meta* to CH_2OAr, 3′ position), 149.2 (*para* to CH_2OAr), 152.6 (*meta* to CO_2H), 171.4 (CO_2H). Anal. Calcd for $C_{67}H_{102}O_{11}$ ($C_{67}H_{99}D_3O_{11}$): C, 74.27; H, 9.49. Found: C, 74.30; H, 9.67.

3. Results and discussion

^2H NMR studies of the benzyl-d_1 deuterated polymethacrylate (PMB$_d$) showed a single isotropic peak appearing above the crystalline-Φ_h transition temperature (ca. 340 K) demonstrating that there is a fast Ar–CDHO bond rotational motion in the columnar mesophase (Fig. 1). Since a more appropriate rotation for our purposes in the preparation of a nanorotor would be correlated rotation of the disc-like molecules in the columns about the columnar axis (the axial rotation) rather than the one observed for PMB$_d$, we invoked the Adam–Gibbs configurational entropy theory as a guide to apply for appropriate modification of the mesogen. The modification of PMB to convert it from a crystalline to a glassy mesogen is an essential step in the proposed development of a molecular nanorotor.

The idea that a glass transition temperature can be introduced by reducing the free volume inside the mesogen (thereby decreasing the conformational freedom of the mesogen group) can be easily tested by the proton NOESY experiment in solution. The Nuclear Overhauser Enhancement is caused by through-space magnetic interactions or dipolar coupling between nuclear spins 'close' in space [12], which give rise to changes in resonance intensities and is intrinsically related to nuclear spin cross-relaxation. For a

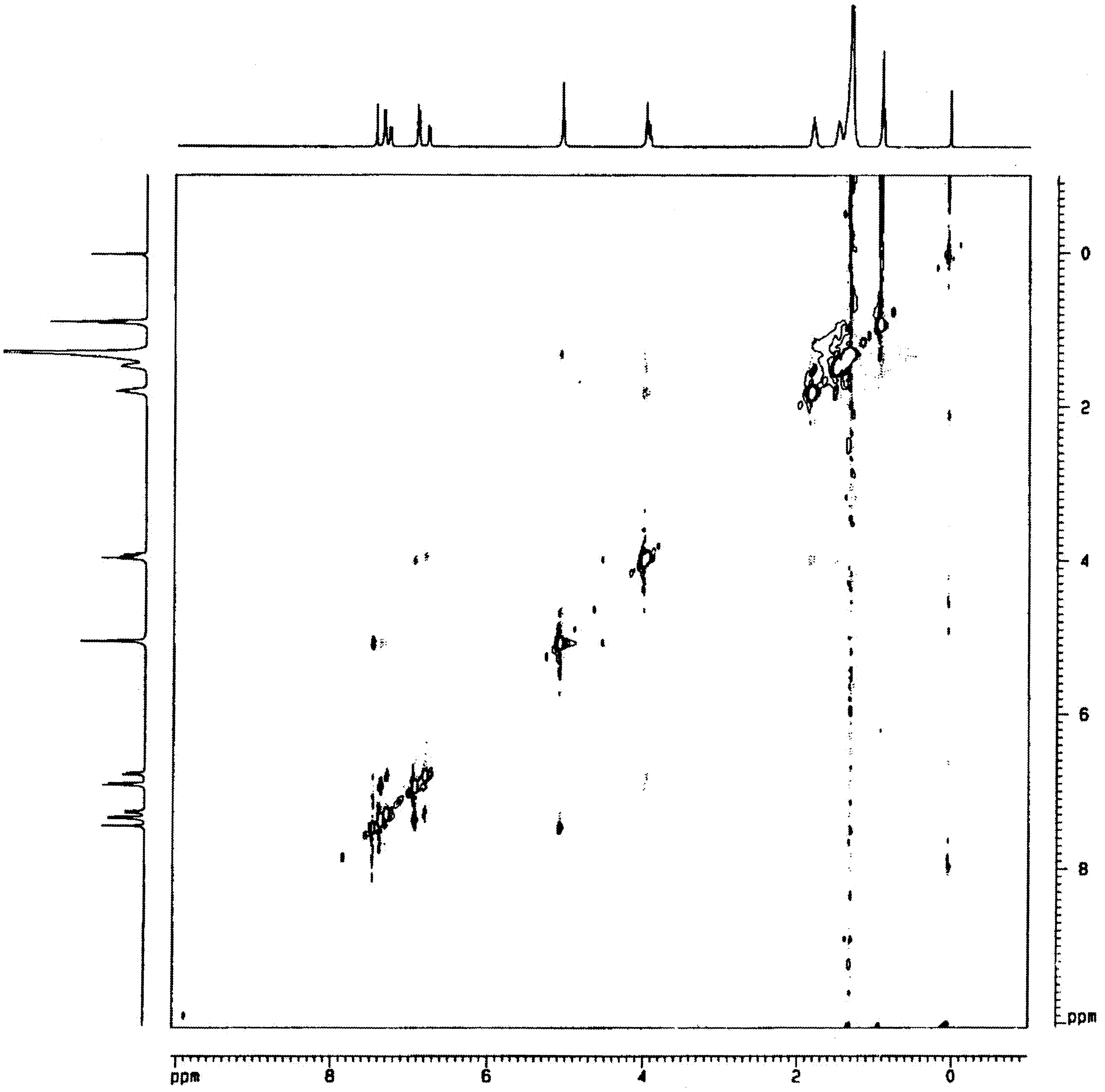


Fig. 2. NOESY spectrum of DOBOB acid (400 MHz).

two-spin system, there are three relaxation pathways. The single-quantum transitions involve the flip of one single spin, for example αα–βα. The other two transitions, αβ–βα (zero-quantum transition, W_o) and αα–ββ (double-quantum transition, W_2), are so-called cross relaxation involving the simultaneous flipping of both (S and I) spins. Molecules which tumble rapidly in solution are likely to favor the higher energy αα–ββ W_2 process and hence exhibit positive NOEs whilst those that tumble slowly will favor the lower energy αβ–βα W_o process and thus display negative NOEs. The sign of the NOEs observed between spatially proximate protons depend on the segmental mobility. Uma et al. reported simultaneous observation of both positive and negative nuclear Overhauser effects (NOEs) in Cys-(Val)$_n$-Trp oligopeptides, of which the negative NOE is owing to the slow motion of local segmental tumbling [13].

A NOESY study of the monodendron DOBOB acid revealed that there are negative NOEs for the benzyl unit: both the methylene (–CH_2O–) protons (with chemical shifts around 4.0 and 5.0 ppm) are correlated with aromatic (C_6H_4O) protons (with chemical shifts from 6.7 to 7.4 ppm) through space (Fig. 2). The negative NOEs are due to slowing of the fast motion of the benzyl unit due to the reduction of free volume caused by the presence of solute molecules with the polymer molecules. Thus, the free volume is directly correlated to the motion of units associated with molecules and the phenomenon can be monitored by NOESY studies.

The induction of the glass transition temperature may require reducing the free volume inside the mesogen. Decreasing the conformational freedom of the mesogen group should result in promoting the correlated segmental motion about the columnar axis that is

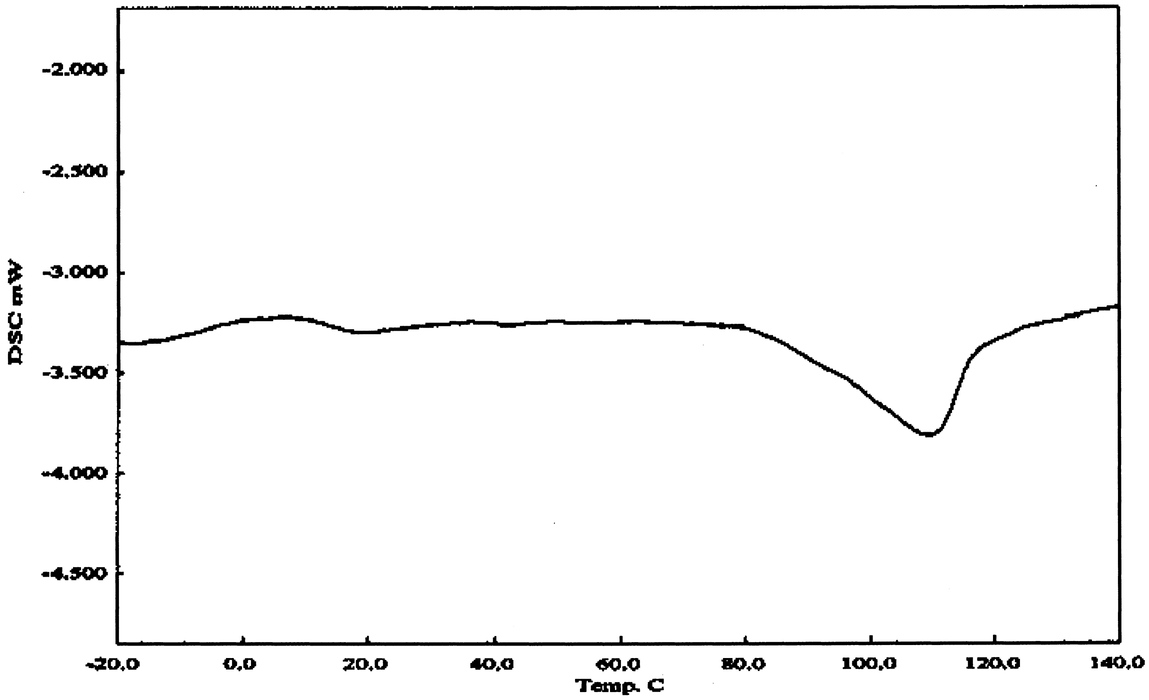


Fig. 3. DSC heating trace of DOVOB acid (15 °C/min).

responsible for the glass transition. Such an effect has been observed in two other similar types of columnar side-group liquid crystalline polymethacrylates synthesized by the Percec group. One involves semifluorination of the alkyl tails of the DOBOB mesogen (VI, VII in Table 1) [14], and the other involves replacing the outer benzene ring of the DOBOB mesogen with a naphthalene unit (VIII, IX in Table 1) [15]. Both types of taper-shaped side-group columnar liquid crystalline polymethacrylates show glass transitions clearly. These mesogens had decreased conformational freedom and thus stabilized columnar mesophases.

The modified mesogen DOV$_d$OB acid showed a glass transition itself (before polymerization) as expected and an isotropic transition (T_g ca. 10 °C, T_{iso} ca. 80 °C) as shown in Fig. 3. Thus, ^{2}H NMR studies of the rotational motion of the vanillyl segment as well as DOVOB$_d$ acid with dideutero benzoate [results to be published] units were conducted. The ^{2}H NMR spectra are similar for DOV$_d$OB acid and DOVOB$_d$ acid as seen from Figs. 4 and 5. At lower

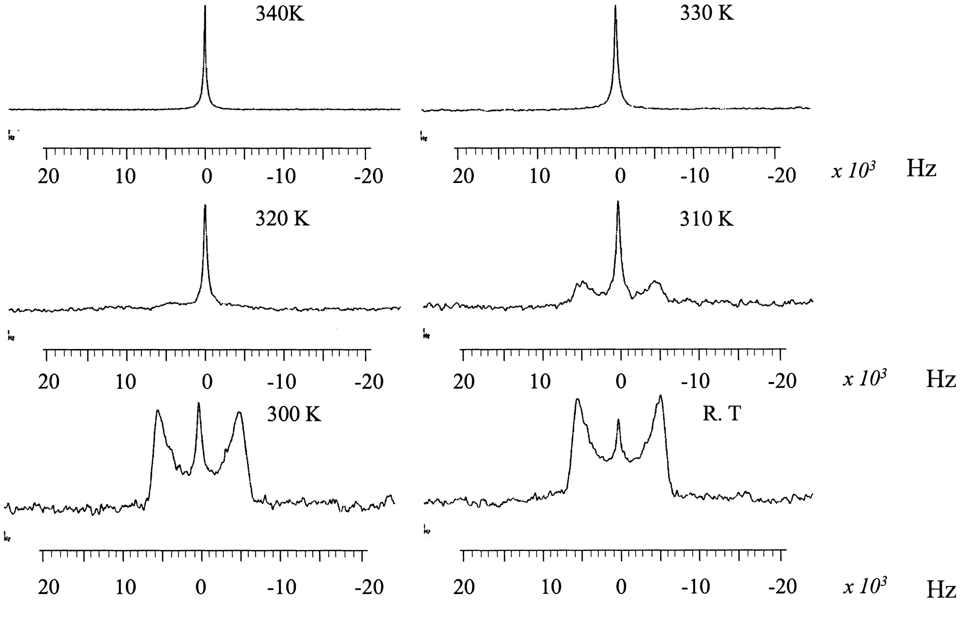


Fig. 4. ^{2}H NMR spectrum of deuterated modified mesogen (DOV$_d$OB acid).

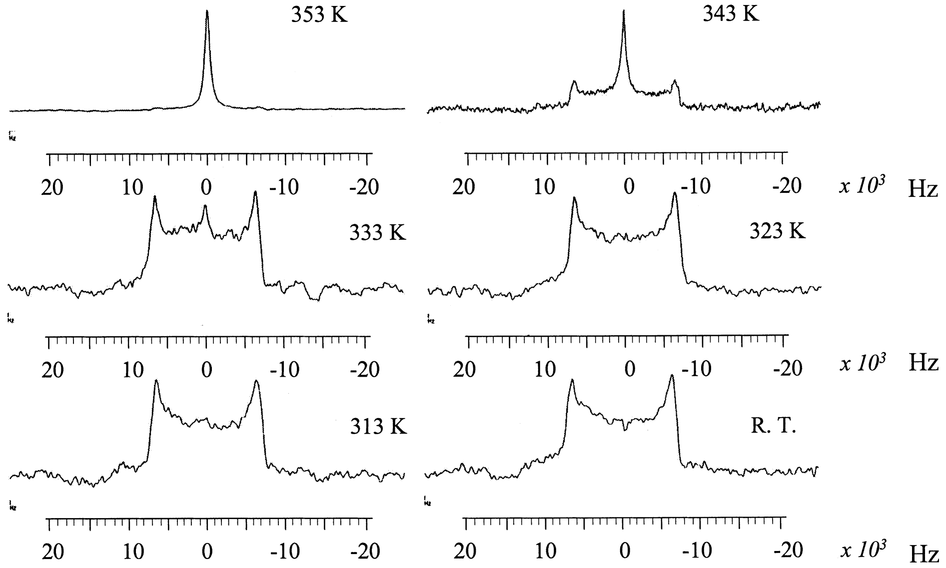


Fig. 5. ^{2}H NMR spectrum of deuterated modified mesogen (DOVOB$_d$ acid).

temperatures rigid Pake powder patterns were observed indicating that slow motions with correlation times longer than 10^{-5} s were present. At higher temperatures, (320 K for DOV$_d$OB acid, 353 K for DOVOB$_d$ acid), a significant reduction in the intensity of the resonance was noted corresponding to motions in the intermediate regime [16]. Close to the T_{iso} (isotropization temperature), the spectra showed a single relatively narrow resonance peak. The loss of the intensity of the Pake pattern around the T_{iso} was likely due to motions in the intermediate time range [17]. Similar spectra have been observed for polystyrene [18–20] and other polymers [21–23]. Spiess et al. reported that as a result of PS segmental motions below and above the T_g, the line shape changed from a Pake powder pattern to a Lorentzian pattern within the narrow temperature range [17, 18]. Results for DOVOB indicate a similar pattern as for PS with a narrowing of the peak followed by a change from a Pake powder pattern to a Lorentzian pattern confirming the presence of a glass transition. Thus, from the DSC results and by interpreting the NMR results, it can be seen that introducing a small group onto the benzyl structure in DOVOB indeed reduced the free volume, slowing the rotational motion of the benzyl unit, and thereby introducing a glass transition.

A similar strategy has been adopted for constructing the triphenylene-based glassy discotic liquid crystalline systems [24–26]. The free volume outside the triphenylene core was reduced by asymmetrically substituting relatively large size groups as one of the six side arms, thereby reducing the associated free volume and destroying the symmetry of the molecule as well. By combining ^{2}H NMR [27] and dielectric spectroscopy [28], it was shown that the glass transition of such columnar discotic phases is connected with the prevention of crystallization. However, this is also analogous to the result of the freezing of the rotational motions of the side arms thereby inducing rotation of the disc-like molecules about the columnar axis. It was demonstrated [29] that the axial rotation is not performed by individual molecules (with low molecular weight mesogens) and that the cooperative coupling of the molecules increases as the glass transition is approached. Motion narrowed Pake powder patterns observed for the triphenylene core based systems have no more than 10 carbons on the alkyl side arms. The simulation results showed that the rate for the axial motion is around several hundred kilo Hertz.

4. Conclusion

The induction of a glass transition for the taper-shaped columnar discotic mesogen 3,4,5-tris(*p*-dodecyloxybenzyloxy)benzoic (DOBOB) acid was achieved by attaching a methoxy group to the benzyl unit. The 3,4,5-tris(*p*-dodecyloxy-*m*-methoxybenzyloxy) benzoic (DOVOB) acid obtained was subsequently used to synthesize a new glassy discotic liquid crystal polymethyacrylate.

Acknowledgements

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