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Synthesis and characterization of a new discotic columnar side-chain liquid crystalline polymer deuterated for NMR analysis

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Abstract

As part of our attempt to prepare molecular spinning machine, we synthesized a new discotic liquid crystalline polymethacrylate based on the taper-shaped monoester of triethylene glycol with 3,4,5-tris(*p*-dodecyloxylbenzyloxy-*m*-methoxybenzyloxy)benzoic acid. The polymethacrylate was deuterated in the benzoic ring for subsequent solid-echo ^{2}H NMR spectroscopy. The *m*-methoxy group was proposed to prevent the rotation of the benzene ring, thereby inducing the cooperative rotational motion of the polymer. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Molecular nano-rotor; Glass transition; Liquid crystalline elastomer

1. Introduction

The goal of molecular nano-technology (MNT) [1] is to establish materials manufacturing at molecular level, so as to improve not only the usage efficiency of both the raw materials and the energy macroscopically, but also to improve the properties of the end-products by means of tuning the microscopic molecular structures. The molecular nano-machine is the key to the MNT revolution. Such a miniaturized mechanical system will function on the basis of a rational organization of molecular nano-systems capable of transferring energy and momentum through molecular translational motions or rotational motions between molecules [2].

The basic idea behind nano-machine has been to tailor a material to function like a machine. The nano-spinning machine (molecular nano-spinnerette) which we envision consists of a membrane containing columnar liquid crystalline macromolecules. As the discotics are made to rotate freely in the desired direction without translational freedom like a nano-rotor, by means of supramolecular non-bonded interactions e.g. hydrogen bonding, they can pull polymeric molecules supplied at the top surface of the membrane, align them within the membrane, and release fiber at the bottom surface. The controllable rotation of such macromolecular nano-rotors would be achieved by the application of an external force field, e.g. a magnetic field.

For amorphous polymers, their backbone cooperative relaxation rotation has been established as a glass–rubber relaxation with the characteristic glass transition temperature (T_g) [3–5]. Therefore, the correlation between the microscopic polymer backbone cooperative relaxation rotation and the macroscopic material glass transition provides a guideline for the molecular design of a nano-rotor. The introduction of deuterium atoms to the polymer allows the characterization of the polymer rotational motion by means of ^{2}H NMR, which has proved to be a powerful and unique technique for studying polymer dynamics [6]. The phenomenon whereby small discotic organic molecules exhibit cooperative axial rotation around the columnar axis has been identified as the motion related to the glass transition process demonstrated by ^{2}H NMR investigation combined with dielectric spectroscopy [7,8].

In an elegant publication, Percec and associates reported that the taper-shaped monoesters of mono-, di-, tri-, and tetraethylene 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 various nano-meter diameters of 5.02, 5.41, 5.98, and 6.00, respectively, at 25 °C (I–IV in Table 1) [9]. 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 tilted angle 40–50° to the backbone) like a self-assembled

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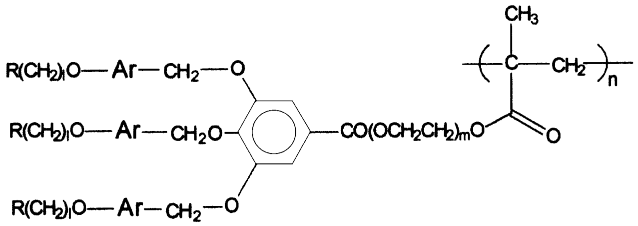
Table 1
Self-assembling columnar LC polymethacrylates with taper-shaped side group



No.	Reference	R	l	Ar	m	d (nm)	M_n(1000)	DSC (°C, kcal/mol, cal/mol/K)
I	[9]	H	12	1,4-C_6H_4	1	5.02	27.7	col127(0.36/0.9)iso
II	[9]	H	12	1,4-C_6H_4	2	5.41	24.6	g36col116(0.41/1.1)iso
III	[9]	H	12	1,4-C_6H_4	3	5.98	44.7	k48(3.32)col113(0.43/1.1)iso
IV	[9]	H	12	1,4-C_6H_4	4	6	69.1	k48(3.75)col103(0.50/1.3)iso
V	[14]	H	18	1,4-C_6H_4	3	5.7	1.3781 (precursor)	k65col75iso
VI	[19]	F	10	1,4-C_6H_4	4	5.79	16.9	g3col66(0.24/0.71)iso
VII	[19]	$F(CF_2)_6$	4	1,4-C_6H_4	4	6.43	22.8	g14col200(0.34/0.72)iso
VIII	[20]	H	10	2,6-$C_{10}H_6$	4	6.19	78.3	g28col139(0.45/1.1)iso
IX	[20]	H	12	2,6-$C_{10}H_6$	4	6.51	32.5	g32col149(0.45/1.1)iso

stacking bowl [10–13] as well as the precursor of 2-[2-(2-hydroxyethoxy)ethoxy)ethyl 3,4,5-tris(*p*-octadecyloxy-benzyloxy)benzoate (V in Table 1) [14]. As a starting point, the model system chosen is the DOBOB mesogen based macromolecule poly{2-[2-(2-methacryloyloxyethoxy)-ethoxy]ethyl 3,4,5-tris(*p*-dodecyloxy-benzyloxy)benzoate} (III in Table 1), or PMB. Unlike poly[2-(2-methacryloyloxy-ethoxy)ethyl 3,4,5-tris(*p*-dodecyloxybenzyloxy]benzoate) (II in Table 1) which exhibited a very weak glass transition at 36 °C as observed from the DSC trace, PMB is highly crystalline and does not form the glassy viscoelastic state [9]. The induction of the glassy state for the columnar structure was the major concern of the molecular design.

Theoretically, the glass transition phenomenon can be described by WLF equation with the free volume concept [15]:

$$\lg a_T = \lg \frac{\tau_c(T)}{\tau_c(T_g)} = -\frac{C_1(T - Tg)}{C_2 + (T - T_g)} \approx \lg \frac{\eta(T)}{\eta(T_g)}$$

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

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

where $f(T) = V_f/(V_0 + V_f)$ is the fractional free volume, and α_f has the dimension of a thermal expansion coefficient, or Adam–Gibbs configurational entropy theory [16]:

$$\tau = \tau_0 \exp(\frac{C\Delta\mu}{TS_c})$$

where $\Delta\mu$ is a free energy barrier per particle to cooperative rearrangements, and S_c is the excess configurational entropy. The ^{2}H 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 [17]. The outer benzyl groups have enough space to undergo ring flips [18]. Our ^{2}H NMR studies of the benzyl-d_1 deuterated polymethacrylate (PMBd) also show the fast isotropic Ar–CDHO bond rotation in mesophase.[1]

Therefore, we theorized that the induction of the glass transition temperature might require reducing the free volume inside the mesogen, thus decreasing the conformational freedom of the mesogen group. As a matter of fact, such an effect has been observed in two other similar types of columnar side-group liquid crystalline polymethacrylates synthesized by the Percec group. One contains semifluorinated alkyl tails of the DOBOB mesogen (VI, VII in Table 1) [19], and the other replaces the outer benzene ring of the DOBOB mesogen with naphthalene unit (VIII, IX in Table 1) [20]. Both types of taper-shaped side-group columnar liquid crystalline polymethacrylates clearly show glass transitions. These mesogens have decreased conformational freedom and thus stabilized columnar mesophases.

In consideration of the ease of the chemical synthesis and the availability of the starting materials, one methoxy group was introduced to the 3′-position of each phenyl ring of the taper-shaped DOBOB mesogen, thus, the syntheses would be carried out by a variation of literature procedures by using vanillyl alcohol as the starting material instead of *p*-hydroxybenzaldehyde. The modified mesogen was expected to stabilize the columnar mesophase and induce a glass transition of the corresponding polymethacrylate.

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[1] Results to be published.

2. Experimental

2.1. Materials

Triethylene glycol (99%), 1-bromododecane (97%), D_2O (98%), trifluoacetic anhydride (98%), methyl 3,4,5-trihydroxybenzoate (97%), $NaBD_4$ (99%), EtOD (98%), D_2SO_4 (98%), tetrabutylammonium hydrogen sulfate (TBAH, 97%), toluenesulfonyl chloride (98%), silical gel (Merck, grade 60, 230–400 mesh, 60 Å), benzene (99%), methacryloyl chloride (98%), methyl methacrylate-d_5 (99% d atom) (all from Aldrich), 4-4-dimethylaminopyridine (DMAP, 98%, Fluka), and the other conventional reagents were used as received. 4-Hydroxy-3-methoxybenzyl alcohol (vanillyl alcohol, 97%, Fluka) was recrystallized from water. Triethylamine (Et_3N) and pyridine were distilled from KOH, and then stored over KOH. 2,2′-Azoisobutyronitrile (AIBN, Aldrich) was recrystallized from MeOH at 4 °C.

2.2. Measurements

^1H and ^{13}C NMR (300 MHz) spectra were recorded on a Varian Gemini 300 spectrometer. Relative molecular weights of polymers were measured by gel permeation chromatography (GPC) with polystyrene standards used for the calibration plot. A Seiko differential scanning calorimeter (DSC220) was used to determine the thermal transitions. A Zeiss polarized optical microscope equipped with a hot stage was used to observe the thermal transitions and to analyze the anisotropic textures, and pictures were taken. Elemental analyses were performed at Atlanta Microlab, Inc. The proton analysis results consist of both protons and deuterons.

2.3. Preparation of p-(n-dodecyloxy)-m-methoxybenzyl alcohol (2)

A mixture of acetone (240 ml), vanillyl alcohol (**1**, 13.0 g, 84.3 mmol), K_2CO_3 (12.5 g, 88.5 mmol), and 1-bromododecane (20 ml, 80.8 mmol) was refluxed in a 500 ml round-bottom flask containing a Teflon-coated magnetic stirring bar for 24 h followed by removing acetone on a rotary evaporator. The residue was dissolved in $CHCl_3$, filtered, and dried over anhydrous $MgSO_4$, to give **2** (25.38 g, 97%) of yellow viscous liquid. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.85 (t, 3H, $C\mathit{H}_3$, $J = 6.7$), 1.25 [m, 18H, $(C\mathit{H}_2)_9$], 1.69 (s, 1H, $CH_2O\mathit{H}$), 1.82 (m, 2H, $C\mathit{H}_2CH_2OAr$), 3.86 (s, 3H, $C\mathit{H}_3O$), 4.00 (t, 2H, $C\mathit{H}_2OAr$, $J = 6.9$), 4.61 (s, 2H, $C\mathit{H}_2OH$), 6.85–6.92 (overlapped m, 3H, $C_6\mathit{H}_3$). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 14.1 ($\mathit{C}H_3$), 22.7 ($CH_3\mathit{C}H_2$), 25.9–29.6 [$(\mathit{C}H_2)_8$], 31.9 ($\mathit{C}H_2CH_2CH_3$), 55.9 ($\mathit{C}H_3O$), 65.3 ($\mathit{C}H_2OH$), 69.1 ($CH_2\mathit{C}H_2OAr$), 110.8 (*ortho* to CH_2OH, 2 position), 112.8 (*meta* to CH_2OH, 5 position), 119.4 (*ortho* to CH_2OH, 6 position), 133.5 (*ipso* to CH_2OH), 148.1 (*meta* to CH_2OH, 3 position), 149.5 (*para* to CH_2OH).

2.4. Preparation of p-(n-dodecyloxy)-m-methoxybenzyl chloride (3)

To a 100 ml round-bottom flask containing a Teflon-coated magnetic stirring bar and dry CH_2Cl_2 (70 ml) solution of **2** (10.0 g, 31.0 mmol) was added freshly distilled $SOCl_2$ (3.0 ml, 41 mmol) dropwise through an addition funnel. After 2 h at room temperature with stirring, the mixture was washed with water, 5% NaOH, water, and dried over anhydrous $MgSO_4$ resulting in **3** (9.37 g, 89%) after rotary evaporation as a yellow solid. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.87 (t, 3H, $C\mathit{H}_3$, $J = 6.7$), 1.25 [m, 18H, $(C\mathit{H}_2)_9$], 1.82 (m, 2H, $C\mathit{H}_2CH_2OAr$), 3.84 (s, 3H, $C\mathit{H}_3O$), 3.97 (t, 2H, $C\mathit{H}_2OAr$, $J = 6.7$), 4.52 (s, 2H, $C\mathit{H}_2Cl$), 6.77–6.88 (overlapped m, 3H, $C_6\mathit{H}_3$). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 13.9 ($\mathit{C}H_3$), 22.5 ($CH_3\mathit{C}H_2$), 25.9–29.5 [$(\mathit{C}H_2)_8$], 31.8 ($\mathit{C}H_2CH_2CH_3$), 46.4 ($\mathit{C}H_2Cl$), 55.7 ($\mathit{C}H_3O$), 68.8 ($CH_2\mathit{C}H_2OAr$), 112.0 (*meta* to CH_2Cl, 5 position), 112.3 (*ortho* to CH_2Cl, 2 position), 120.9 (*ortho* to CH_2Cl, 6 position), 129.7 (*ipso* to CH_2Cl), 148.7 (*para* to CH_2Cl), 149.3 (*meta* to CH_2Cl, 3 position).

2.5. Preparation of 3,4,5-trihydroxy-d_3-benzoic-d_2 acid-d (5)

A D_2O (60.0 ml) solution of trifluoroacetic anhydride (60.0 ml) and methyl 3,4,5-trihydroxy benzoate **4** (9.2 g, 50.0 mmol) was refluxed in a 250 ml round-bottom flask for 20 h and then cooled down to room temperature White crystals (8.1 g, 92%) were obtained from the recrystallization and used without further purification. ^1H NMR, δ (DMSO, TMS, ppm): 9.18 (broad s, 3H, $O\mathit{H}$), 12.20 (broad s, 1H, $COO\mathit{H}$). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 108.8 (*ortho* to CO_2H), 120.3 (*ipso* to CO_2H), 137.9 (*para* to CO_2H), 145.2 (*meta* to CO_2H), 167.4 ($\mathit{C}O_2H$).

2.6. Preparation of ethyl 3,4,5-trihydroxy-d_3-benzoate-d_2 (6)

In a 100 ml round-bottom flask, ethyl alcohol-d (40 ml) solution of **5** (8.0 g, 45.4 mmol) with three drops of D_2SO_4 was refluxed for 30 h, followed by removing ethanol on a rotary evaporator. The residue was redissolved In ethyl acetate, washed with H_2O and dried over anhydrous $MgSO_4$ to give **6** (4.03 g, 44%) of a white solid. ^1H NMR, δ (DMSO, TMS, ppm): 1.25 (t, 3H, $C\mathit{H}_3$, $J = 7.2$), 4.18 (q, 2H, $C\mathit{H}_2$, $J = 7.2$). ^{13}C NMR, δ (DMSO, TMS, ppm): 14.3 ($\mathit{C}H_3$), 60.1 ($\mathit{C}H_2$), 108.4 (*ortho* to CO_2H), 119.5 (*ipso* to CO_2H), 138.5 (*para* to CO_2H), 145.5 (*meta* to CO_2H), 165.9 ($\mathit{C}O_2H$).

2.7. Preparation of ethyl 3,4,5-tris[p-(n-dodecyloxy)-m-methoxybenzyloxy]benzoate-d_2 (7)

A mixture of DMF (80 ml) and K_2CO_3 (14.0 g, 101 mmol) in a 250 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 **6** (2.03 g, 10 mmol) the temperature was raised to 70 °C, followed by adding the DMF (10 ml) solution of **3** (10.24 g, 30.0 mmol) quickly through an addition funnel. The mixture was kept at 70 °C for additional 4 h and then poured into H_2O, acidified with aq. HCl. After filtration, the residue was recrystallized from EtOH to give **7** as a white solid (5.12 g, 46%). ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, CH_3, $J = 6.9$), 1.25 [m, 54H + 3H, $(CH_2)_9$, CH_3, $J = 7.2$], 1.83 (m, 6H, CH_2CH_2OAr), 3.61 and 3.80 (ss, 3H + 6H, CH_3O), 3.98 (tt, 6H, RCH_2Oar, $J = 6.6$), 4.34 (q, 2H, CH_2, $J = 7.2$), 5.03–5.05 (ss, 6H, $ArCH_2OAr$), 6.71–7.00 (overlapped m, 9H, C_6H_3). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 14.0 ($CH_2CH_2CH_3$), 14.3 ($CO_2CH_2CH_3$), 22.5 ($CH_3CH_2CH_2$), 25.8–29.5 [$(CH_2)_8$], 31.8 ($CH_2CH_2CH_3$), 55.7 (CH_3O), 60.9 ($ArCO_2CH_2$), 68.9 (CH_2CH_2OAr), 71.3–74.8 ($ArCH_2$-OAr), 109.0 (*ortho* to CO_2CH_2), 111.4 (*ortho* to CH_2OAr, $2'$ position), 112.2 (*meta* to CH_2OAr, $5'$ position), 120.5 (*ortho* to CH_2OAr, $6'$ position), 125.3 (*ipso* to CO_2CH_2), 129.5 (*ipso* to CH_2OAr), 142.3 (*para* to CO_2CH_2), 148.4 (*meta* to CH_2OAr, $3'$ position), 149.3 (*para* to CH_2OAr), 152.6 (*meta* to CO_2CH_2), 165.9 ($ArCO_2CH_2$). Anal. Calcd for $C_{69}H_{106}O_{11}(C_{69}H_{104}D_2O_{11})$: C, 74.56; H, 9.61. Found: C, 74.79; H, 9.82.

2.8. Preparation of 3,4,5-tris[p-(n-dodecyloxy)-m-methoxybenzyloxy]benzoic-d_2 acid (8)

In a 100 ml round-bottom flask, a 90% ethanol–water solution (30 ml) of KOH (1.68 g, 30 mmol) and **7** (3.34 g, 3.00 mmol) was refluxed for 1 h, then poured into H_2O (50 ml), acidified with aq. HCl. The resulting precipitate was redissolved in $CHCl_3/CH_3OH$ mixture (95:5 ml) with acidification (aq. HCl), washed with H_2O, and dried over anhydrous $MgSO_4$ to give **8** (3.01 g, 92%) as an orange liquid. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, CH_3, $J = 6.9$), 1.27 [m, 54H, $(CH_2)_9$], 1.84 (m, 6H, CH_2CH_2OAr), 3.62 and 3.82 (ss, 3H + 6H, CH_3O), 4.00 (tt, 6H, RCH_2OAr), 5.06–5.08 (ss, 6H, $ArCH_2OAr$), 6.72–7.02 (overlapped m, 9H, C_6H_3). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 14.3 (CH_3), 22.9 (CH_3CH_2), 26.2–29.9 [$(CH_2)_8$], 32.1 ($CH_2CH_2CH_3$), 55.9 (CH_3O), 69.3 (CH_2CH_2OAr), 71.6–75.2 ($ArCH_2OAr$), 109.8 (*ortho* to CO_2H), 111.4 (*ortho* to CH_2OAr, $2'$ position), 112.2 (*meta* to CH_2OAr, $5'$ position), 120.6 (*ortho* to CH_2OAr, $6'$ position), 124.1 (*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), 171.6 (CO_2H). Anal. Calcd for $C_{67}H_{102}O_{11}(C_{67}H_{100}D_2O_{11})$: C, 74.27; H, 9.49. Found: C, 74.05; H, 9.52.

2.9. Preparation of 2-[2-(2-hydroxyethoxy)ethoxy]ethyl 3,4,5-tris[p-(n-dodecyloxy)-m-methoxybenzyloxy]benzoate-d_2 (9)

A mixture of THF (18.0 ml), **8** (3.01 g, 2.77 mmol), TEG(1.50 ml, 11.1 mmol), TsCl (0.526 g, 2.76 mmol), DMAP (0.11 g, 0.59 mmol), TBAH (0.110 g, 0.34 mmol), and K_2CO_3 (1.68 g, 12.2 mmol) was kept at 45 °C for 20 h in a 50 ml round-bottom flask containing a magnetic stirring bar, then cooled down to room temperature, and transferred into H_2O (540 ml) slowly with stirring. After acidification to pH 1 with aq. HCl, the mixture was extracted with CH_2Cl_2, washed with H_2O, and dried over anhydrous $MgSO_4$. The crude product was column chromatographed (silica gel, 9:1 CH_2Cl_2/CH_3COCH_3) resulting in **9** (1.99 g, 59%) as a yellow viscous liquid. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.85 (t, 9H, CH_3, $J = 6.9$), 1.25 [m, 54H, $(CH_2)_9$], 1.82 (m, 6H, CH_2CH_2OAr), 3.56–3.85 [m, 9H + 10H, CH_3O + $CH_2O(CH_2CH_2O)_2H$], 3.95 (tt, 6H, RCH_2OAr), 4.45 (t, 2H, CO_2CH_2, $J = 4.8$), 4.98–5.04 (ss, 6H, $ArCH_2OAr$), 6.67–7.04 (overlapped m, 9H, C_6H_3). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 14.0 (CH_3), 22.5 (CH_3CH_2), 25.8–29.5 [$(CH_2)_8$], 31.8 ($CH_2CH_2CH_3$), 55.7 (CH_3O), 61.5 (CH_2OH), 63.9 ($ArCO_2CH_2$), 68.9 (CH_2CH_2OAr), 69.2–71.3 (CH_2OCH_2-CH_2OCH_2), 72.4–74.8 ($ArCH_2OAr$), 109.1 (*ortho* to CO_2CH_2), 111.4 (*ortho* to CH_2OAr, $2'$ position), 112.5 (*meta* to CH_2OAr, $5'$ position), 120.6 (*ortho* to CH_2OAr, $6'$ position), 124.8 (*ipso* to CO_2CH_2), 129.6 (*ipso* to CH_2OAr), 142.1 (*para* to CO_2CH_2), 148.4 (*meta* to CH_2OAr, $3'$ position), 149.3 (*para* to CH_2OAr), 152.7 (*meta* to CO_2CH_2), 166.0 ($ArCO_2CH_2$). Anal. Calcd for $C_{73}H_{114}O_{14}(C_{73}H_{112}D_2O_{14})$: C, 72.12; H, 9.44. Found: C, 72.39; H, 9.48.

2.10. Preparation of 2-[2-(2-methacryloyloxyethoxy)ethoxy]ethyl 3,4,5-tris[p-(n-dodecyloxy)-m-methoxybenzyloxy]benzoate-d_2 (10)

To a 50 ml round-bottom flask containing a dry CH_2Cl_2 (7.4 ml) solution of **9** (0.9 g, 0.74 mmol) and methacryloyl chloride (0.3 ml, 3 mmol) was added dry TEA (0.62 ml) dropwise. The mixture was stirred at room temperature for 2 h, then poured into H_2O (150 ml), extracted with CH_2Cl_2, washed with 5% HCO_2H, followed by H_2O, and dried over anhydrous $MgSO_4$, followed by rotary evaporation. The crude product was purified by column chromatography (silica gel, 19:1 CH_2Cl_2/CH_3COCH_3) resulting in **10** (0.60 g, 63%) as a yellowish waxy solid. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.87 (t, 9H, CH_3, $J = 6.6$), 1.26 [m, 54H, $(CH_2)_9$], 1.82 (m, 6H, CH_2CH_2OAr), 1.92 [s, 3H, $CH(CH_3){=}CH_2$], 3.58-3.84 (m, 9H + 8H, CH_3O + $CH_2OCH_2CH_2OCH_2$), 3.95 (tt, 6H, RCH_2OAr), 4.27 (t, 2H, CH_2CO_2, $J = 4.8$), 4.45 (t, 2H, CO_2CH_2, $J = 4.8$), 5.02–5.05 (ss, 6H, $ArCH_2OAr$), 5.53 [m, 1H, $C(CH_3){=}CH_2$], 6.10 [s, 1H, $C(CH_3){=}CH_2$], 6.70–7.00 (overlapped m, 9H, C_6H_3). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 14.0 (CH_3), 18.2 [$CH_2{=}C(CH_3)CO_2$], 22.7 (CH_3CH_2), 25.9–29.5 [$(CH_2)_8$], 31.8 ($CH_2CH_2CH_3$), 55.5 (CH_3O), 63.6 [$CH_2OCOC(CH_3){=}CH_2$], 64.0 ($ArCO_2CH_2$), 69.0 (CH_2CH_2OAr), 69.1–70.6 ($CH_2OCH_2CH_2OCH_2$), 71.3–74.8 ($ArCH_2OAr$), 109.1 (*ortho* to CO_2CH_2), 111.4 (*ortho* to CH_2OAr, $2'$ position), 112.2 (*meta* to CH_2OAr, 5′ position), 120.6 (*ortho* to CH_2OAr, 6′ position), 124.8 [CH_2=C(CH_3)CO], 125.7 (*ipso* to CO_2CH_2), 129.5 (*ipso* to CH_2OAr), 136.1 [CH_2=*C*(CH_3)CO], 142.1 (*para* to CO_2CH_2), 148.4 (*meta* to CH_2OAr, 3′ position), 149.3 (*para* to CH_2OAr), 152.6 (*meta* to CO_2CH_2), 166.0 [$CH_2OCOC(CH_3)=CH_2$], 167.1 (Ar*C*O_2CH_2). Anal. Calcd for $C_{77}H_{118}O_{15}(C_{77}H_{116}D_2O_{15})$: C, 72.04; H, 9.26. Found: C, 72.27; H, 9.28.

*2.11. Preparation of poly{2-[2-(2-methacryloyloxyethoxy)ethoxy]ethyl 3,4,5-tris[p-(n-dodecyloxy)-m-methoxybenzyloxy]benzoate-d₂} (**11**)*

A 50 ml Schlenk tube containing a Teflon-coated magnetic stirring bar was charged with a benzene (2.5 ml) solution of **10** (1.0 g, 0.778 mmol) and AIBN (0.005 g, 0.0304 mmol) and sealed with a rubber septum. The solution was subjected to five freeze–pump–thaw cycles, and stirred at 68 °C for 10 h, after which the mixture was diluted with $CHCl_3$ and precipitated into CH_3OH three times to give **11** (0.58 g, 58%) of a white elastic solid. Anal. Calcd for $C_{77}H_{118}O_{15}(C_{77}H_{116}D_2O_{15})$: C, 72.04; H, 9.26. Found: C, 71.10; H, 9.28 (corresponding to $\{C_{77}H_{116}D_2O_{15} + CH_3OH\}_n$). $M_n = 176{,}284$, PDI = 1.02.

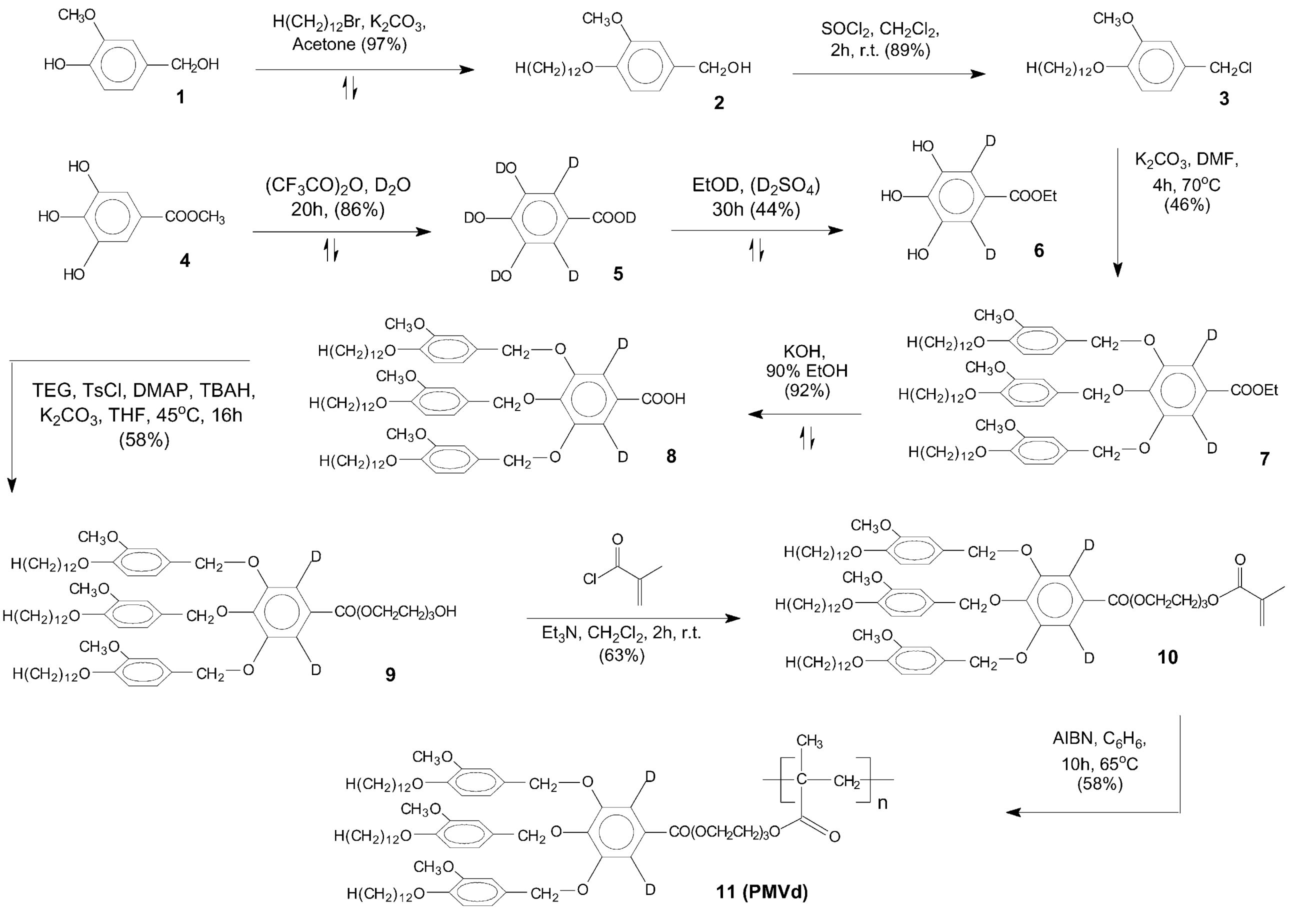
3. Results and discussion

3.1. Preparation of monomers and polymers

Scheme 1 outlines the synthesis of monomer and polymer. The deuterons were introduced into **10** by H/D exchange of methyl 3,4,5-trihydroxybenzoate in a D_2O/$(CF_3CO)_2O$ mixture together with ester hydrolysis, followed by reesterification in EtOD catalyzed by D_2SO_4. ^1H NMR spectral analysis of compound **7** (ETHBd) indicated that deuteration in the 2 and 6 position of the gallate unit occurs to an extent greater than 90%, which is maintained in the following steps without significant exchange occurring since no strong acidic conditions are involved. The radical polymerization was carried out in benzene at 65 °C with AIBN as the initiator.

3.2. Characterization of the deuterated intermediates

In the solution ^1H NMR spectrum of compound **8** (DOVOBa), two peaks appear for two types of methoxy groups at 3.61 and 3.80 ppm (Fig. 1), while the chemical shift difference between the two types of the corresponding protons on the outer benzene ring of DOBOB mesogen is less than 0.05 ppm (Fig. 2) [9]. In the HMQC spectrum



Scheme 1. Synthesis of mesogen-deuterated modified system (PMVd).

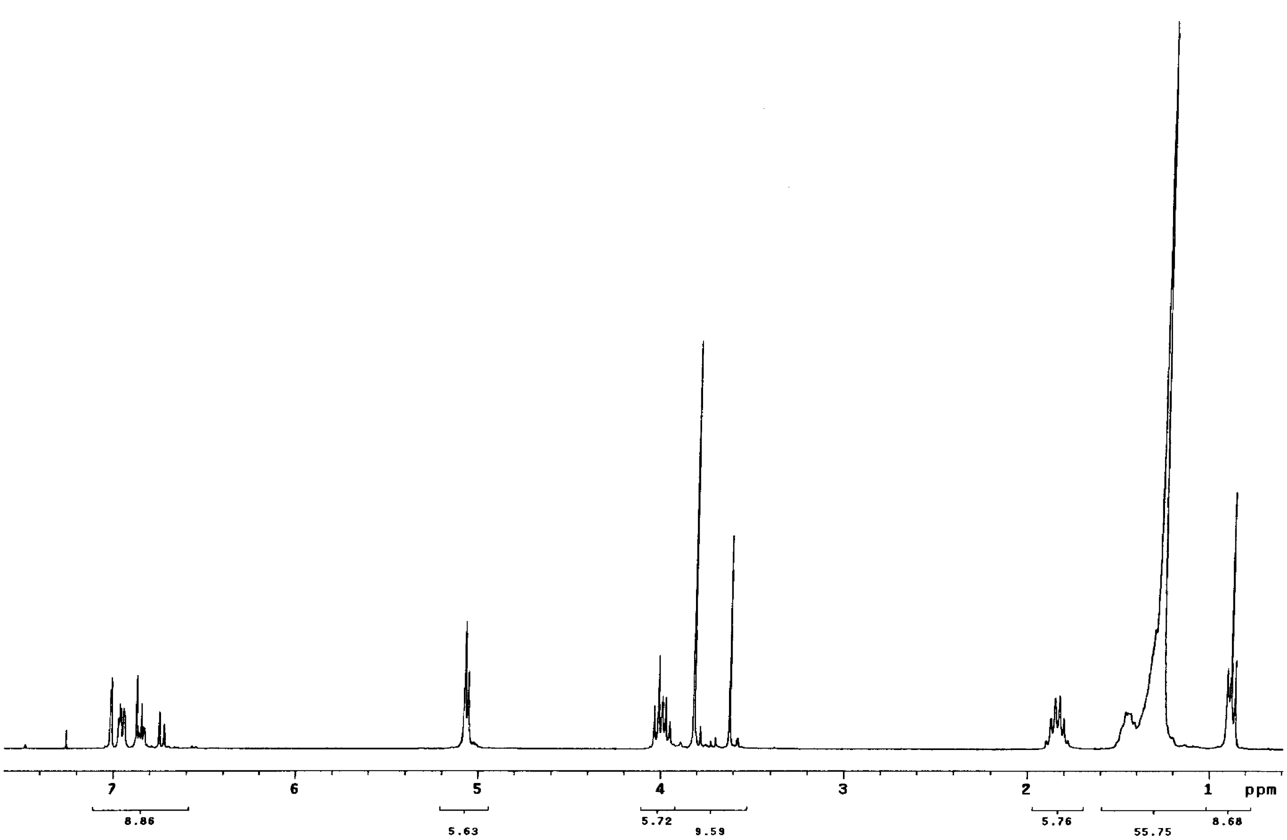


Fig. 1. ^{1}H NMR spectrum of 3,4,5-tris[*p*-(*n*-dodecyloxy)-*m*-methoxybenzyloxy]benzoic acid (DOVOBa) (300 MHz, $CDCl_3$, TMS).

(Fig. 3), these points are correlated to the ^{13}C signal of the methoxy group, which is supported by DEPT analysis (Fig. 4). Similar chemical shift dispersion is observed for the same monodendrimer structure based on vanillyl alcohol in which the dodecyl tail is replaced by the shorter ethyl group (results to be published elsewhere). Moreover, similar chemistry shift dispersion is also observed for another CH_3O–Ar group in a monodendron structure with a

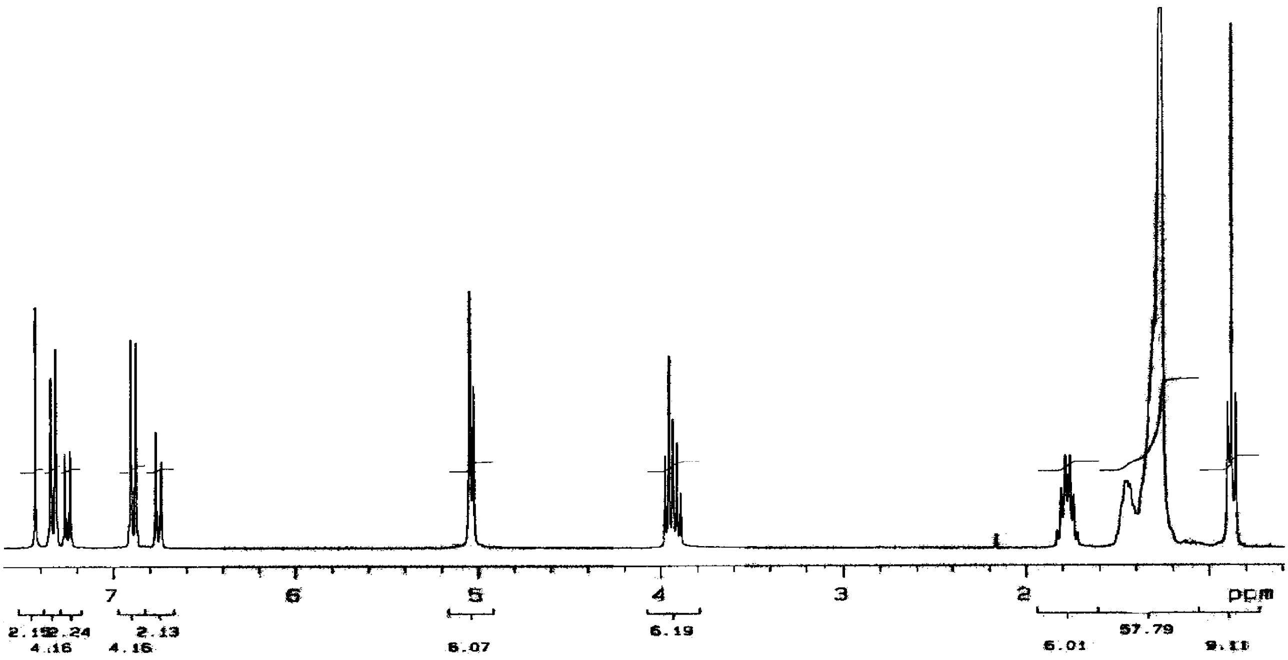


Fig. 2. ^{1}H NMR spectrum of 3,4,5-tris[*p*-(*n*-dodecyloxy)benzyloxy]benzoic acid (DOBOBa) (300 MHz, $CDCl_3$, TMS).

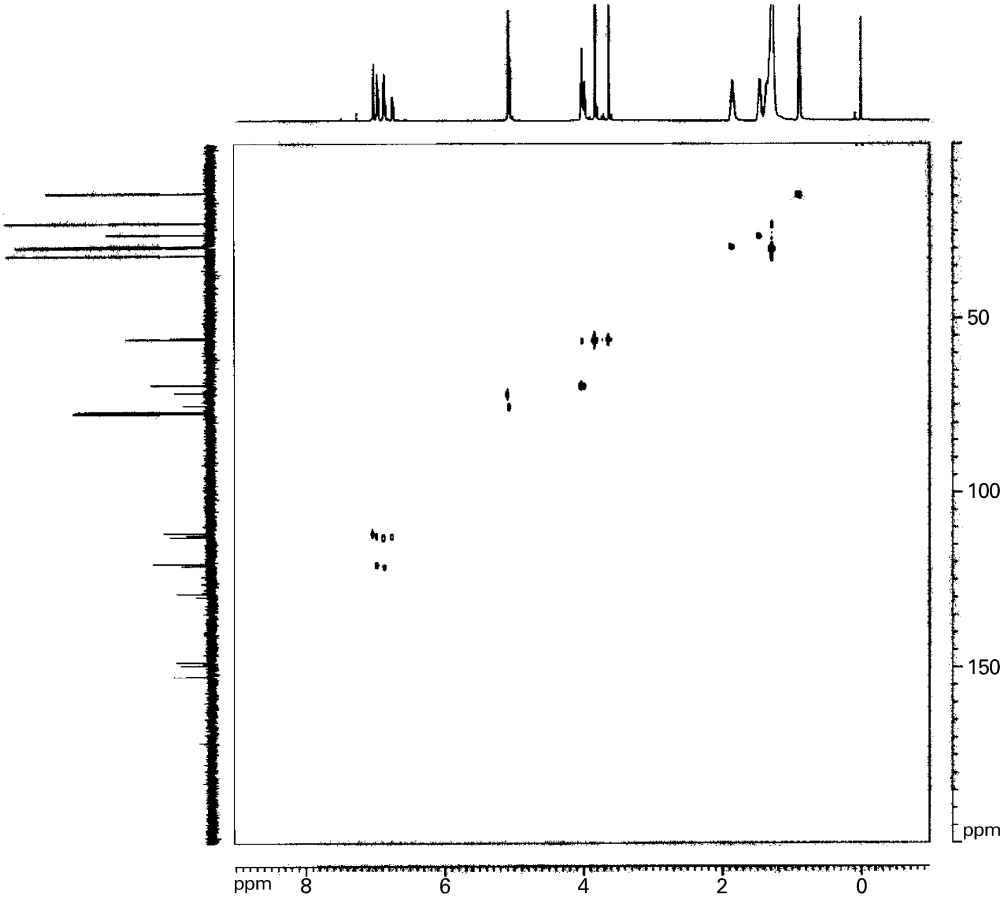


Fig. 3. HMQC spectrum of 3,4,5-tris[*p*-(*n*-dodecyloxy)-*m*-methoxybenzyloxy]benzoic acid (DOVOBa) (400 MHz, $CDCl_3$, TMS).

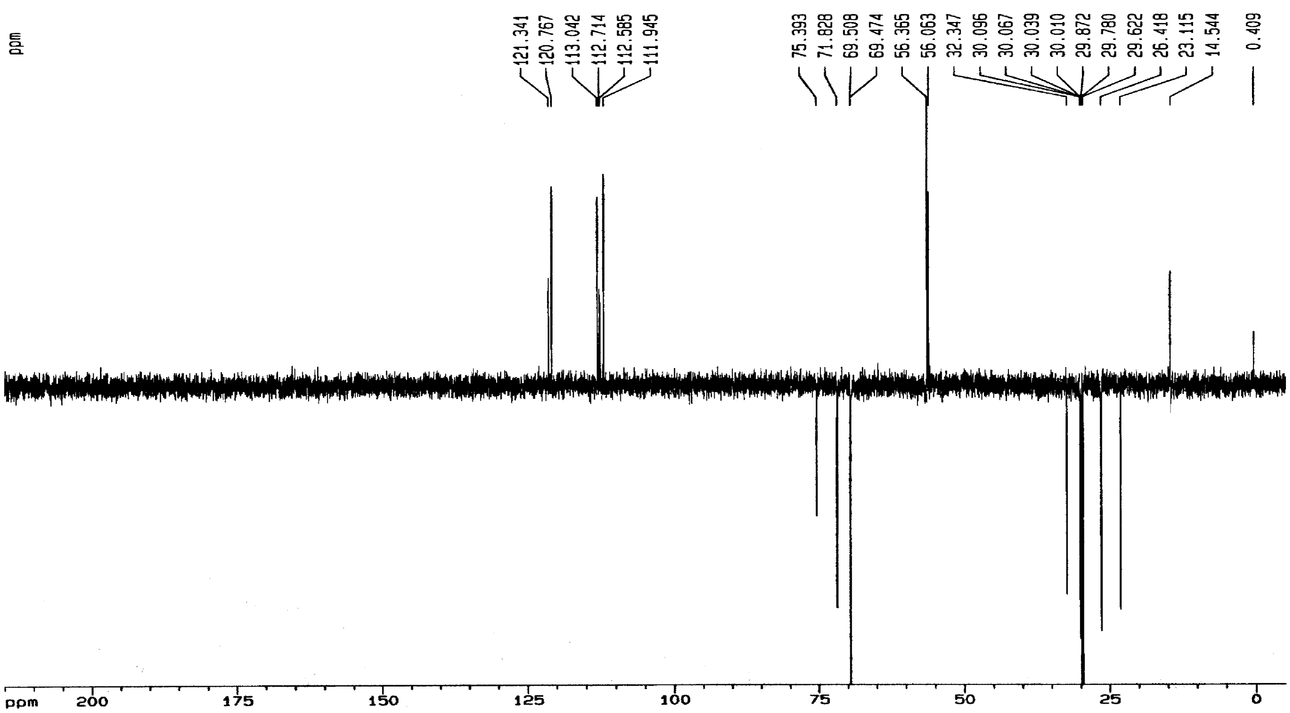


Fig. 4. DEPT spectrum of 3,4,5-tris[*p*-(*n*-dodecyloxy)-*m*-methoxybenzyloxy]benzoic acid (DOVOBa) (400 MHz, $CDCl_3$, TMS).

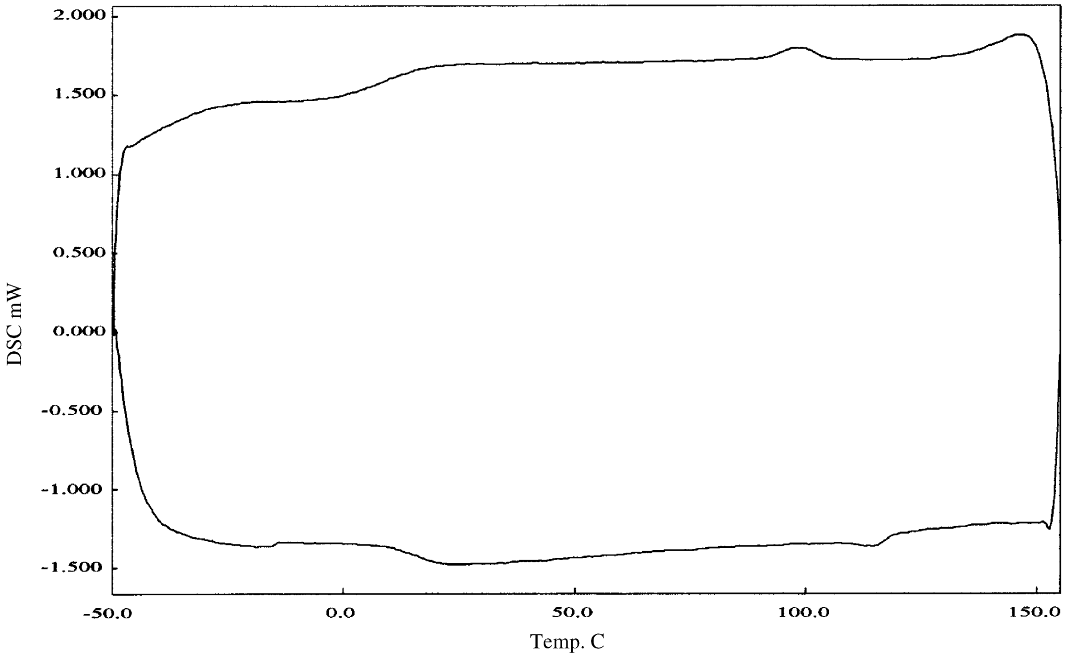


Fig. 5. DSC heating trace of PMVd (+10 °C/min).

crowded environment [21]. The attachment of methacryloyl unit is also indicated by ^{13}C NMR data. The disappearance of the signal at 61.7 ppm ($-CH_2CH_2OH$) and the appearance of the signal at 63.7 ppm ($-CH_2CH_2OCOC(Me){=}CH_2$) together with the signals corresponding to the structural unit of $RCH_2OCOC(CH_3){=}CH_2$ (166.2, 136.1, 18.3, 124.8 ppm) confirms the structure of the monomer.

3.3. Characterization of polymer

GPC analysis indicated that the degree of polymerization for the mesogen-deuterated polymethacrylate (PMVd) was ca. 130. The elemental analysis results were consistent with the theoretical values.

In the DSC trace (Fig. 5) of the mesogen deuterated polymethacrylate (PMVd), at a heating rate of 10 °C/min, a glass transition centered at 15 °C (290 K) is observed as expected, in addition to an LC-isotropic transition at ca. 120 °C (390 K). Thermoplastic elastomers (TPEs), in which the hard domain results from secondary intermolecular forces, also show similar thermal diagrams [22]. Such thermal diagrams were also reported for other self-assembling columnar SGLCPs (VI–IX in Table 1) by the Percec group, in which various structural units from the model DOBOB-based columnar SGLCP are incorporated including alkyl tails with fluoro atoms and outer naphthalene groups [19,20]. The polarized optical micrograph of PMVd under crossed polars at room temperature (Fig. 6) is significantly different from PMBd (Fig. 7) because of the

Fig. 6. Mesophase texture of PMVd at room temperature under POM.

Fig. 7. Mesophase texture of PMBd at 350 K under POM.

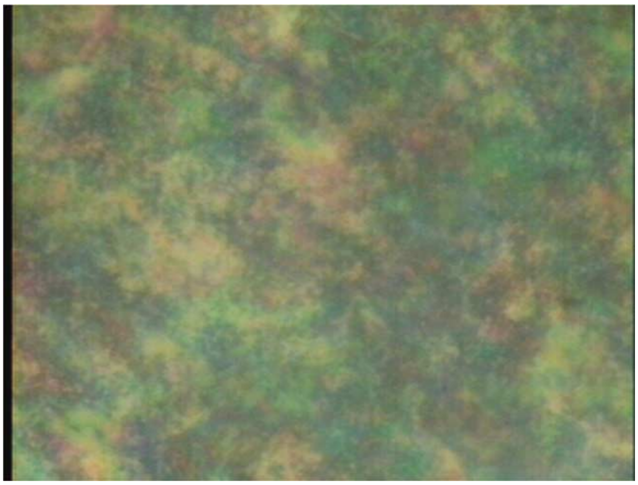


Fig. 8. Mesophase texture of DOVOBa (**8**) at r.t. under POM.

different mesogens (Fig. 8: DOVOBa vs. Fig. 9: DOBOBa). The unique intramolecular interaction between the vanillyl units reduces the excess entropy of the modified mesogen thus inducing the glass transition of the columnar SGLCP, which involves mainly the onset of a cooperative relaxation rotational motion with large amplitude in the polymer. The deuterated polymethacrylate is not a semicrystalline powder but instead a soft elastic solid. It displayed the polydomain to monodomain transition under a mechanical field at room temperature, the so-called mechanico-optical property [23,24] as the bulk material became transparent instead of turbid during this transition. These properties suggested that these side group polymethacrylates based on the modified DOBOB mesogen belong to the class of liquid crystalline elastomers (LCEs) [25–29]. In addition to lightly chemically cross-linked LCE networks proposed by De Gennes [30] and first synthesized by the Finkelmann group [31], a novel LCE resulting from physical cross-linking has been synthesized as a thermoplastic copolyurethane with liquid crystalline moieties pendant to the soft polysiloxane segment [32].

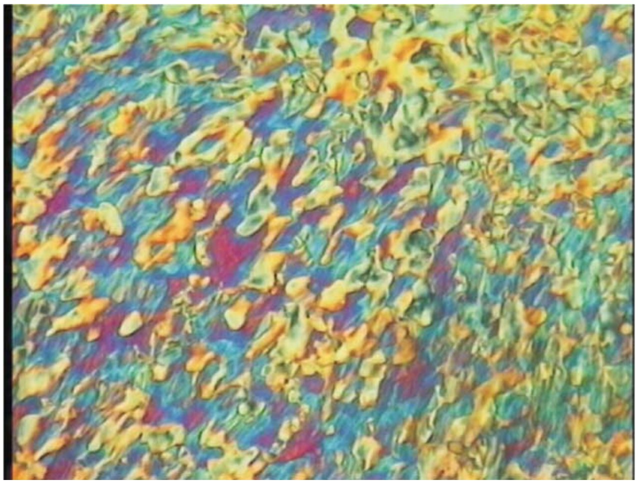


Fig. 9. Mesophase texture of DOBOBa at 345 K under POM.

4. Conclusion

In summary, a deuterated self-assembling columnar liquid crystalline polymethacrylate based on the taper-shaped DOBOB-modified mesogen (DOVOB) side group has been synthesized successfully and characterized by elemental analysis, proton and carbon nuclear magnetic resonances, GPC, DSC, and polarized optical microscope. These polymethacrylates display different phase transitions than their DOBOB-based counterpart that is a semicrystalline powder. The new polymethacrylates show the liquid crystalline mesophase at room temperature and a glass transition, and therefore they belong to the family of thermoplastic liquid crystalline elastomers. The DSC result suggests that the configurational entropy of the modified mesogen is reduced as expected from the molecular design using the Adam–Gibbs theory as a guideline, and thus certain strong intramolecular interactions exist inside the modified mesogen, which moreover provide the physical cross-linking through self-assembling which results in the hard domain inside the columnar LC structure. The capability of exhibiting cooperative rotational motion, which is the molecular dynamics of the glass transition, renders the designed polymethacrylate as a molecular nano-rotor candidate for the construction of molecular nano-spinnerets. ^{2}H NMR characterization of the rotation dynamics of the deuterated DOBOB mesogen and the modified mesogen structure are both in progress.

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