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Synthesis and properties of regioregular polyethers and polyesters with (η^4-cyclobutadiene)cobalt moieties in the main chain[1]

I.L. Rozhanskii[2a], I. Tomita[b], T. Endo[a,*]

[a]*Research Laboratory of Resources Utilisation, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*
[b]*Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan*

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Abstract

Regioregular organocobalt polyethers (**3** and **4**) and polyesters (**5**–**8**) have been prepared by the polycondensation of regioisomerically pure (η^4-tetraarylcyclobutadiene)cobalt-containing bis-phenols (**9** and **10**) with aliphatic or aromatic comonomers. The diols (**9**) offered rigid-rod *p*-terphenyl-like structural units, while their isomers (**10**) led to 90° kinks in polymeric backbones. The polymers (**3**, **5** and **7** = 'odd' series) were derived from the bis-phenols (**9**), while their isomers (**4**, **6** and **8** = 'even' series) resulted from **10**. Most of the polymers (**3**–**8**) exhibited good solubilities in common organic solvents. In the case of the isomeric polyesters with aromatic backbones (**7** and **8**), the latter were more soluble, indicative of their higher configuration entropies. Glass transition temperatures of the 'odd' and 'even' isomers were similar, irrelative to the kinks in their backbones, but they showed good correlation with aliphatic-to-aromatic mass ratios and rigidities of the main chains. The polymers of the 'odd' series exhibited crystalline and liquid crystalline (polyesters, **7**) phases, while their 'even' isomers remained amorphous. Correlations between mesomorphic properties and the structure of the repeating units have been discussed.

Keywords: Organocobalt polymers; Polycondensation; Liquid crystal polyesters

1. Introduction

An incorporation of transition metal complexes into polymer backbones can greatly extend the scope of a macromolecular design, based on unique properties of organometallic compounds and versatile methods of their synthesis. Metal-containing polymers are regarded as promising materials for non-linear optics and optoelectronics, as well as polymeric catalysts or precursors for functional polymers (for recent reviews, see Refs. [2–5]. Recently, several series of polymers bearing (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt moieties have been synthesised in our [1,6–9] and Bunz [10,11] groups. In particular, these units have been used as building blocks for organometallic π-conjugated polymers [6,7,9–11]. In the previous work, we have reported the reaction of (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt (**1**) with various diynes, which leads to the formation of phenylated polymers (**2**) bearing statistically distributed isomeric repeating units (Scheme 1) [6–8]. Although the randomness of the backbone structure of **2** may facilitate their solubility in organic solvents, it may preclude the formation of liquid crystalline phases, which are desirable in a number of applications. Another limitation of this approach is the difficulty in maintaining feed ratios of monomers, because **1** is air-sensitive and it is hard to achieve purity. In order to control the regularity of the main chain linkage (e.g. by employing the steric factor), the polycondensation was carried out with designed diynes which, however, attained as high as 90% selectivity [12].

Alternatively, the above limitations may be overcome, if stable regioisomerically pure (η^4-cyclobutadiene)cobalt-containing monomers, are employed in the polymerisation step instead of **1**. A variety of common polycondensation reactions might be applied, depending on the functional groups in monomers. In this paper, we describe the synthesis of organocobalt polyethers (**3** and **4**) and polyesters (**5**–**8**) by the polycondensation of regioisomerically pure bis-phenols possessing the organocobalt cores (**9** and **10**) and various bifunctional comonomers (Scheme 2, Scheme 3).[3]

* Corresponding author.
[1] A part of this work has been communicated in Ref. [1].
[2] Present address: Tsukuba Research Laboratory, JSR Corporation, 25 Miyukigaoka, Tsukuba, Ibaraki 305, Japan.
[3] Polyesters with all-aromatic rigid-rod backbones (**7**) were reported in the preliminary communication (see Ref. [1]).

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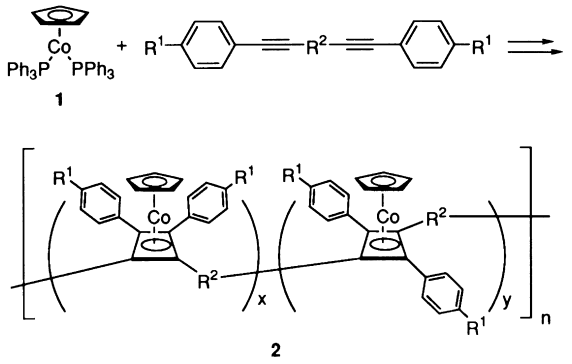
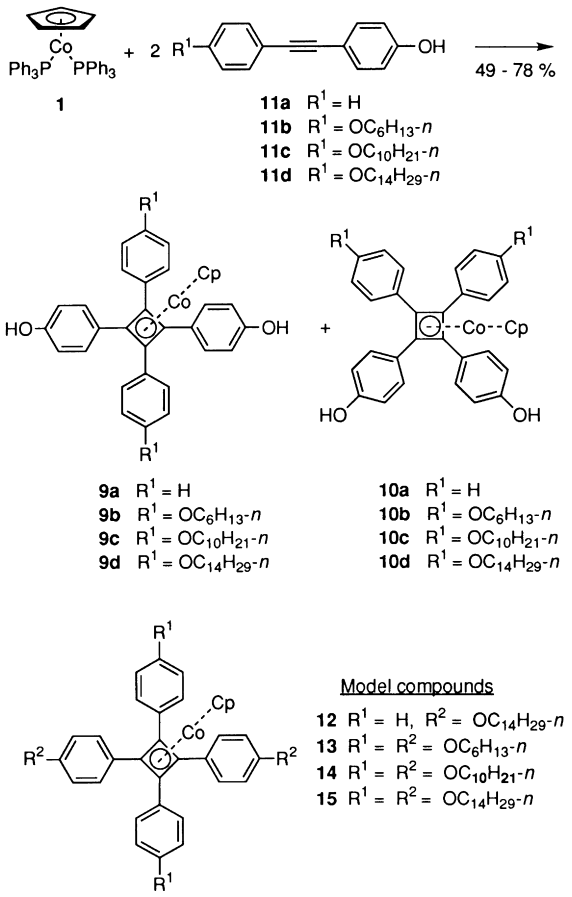


Scheme 1. Previous work (Refs. [7, 8]).

In addition to the interest in the polymers (**3**–**8**) as new materials bearing organometallic species, they may also be considered as convenient model systems for the study of the structure-property relations in condensation polymers. Since the parent (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt complex is known to possess nearly tetragonal symmetry [13], the polymers (**3**, **5** and **7**) are assumed to bear rigid-rod *p*-terphenyl-like moieties, while the corresponding units in **4**, **6** and **8** are bent by 90°. As a consequence, 'odd' and 'even' rows of the polymers (**3**–**8**) might represent two limiting cases of the main-chain geometry, as it may be visualised by the 'cross-and-stick' models (Fig. 1). Since the only structural difference between **9** and **10** is the position of functional groups (which are rather distant from each other), one can neglect possible effects of steric hindrance or different reactivity of monomers. By varying length and rigidity of spacers, conclusions may be drawn about the influence of the backbone structure on the physical properties of polymers. Such model considerations might be useful in the design of novel, commercially important, high-performance polymers, because many of them are produced from mixtures of stiff and bent structural units.

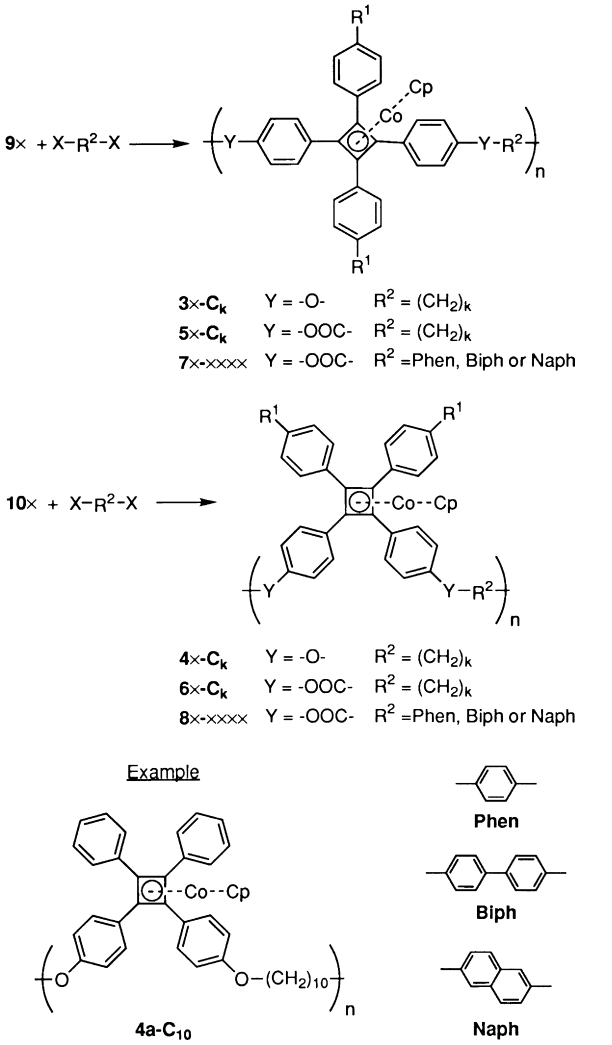


Scheme 2. Synthesis of monomers and model compounds.

2. Results and discussion

2.1. Bis-phenols *9* and *10*

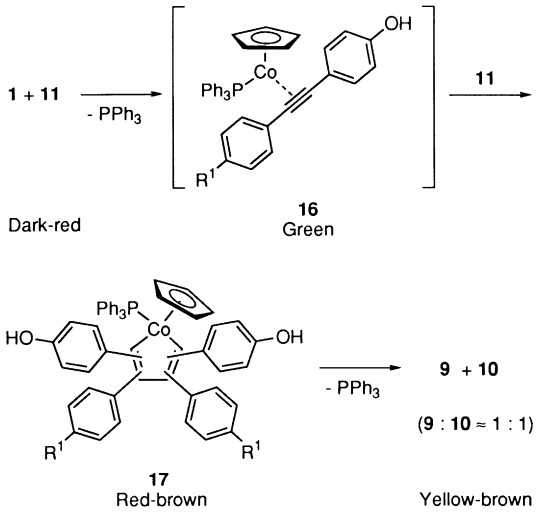
The organocobalt bis-phenols (**9** and **10**) were prepared by the previously reported procedures with slight



Scheme 3. Synthesis and designation of polymers.

modifications [8,14]. In agreement with the known mechanism, the reaction of **1** with ethynylphenols (**11**) led to the formation of green-coloured mono-adducts (**16**) in the early stage, which reacted with the second equivalent of **11** to give mixtures of isomeric cobaltacyclopentadiene-containing diols (**17**), as it could be monitored by the colour changes of the reaction mixture (Scheme 4). Unstable intermediates (**17**) were converted to the mixtures of **9** and **10** in situ by heating the reaction solutions in DMF. Bis-phenols (**9** and **10**, with ratios of two isomers being close to 1:1) were isolated by the column chromatography on silica gel in 24%–44% yields.

The physical properties of **9** and **10** indicate the systematic difference between isomeric diols. The bis-phenols (**9**) are less polar (judging from higher R_fs), crystallise more easily, and exhibit higher melting points (MP), compared with the corresponding **10**. For instance, **9c** and **9d** readily precipitated as crystals upon removal of the solvent by the rotary evaporator, while **10c** and **10d** did not crystallise at all and were isolated as amorphous solids. Bis-phenols (**9a**–**9c**, **10a**–**10b**) appeared as dimorphic yellow-brown crystals exhibiting two melting points. Ratios of stable (higher MP) and metastable (lower MP) crystalline phases in isolated products depended on the rates of crystallisation, with higher content of the higher-melting crystal forms for slower rates. The bis-phenol (**9d**) showed the single crystalline phase. All isolated diols (**9** and **10**) are quite stable both as solids and in solutions. No deterioration took place during their prolonged ($>$ 1 year) storage in air at room temperature. Both **9** and **10** are soluble in a variety of solvents (THF, DMF, DMSO, CH_2Cl_2, 1,4-dioxane, etc.) and do not decompose under the action of bases and non-oxydizing acids. In view of their stability and ease of handling, monomers (**9** and **10**) can be employed in conventional polycondensation reactions without particular limitations.



Scheme 4. Mechanism of organocobalt bis-phenols formation.

2.2. Model compounds **12**–**15**

Alkoxy-substituted organocobalt repeating units in **3**–**8** might be regarded as potential mesogenes, since they bear nearly flat extended aromatic cores and several lateral aliphatic chains, which are the common features with the known organometallic discotic liquid crystals [15]. However, polymers (**2**) did not exhibit any mesomorphism [8]. It was not clear from the previous study, whether (η^5-cyclopentadienyl)(η^4-tetraarylcyclobutadiene)cobalt groups were intrinsically non-mesogenic or whether they lost these properties after polymerisation. In the course of this work, several model compounds (**12**–**15**) were synthesised to elucidate the inherent thermal properties of repeating units.

Model (η^5-cyclopentadienyl)(η^4-tetraarylcyclobutadiene)cobalt complexes with two (**12**) or four (**13**–**15**) linear alkoxy substituents were obtained from bis-phenols (**9a**, **10b**–**10d**) by the Williamson ether synthesis in 56%–68% yields (Scheme 2). The results of the DSC and the polarising microscopic study of their thermal behaviours are summarised in Table 1. Although none of the model compounds exhibited mesomorphic properties, the crystalline polymorphism and multiple melting were typical for the tetraalkoxy-substituted complexes (**13**–**15**). It was found that the compounds (**12**–**14**) showed a tendency to supercooling and glass formation. Probably high melt viscosities may inhibit the rapid crystallisation of these complexes. The compound (**15**) exhibited somewhat more complicated thermal behaviour, with two or three melting endotherms of variable intensities registering from freshly crystallised (Et_2O–hexane) samples. The slower the heating rates, the greater the content of the higher-melting polymorph (Fig. 2a, Fig. 2b), indicative of slow second-order transitions between different crystal forms. On cooling from the isotropic liquid, **15** did not form glass, but crystallised as the lower-melting phase (MP = 7.5°C). Only the latter crystal form was observed in subsequent thermal cycles (Fig. 2c), and it could not be converted to the higher-melting one, even after several hours of annealing.

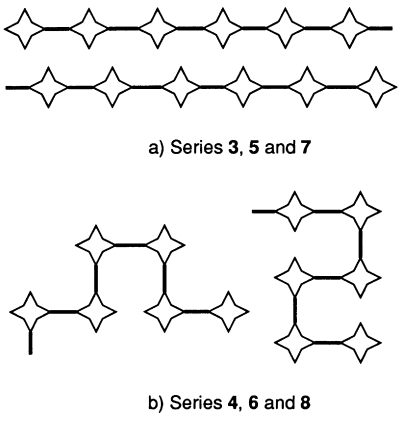


Fig. 1. 'Cross-and-stick' representations of isomeric organocobalt polymers derived from bis-phenols (**9** or **10**).

Table 1
Transitional properties of model compounds

Compound designation	Transition parameters[a] First heating	Second heating
12	MP = 76; $\Delta H_m = 62$	$T_g = -19$
13[b]	MP = 131; $\Delta H_m = 43$	$T_g = -10$; $MP_2 = 120$; $MP_1 = 128$; $\Sigma\Delta H_m = 40$
14	$T_{Cr-Cr} = -16$; $\Delta H_{Cr-Cr} = 12$; MP = 64; $\Delta H_m = 25$	$T_g = -33$
15	$MP_3 = 6$; $MP_2 = 38.5$; $MP_1 = 47$; $\Sigma\Delta H_m = 90$	MP = 7.5; $\Delta H_m = 41$

[a]Temperatures in °C; enthalpies in kJ mol^{-1}
[b]Formed glass on cooling, recrystallised on repeated heating

According to the study of model compounds, the formation of columnar mesophases in polymers (**3**–**8**) seems unlikely, because four aliphatic chains per aromatic core in **13**–**15** might not be sufficient to promote the genuine liquid crystallinity in these complexes. However, the observed multiple melting of **13**–**15** could manifest a borderline between mesomorphic and non-mesomorphic compounds. One can expect that mesophases might be induced by the copolymerisation of (η^4-cyclobutadiene)cobalt units with other mesogenes and/or by the construction of regular rigid-rod backbones.

2.3. *Polymers* 3–8

Two series' of isomeric polyethers (**3** and **4**) were obtained by the condensation of diols (**9** and **10**) with α,ω-dibromoalkanes under Williamson ether synthesis conditions, respectively. The obtained polymers were purified by the precipitation into *n*-hexane, followed by filtration or centrifugation, depending on whether they gave filtrable or adhesive precipitates. Their properties are summarised in Table 2. The regioregular polyethers of these series may be compared with their random isomers **2**.[4] Apart from some difference in molecular weights, isomeric polymers (**2**, **3** and **4**) exhibited similar (within $\pm$ 12°C) glass transition and degradation temperatures. The latter were typically in the range of 400°C–420°C, as measured from the maxima of exothermic peaks in DTA curves. According to DSC measurements and polarising microscopic observations, some polyethers (**2** and **3**, but not **4**) were partly crystallised upon solution-casting, but the crystal phases disappeared irreversibly after melting. Similar to the model compounds (**12**–**15**), no mesophases were found in polyethers (**3** and **4**).

The aforementioned synthesis of polyethers (**3** and **4**) was carried out to obtain polymers, which could model main-chain discotic polymeric liquid crystals. When bifunctional acyl chlorides were used as comonomers, the resulting polyesters (**5**–**8**) may have varied the main-chain rigidity in the broader range. Aromatic spacers (*p*-phenylene, biphenyl-4,4′-diyl and naphthalene-2,6-diyl) are especially attractive because of their mesogenic abilities. Accordingly, polyesters (**5**–**8**) were synthesised by the interfacial esterification, using quaternary ammonium salt as a phase-transfer catalyst. To attain the maximum comparability, the reaction conditions were essentially the same throughout all of the polycondensations. The bis-phenols (**9** or **10**) were first dissolved (or dispersed to fine emulsions) in 1:2 mixtures of 1,4-dioxane and aq. 1 N NaOH. After addition of CH_2Cl_2 solutions of acyl chlorides, the polycondensation reactions proceeded quite rapidly, judging from the immediate formation of yellow precipitates. In the most cases, the dilution of the reaction mixtures with methanol, filtration and washing of precipitates with water and methanol were sufficient to yield pure polyesters, as confirmed by their ^{1}H n.m.r. spectra and g.p.c. traces. If some admixtures were still present in the so-isolated products, the samples of polyesters were dissolved in the minimal amount of CH_2Cl_2, and the similar purification procedures were repeated once more.

The structures of the polyesters (**5–8**) were confirmed by their i.r. and ^{1}H n.m.r. spectra. Isomeric polymers (**5** and **6**, or **7** and **8**, respectively) showed nearly indistinguishible i.r. spectra. Similarly, ^{1}H n.m.r. spectra of 'odd' and 'even' rows of **5**–**8** exhibited similar features, except for systematic differences in chemical shifts of protons at 7.6–6.8 ppm (phenylene groups of organocobalt cores), indicating thereby the regioregularity of their backbones (Fig. 3, as a representative example).

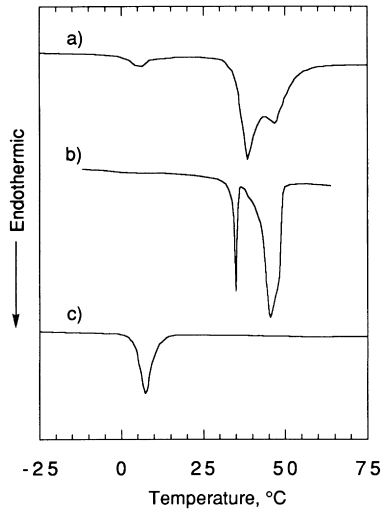


Fig. 2. DSC thermograms of **15**: (a) first heating, 20°C min^{-1}; (b) first heating, 0.5°C min^{-1}; and (c) second heating, 10°C min^{-1}.

[4] Molecular weights and thermal properties of the relevant polyethers (**2**) of Ref. [8] are listed in Table 2. For convenience, the notation of the recent paper is followed.

Table 2
Molecular weights and thermal properties of organocobalt polymers (**2**–**8**)

Polymer designation[a]	$\bar{M}_n$, ($\bar{M}_w/\bar{M}_n$)[b]	T_m(°C)[c]	T_g(°C)[d]	Mesophase temperature range (°C)[e]	Polymer designation	$\bar{M}_n$, $\bar{M}_w/\bar{M}_n$)[b]	T_m(°C)[c]	T_g(°C)[d]
3a-C$_6$	5000 (1.29)		100 (103)		**4a-C$_6$**	2300 (1.13)		95 (n.d.)[g]
2a-C$_6$[f]	7800 (1.27)	60	119 (128)					
3a-C$_{10}$	3600 (1.73)	55	90 (100)		**4a-C$_{10}$**	1500 (1.38)		76 (79)
2a-C$_{10}$[f]	9800 (1.41)	75, 128	65 (n.d.)[g]					
3d-C$_6$	6100 (1.94)	70	6 (n.d.)[g]		**4d-C$_6$**	3200 (1.29)		20 (30)
2d-C$_6$[f]	6300 (1.16)	25	0 (n.d.)[g]					
3d-C$_9$	5900 (1.61)		21 (21)		**4d-C$_9$**	4300 (1.52)		19 (29)
2d-C$_9$[f]	12800 (1.50)		− 11 (− 7)					
3d-C$_{10}$	6100 (1.70)		9 (32)		**4d-C$_{10}$**	5400 (1.51)		10 (n.d.)[g]
5d-C$_4$	13400 (1.86)	149	40 (50)		**6d-C$_4$**	7300 (1.41)		46 (47)
5d-C$_7$	8400 (1.48)	149	14 (20)		**6d-C$_7$**	7900 (1.41)		26 (13)
5d-C$_8$	8700 (1.46)	124	12 (16)		**6d-C$_8$**	6600 (1.44)		19 (10)
7a-Biph	7200 (1.86)		no transitions		**8a-Biph**	5700 (1.26)		no transitions
7b-Biph	10700 (1.73)	73	145 (130)	140 to > 250	**8b-Biph**	8200 (1.32)	75	142 (154)
7c-Biph	22500 (3.08)	73	115 (122)	125 to > 250	**8c-Biph**	11400 (1.42)	70	116 (137)
7d-Biph	19700 (5.45)	82	100 (111)	110 to > 250	**8d-Biph**	16300 (1.79)	70	106 (123)
7c-Phen	13300 (1.93)	72	90 (101)	115–175	**8c-Phen**	8500 (1.29)	62	92 (101)
7d-Phen	12500 (2.36)	68, 146	80 (n.d.)[g]	110–160	**8d-Phen**	11000 (1.28)		81 (93)
7c-Naph	17200 (1.93)	52, 224	103 (100)	120–225	**8c-Naph**	11100 (1.51)		106 (115)
7d-Naph	17800 (2.19)	71, 192	82 (105)	110–200	**8d-Naph**	13600 (1.47)	69	84 (112)

[a]Polymer structures according to Scheme 3
[b]Estimated from GPC (TBF, polystyrene standard)
[c]Determined by DSC in the first heating
[d]Determined by DSC in the second heating. Data of the first heating are given in the parentheses
[e]Determined from polarising microscopic observations in the first heating, 10°C min^{-1}
[f]Isomeric polyethers with random backbones, data of ref. [8]
[g]Not detected

In cases of polyesters with all-aromatic main chains (**7** and **8**), g.p.c. showed higher molecular weights and polydispersity indices for the polymers (**7**), compared with their isomers (**8**). This effect might be due to the difference in the molecular shape for different isomers, because persistence lengths of 'odd' polymers with stiff spacers are expected to be higher (Fig. 1). In agreement with this proposition, g.p.c. analysis showed that peaks of oligomers of polyesters (**7**) appeared at shorter retention times, compared with those of **8** (Fig. 4). In the particular example of **7b-Biph** and **8b-Biph**, number-averaged degrees of polymerisation ($\bar{P}_n$) were estimated independently from their ^{1}H n.m.r. spectra.[5] Both **7b-Biph** and **8b-Biph** exhibited similar $\bar{P}_n$s (7.0 and 8.5, respectively), supporting the above proposition. It may be concluded that g.p.c.-estimated $\bar{M}_n$s of polyesters (**7**) deviate regularly from those values for **8**, because of their distinct molecular dimensions rather than due to different polymerisabilities. Polymers with flexible spacers (**3**–**6**) exhibited similar trends, although less prominent. One might speculate about the formation of cyclic oligomers in the series **4** and **6**, as an alternative explanation of the difference in molecular weights. However, g.p.c. curves of the isolated products were unimodal (similar to those of Fig. 4), with no peaks assignable apparently to cyclic species. Although the possibility of the formation of macrocycles cannot be entirely ruled out, it is unlikely that they contribute to the molecular weight distributions in a measurable extent.

One can expect that solubilities of regioregular polymers (**3**–**8**) may be affected by the main-chain geometry. In cases of polymers with aliphatic spacers (**3**–**6**), both 'odd' and 'even' rows exhibited very good solubilities in common organic solvents (toluene, ether, THF, $CHCl_3$, DMF, etc.) with no qualitative distinction between different isomers. Polyesters with all-aromatic backbones and pendant alkoxy groups (**7b**–**7d** and **8b**–**8d**) were also soluble in the same solvents as polymers **3**–**6**, indicating the good solubilisation effect of lateral aliphatic moieties. A difference between **7** and **8** was mostly in the rate of dissolution. While polyesters with stiff repeating units (**7**) required at least 30 min stirring at room temperature, to obtain their 10 wt% solutions in $CHCl_3$, the same process took ca. 5 min for their bent isomers (**8**). The most striking effect was exhibited by the fully aromatic polyesters (**7a-Biph** and **8a-Biph**). The former (**7a-Biph**) was found practically insoluble at room temperature in all of the examined organic solvents.[6] It was

[5] Estimations were based on the relative intensities of bands from both carboxylic acid (a′ and b′, Fig. 3) and phenol (d′ and e′, respectively) end groups, which were clearly resolved in the given n.m.r. spectra.

[6] It was possible to record g.p.c. traces from very diluted THF solutions of **7a-Biph** using a u.v. detector, because of the high molar extinction of aromatic cor.es

dissolved at elevated temperatures in *o*-dichlorobenzene and nitrobenzene, but precipitated from solutions on cooling. In contrast, its isomer (**8a-Biph**) was readily soluble in a variety of solvents (such as, toluene, THF, $CHCl_3$, DMF). Ibis model example emphasises an importance of the entropy factor in the solution behaviour of polymers, because **8a-Biph** has the same chemical composition and approximately the same $\overline{P}_n$ as **7a-Biph**, but it can form a bigger number of conformational isomers.

Except for all-aromatic polyesters (**7a-Biph** and **8a-Biph**), polymers (**3**–**8**) exhibited distinct glass transitions in the DSC charts. Comparing T_gs of the two rows of the isomeric polymers (Table 2), one can note an obvious independence of T_g values on the geometry of the organometallic repeating units. In many instances, T_gs of stiff and bent isomers markedly coincided. A crucial factor was found to be the content of aliphatic moieties, judging from good correlations between T_gs of polymers (**3**–**8**) and the mass fractions of the methylene groups (Fig. 5). Another governing factor is the rigidity of the polymeric main chain, as it may be concluded from the regular shifts of the fitting lines in the series of polymers with rigid (**7** and **8**) and semi-rigid (**3**–**6**) backbones, as well as model compounds (**12**–**14**).

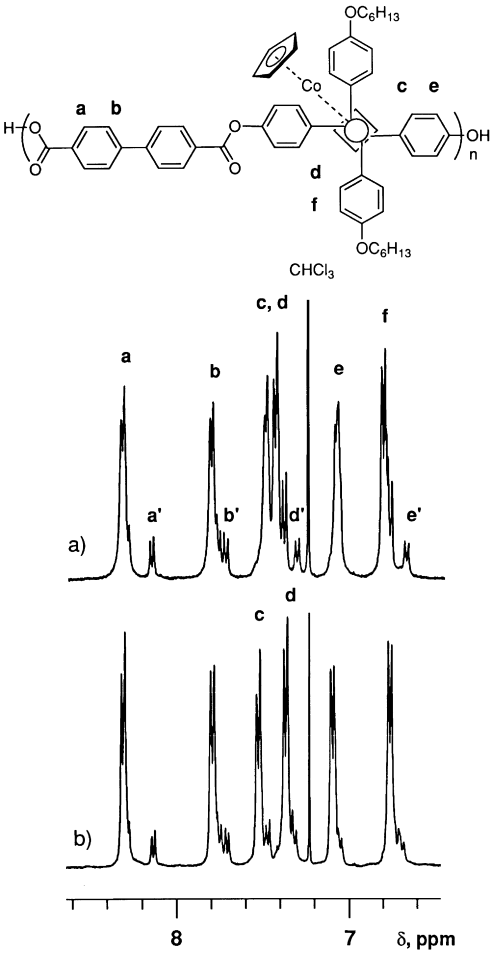


Fig. 3. ^{1}H NMR spectra of: (a) **7b-Biph;** and (b) **8b-Biph**, in the regions of aromatic protons. Primed indices denote bands of end groups.

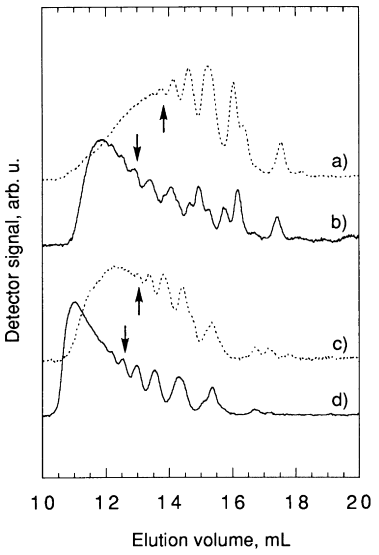


Fig. 4. G.p.c. traces of: (a) **8a-Biph**; (b) **7a-Biph**; (c) **8b-Biph**; and (d) **7b-Biph**. Arrows indicate the peaks of hexamers.

The above observations are consistent with the proposition, that T_gs of the given aliphatic–aromatic polymers are defined mostly by the local mobilities of structural units, with the peculiarities of main chains (i.e. degrees of polymerisation, conformations or persistence lengths) being of secondary importance.

All of the examined polymers (except for poorly soluble **7a-Biph**) exhibited good film-forming properties, to give clear transparent films on casting from $CHCl_3$ or THF solutions. DSC measurements of freshly prepared films detected endothermic transitions in a number of polymers of the 'odd' series, probably indicating melting of some ordered phases. The polymers with flexible spacers (**3** and **5**) might be partially crystalline, judging from the presence of turbid birefringent domains in the corresponding samples. An absence of crystalline phases in the polymers (**4** and **6**) correlates with the poor crystallisability of the corresponding bis-phenols (**10**).

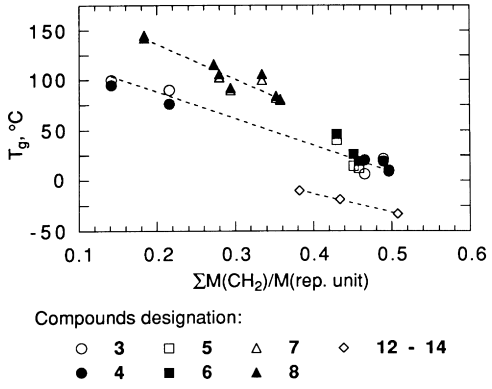


Fig. 5. Glass transition temperatures of polymers (**3**–**8**) and model compounds (**12**–**14**) as a function of the content of aliphatic moieties (calculated as a total mass of CH_2 groups in a repeating unit divided by the mass of the latter).

As communicated previously, the rigid-rod polyesters (**7**) exhibited thermotropic mesophases at the temperatures above their T_gs [1]. One can note that the stability ranges of mesophases in the polymers (**7**) apparently correlated with aspect ratios of comonomers, being the broadest for Biph units and the narrowest for Phen. This effect could assign aromatic comonomers as an important driving force to induce liquid crystallinity. Although the structural parameters of mesophases are yet to be determined, there is an obvious resemblance in the transitional behaviour between the polyesters (**7**) and so-called 'hairy-rod' polymers, which can form a variety of layered mesophases [16]. Thus, endothermic peaks at 50°C–80°C might be assigned as order–disorder transitions of aliphatic side chains in the microphase-separated domains. Therefore, another important factor should be an overall elongated shape of the macromolecules, since it facilitates the anisotropic packing. The latter proposition may be also supported by the absence of any mesomorphism in the polyesters (**8**), which formed isotropic fluids above their T_gs.

The common feature in the thermal behaviour of the polymers (**3**, **5** and **7**) is an irreversibility of crystal or liquid crystal phases after melting. Since the same effect was also observed in the model compounds (**12**–**14**), it may originate from high melt viscosities. One of the ways to reduce their values and to promote the enantiotropic mesophases might be an introduction of additional pendant group or branched substituents. Transition temperatures could be tuned by the ratios of aliphatic-to-aromatic moieties and an appropriate choice of comonomers. The further work is in progress.

3. Conclusions

1. Thermally and chemically stable (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt-containing bis-phenols (**9** and **10**) could be obtained in a high regioisomeric purity, and their applicability to the polymer synthesis was established.
2. Regioregular polyethers and polyesters were prepared independently from either **9** or **10**, and the properties of isomeric polymers have been compared. The obtained polymers (**3**–**8**) were regarded as convenient models for high-performance condensation polymers, due to their unique geometry.
3. Glass transition temperatures of the polymers (**3**–**8**) correlated with the content of aliphatic moieties and rigidities of main chains, but were not sensitive to the kinks in the backbones.
4. Solubilities of the all-aromatic random-coil polyesters **8** were higher, compared with their rigid-rod isomers **7**, presumably due to the entropy factor.
5. An introduction of rigid-rod units **9** promoted crystalline or liquid-crystalline phases into corresponding polymers, while the bent monomers **10** suppressed crystallisation and favoured glass formation.

4. Experimental section

4.1. Materials and instruments

(η^5-Cyclopentadienyl)bis(triphenylphosphine)cobalt (**1**) and ethynylphenols (**11a**–**11d**) were synthesised according to the published procedures [14,17]. 2,6-Naphthalenedicarbonyl dichloride was prepared from 2,6-Naphthalenedicarboxylic acid by the reaction with thionyl chloride and recrystallised from chloroform. Tetrahydrofuran (THF) was dried over sodium and distilled under nitrogen prior to use. α,ω-dibromo-*n*-alkanes and α,ω-bis(chlorocarbonyl)-*n*-alkanes were distilled under reduced pressure. Terephthaloyl chloride and 4,4′-biphenyldicarbonyl dichloride were recrystallised from chloroform. Other reagents (from Tokyo Kasei Kagaku or Kanto Chemicals) were used as received.

^{1}H n.m.r. spectra were recorded on a JEOL JNM-EX400 and/or a JNM-EX90 spectrometer (400 and 90 MHz, respectively) in $CDCl_3$ or DMSO-d_6 (tetramethylsilane as an internal standard). I.r. spectra were obtained on a Jacso FT/IR-5300 spectrometer from KBr pellets or neat films cast onto KBr plates. Gel permeation chromatographic (g.p.c.) analyses were performed on a Tosoh HLC-8020 (tandem columns with TSK-G2500HXL + TSK-G3000HXL or TSK-G4000HXL + TSK-G5000HXL gels, THF as eluent) using standard polystyrene as a reference. Thermogravimetric (TG) and differential thermal analyses (DTA) were carried out on a Seiko TG/DTA 220 instrument at a heating rate of 10°C min^{-1} under nitrogen. Differential scanning calorimetry (d.s.c.) analyses were carried out on a Seiko SSC/220C and/or a DuPont DSC2000 instrument at a scanning rate of 20°C min^{-1}. Melting points (MP) and glass transition temperatures (T_g) were determined from DSC thermograms, as temperatures corresponding to maxima of endothermic peaks and baseline inflection points, respectively. Polarising microscopic observations were performed on an Olympus BH-2 microscope equipped with a Mettler FP90 hot stage.

4.2. Synthesis

4.2.1. Bis-phenols **9** and **10** (Typical procedure for **9d** and **10d**)

The cobalt(I) complex **1** (1.72 g, 2.65 mmol) was placed into a 200 ml 3-necked flask equipped with a reflux condenser and a magnetic stirrer bar, under nitrogen. To the flask was added a solution of **11d** (2.15 g, 5.30 mmol) in THF (35 ml) via a syringe. After stirring at 50°C for 20 h, the reflux condenser was replaced by the distillation apparatus, DMF (70 ml) was added, and the reaction mixture was

stirred at 120°C (oil bath temperature) for 3 h, under nitrogen. THF was partially distilled off during this procedure. The residual solvent was removed under reduced pressure and the reaction products were separated by the column chromatography (SiO_2, benzene–*n*-hexane–diethyl ether = 4:1:1). Triphenylphosphine was observed as the first colourless band, the next one was **9d** (yellow-brown), then recovered **11d** (colourless) and, finally, **10d** (yellow-brown). The fraction containing **9d** was flushed through the column (SiO_2, *n*-hexane–diethyl ether = 2:1) to remove traces of PPh_3 and **lld**. After removal of the solvent under reduced pressure and drying in a vacuum oven (60°C, 6 h), **9d** (0.91 g, 37%) and **10d** (1.03 g, 41%) were isolated as yellow crystals and a brown resin, respectively.

9d: MP = 114°C; $R_f = 0.86$ (benzene–*n*-hexane–Et_2O = 4:1:1); i.r. (KBr, cm^{-1}) 3410 (OH), 2924, 2853 (C–H), 1607, 1514 (C=C), 1242 (=C–O–); ^{1}H n.m.r. (400 MHz, $CDCl_3$) δ 7.35–7.30 (8 H, C_6H_4 *meta* to –OH and –OR), 6.74 (*d*, $J = 8.4$ Hz, 4 H, C_6H_4 *ortho* to –OR), 6.67 (*d*, J = 8.2 Hz, 4 H, C_6H_4 *ortho* to –OH), 5.05 (*s*, 2 H, –OH), 4.57 (*s*, 5 H, C_5H_5), 3.95 (*br*, 4 H, $-OCH_2-$), 1.79–1.27 (48 H, $-CH_2-$), 0.88 (*br*, 6 H, $-CH_3$).

10d: $T_g = 27$°C; $R_f = 0.41$ (benzene–*n*-hexane–Et_2O = 4:1:1); i.r. (KBr, cm^{-1}) 3414 (OH), 2924, 2853 (C–H), 1606, 1514 (C=C), 1242 (=C–O–); ^{1}H n.m.r. (400 MHz, $CDCl_3$) δ 7.35–7.30 (8 H, C_6H_4 *meta* to –OH and –OR), 6.74 13 (*d*, $J = 8.2$ Hz, 4 H, C_6H_4 *ortho* to –OR), 6.69 (*br*, 4 H, C_6H_4 *ortho* to –OH), 5.22 (*s*, 2 H, –OH), 4.57 (*s*, 5 H, C_5H_5), 3.95 (*br*, 4 H, $-OCH_2-$), 1.79–1.27 (48 H, $-CH_2-$), 0.88 (*br*, 6 H, $-CH_3$).

9a: yield, 44%; $MP_1 = 264$°C, $MP_2 = 184$°C; $R_f = 0.48$ (benzene–*n*- hexane–Et_2O = 4:1:1); i.r. (KBr, cm^{-1}) 3436 (OH), 1611, 1516 (C=C), 1258, 1235 (=C–O–); ^{1}H n.m.r. (90 MHz, DMSO-d_6) δ 9.46 (*br*, 2 H, –OH), 7.36–7.16 (14 H, C_6H_5 and C_6H_4 *meta* to –OH), 6.67 (*d*, $J = 8.6$ Hz, 4 H, C_6H_4 *ortho* to –OH), 4.59 (*s*, 5 H, C_5H_5).

10a: yield, 31%; $MP_1 = 237$°C, $MP_2 = 137$°C; $R_f = 0.24$ (benzene–*n*- hexane–Et_2O = 4:1:1); i.r. (KBr, cm^{-1}) 3443 (OH), 1611, 1514 (C=C), 1258, 1221 (=C–O–); ^{1}H n.m.r. (90 MHz, DMSO-d_6) δ 9.46 (*br*, 2 H, –OH), 7.56–7.18 (14 H, C_6H_5 and C_6H_4 *meta* to –OH), 6.65 (*d*, $J = 8.4$ Hz, 4 H, C_6H_4 *ortho* to –OH), 4.59 (*s*, 5 H, C_5H_5).

9b: yield, 32%; $MP_1 = 156$°C, $MP_2 = 69$°C; $R_f = 0.70$ (benzene–*n*- hexane–Et_2O = 4:1:1); i.r. (KBr, cm^{-1}) 3422 (OH), 2930, 2859 (C–H), 1607, 1514 (C=C), 1242 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.40–7.20 (8 H, C_6H_4 *meta* to –OH and –OR), 6.71 (*d*, $J = 8.8$ Hz, 8 H, C_6H_4 *ortho* to –OR and –OH), 4.90 (*s*, 2 H, –OH), 4.57 (*s*, 5 H, C_5H_5), 3.95 (*t*, $J = 6.0$ Hz, 4 H, $-OCH_2-$), 1.79–1.37 (16 H, –CH2–), 0.88 (*br*, 6 H, $-CH_3$).

10b: yield, 38%; $MP_1 = 104$°C, $MP_2 = 50$°C; $R_f = 0.32$ (benzene–*n*- hexane–Et_2O = 4:1:1); i.r. (KBr, cm^{-1}) 3418 (OH), 2930, 2859 (C–H), 1607, 1514 (C=C), 1242 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.31–7.17 (8 H, C_6H_4 *meta* to –OH and –OR), 6.68 (*d*, $J = 8.4$ Hz, 8 H, C_6H_4 *ortho* to –OR and –OH), 5.32 (*s*, 2 H, –OH), 4.57 (*s*, 5 H, C_5H_5), 3.95 (*t*, $J = 6.0$ Hz, 4 H, $-OCH_2-$ 1.79–1.37 (16 H, $-CH_2-$), 0.88 (*br*, 6 H, $-CH_3$).

9c: yield, 24%; $MP_1 = 163$°C, $MP_2 = 61$°C; $R_f = 0.79$ (benzene–*n*- hexane–Et_2O = 4:1:1); i.r. (KBr, cm^{-1}) 3418 (OH), 2925, 2855 (C–H), 16091) 1514 (C=C), 1242 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.36–7.17 (8 H, C_6H_4 *meta* to –OH and –OR), 6.67 (*d*, $J = 8.4$ Hz, 8 H, C_6H_4 *ortho* to –OR and –OH), 4.78 (*s*, 2 H, –OH), 4.57 (*s*, 5 H, C_5H_5), 3.95 (*t*, $J = 6.0$ Hz, 4 H, $-OCH_2-$) 1.79–1.27 (32 H, $-CH_2-$), 0.88 (*br*, 6 H, $-CH_3$).

10c: yield, 25%; $T_g = 44$°C; $R_f = 0.37$ (benzene–*n*-hexane–Et_2O 4:1:1); i.r. (KBr, cm^{-1}) 3418 (OH), 2924, 2855 (C–H), 1609, 1514 (C=C), 1242 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.36–7.21 (8 H, C_6H_4 *meta* to –OH and –OR), 6.67 (*d*, $J = 8.4$ Hz, 8 H, C_6H_4 *ortho* to –OR and –OH), 4.90 (*s*, 2 H, –OH), 4.57 (*s*, 5 H, C_5H_5), 3.95 (*t*, J = 6.0 Hz, 4 H, $-OCH_2-$), 1.79–1.27 (32 H, $-CH_2-$),0.88 (*br*, 6 H, $-CH_3$).

4.2.2. Model compounds **12**–**15** *(Typical procedure for* **15***)*

The bis-phenol **10d** (200 mg, 0.21 mmol), 1-bromotetradecane (178 mg, 0.64 mmol), K_2CO_3 (160 mg, 1.16 mmol), and DMF (1.0 ml) were placed into a test-tube equipped with a reflux condenser and a magnetic stirrer bar. After stirring at 110°C, for 3 h, the mixture was poured into 5% aq. $NaHCO_3$ (50 ml), stirred for 40 min, and extracted 4 times with *n*-hexane (20 ml). After reducing the volume of the organic phase under reduced pressure, **15** was isolated by the column chromatography (SiO_2, *n*-hexane: diethyl ether = 8:1) as soft yellow crystals (188 mg, 66%, MP = 46°C), i.r. (KBr, cm^{-1}) 2922, 2853 (C–H), 1607, 1514 (C=C), 1244 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.36 (*d*, $J = 8.8$ Hz, 8 H, C_6H_4 *meta* to –OR), 6.73 (*d*, J = 8.8 Hz, 8 H, C_6H_4 *ortho* to –OR), 4.57 (*s*, 5 H, C_5H_5), 3.95 (*t*, $J = 6.3$ Hz, 8 H, $-OCH_2-$), 1.79–1.27 (96 H, $-CH_2-$), 0.88 (*t*, $J = 5.8$ Hz, 12 H, $-CH_3$).

12: yield, 56%; MP = 76°C; i.r. (neat, cm^{-1}) 2924, 2853 (C–H), 1607, 1514 (C=C), 1244 (=C–O–); ^{1}H n.m.r. (400 MHz, $CDCl_3$) δ 7.43 (*d*, $J = 8.0$ Hz, 4 H, C_6H_5 2,6-positions), 7.38 (*d*, $J = 8.4$ Hz, 4 H, C_6H_4 *meta* to –OR), 7.19 (*br*, 6 H, C_6H_5 3,4,5-positions), 6.75 (*d*, $J = 8.8$ Hz, 4 H, C_6H_4 *ortho* to –OR), 4.59 (*s*, 5 H, C_5H_5), 3.95 (*t*, J = 6.4 Hz, 4 H, $-OCH_2-$), 1.79–1.27 (32 H, $-CH_2-$), 0.88 (*t*, J = 6.6 Hz, 6 H, $-CH_3$).

13: yield, 59%; MP = 128°C; i.r. (neat, cm^{-1}) 2930, 2859 (C–H), 1607, 1514 (C=C), 1242 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.36 (*d*, $J = 8.8$ Hz, 8 H, C_6H_4 *meta* to –OR), 6.73 (*d*, $J = 8.8$ Hz, 8 H, C_6H_4 *ortho* to –OR), 4.57 (*s*, 5 H, C_5H_5), 3.95 (*t*, $J = 6.3$ Hz, 8 H, $-OCH_2-$), 1.79–1.38 (32 H, $-CH_2-$), 0.92 (*t*, $J = 5.8$ Hz, 12 H, $-CH_3$).

14: yield, 68%; MP = 64°C; i.r. (neat, cm^{-1}) 2926, 2855 (C–H), 1607, 1514 (C=C), 1242 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.36 (*d*, $J = 8.8$ Hz, 8 H, C_6H_4 *meta* to –OR), 6.73 (*d*, $J = 8.8$ Hz, 8 H, C_6H_4 *ortho* to –OR), 4.57 (*s*, 5 H, C_5H_5), 3.95 (*t*, $J = 6.1$ Hz, 8 H, $-OCH_2-$), 1.79–1.27 (64 H, $-CH_2-$), 0.88 (*t*, $J = 6.0$ Hz, 12 H, $-CH_3$).

4.2.3. Polyethers **3** *and* **4** *(Typical procedure for* **3a-C$_{10}$***)*

The bisphenol **9a** (51 mg, 0.10 mmol), 1,10-dibromodecane (30 mg, 0.10 mmol), K_2CO_3 (70 mg, 0.52 mmol) and DMF (0.5 ml) were placed into a test-tube equipped with the reflux condenser and the magnetic stirrer bar. After stirring at 125°C for 20 h, the mixture was poured into 5% aq. $NaHCO_3$ (30 ml), stirred for 40 min, filtered, and washed successively with water and methanol, and then with *n*-hexane. The crude product thus obtained was dissolved in a minimal amount of CH_2Cl_2 and reprecipitated into *n*-hexane, followed by filtration and drying *in vacuo* to afford **3a-C$_{10}$** (52 mg, 80%) as a yellow powder. i.r. (KBr, cm^{-1}) 3057, 2926, 2853 (C–H), 1605, 1512 (C=C), 1242 (=C–O–); ^{1}H n.m.r. (400 MHz, $CDCl_3$) δ 7.43 (*d*, J = 8.0 Hz, 4 H, C_6H_5 2,6-positions), 7.38 (*d*, J = 8.4 Hz, 4 H, C_6H_4 *meta* to –OR), 7.19 (*br*, 6 H, C_6H_5 3,4,5 -positions), 6.76 (*d*, J = 8.4 Hz, 4 H, C_6H_4 *ortho* to –OR), 4.60 (*s*, 5 H, C_5H_5), 3.95 (*br*, 4 H, $-OCH_2-$), 1.79–1.26 (16 H, $-CH_2-$).

4a-C$_{10}$: yield, 68%; i.r. (KBr, cm^{-1}) 3057, 2928, 2855 (C–H), 1607, 1508 (C=C 1244 (=C–O–); ^{1}H n.m.r. (400 MHz, $CDCl_3$) δ 7.45 (*m*, 4 H, C_6H_5 2,6-positions), 7.36 (*d*, J = 8.4 Hz, 4 H, C_6H_4 *meta* to –OR), 7.20 (*m*, 6 H, C_6H_5 3,4,5-positions), 6.75 (*d*, J = 8.8 Hz, 4 H, C_6H_4 *ortho* to –OR), 4.60 (*s*, 5 H, C_5H_5), 3.95 (*br*, 4 H, $-OCH_2-$), 1.79–1.26 (16 H, $-CH_2-$).

3a-C$_6$: yield, 88%; i.r. (KBr, cm^{-1}) 3057, 2936, 2863 (C–H), 1605, 1512 (C=C 1242 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.46–7.19 (14 H, C_6H_5, C_6H_4 *meta* to –OR), 6.75 (*d*, J = 8.6 Hz, 4 H, C_6H_4 *ortho* to –OR), 4.60 (*s*, 5 H, C_5H_5), 3.96 (*t*, J = 6.0 Hz, 4 H, $-OCH_2-$), 1.79–1.36 (8 H, $-CH_2-$).

4a-C$_6$: yield, 62%; i.r. (KBr, cm^{-1}) 3057, 2932, 2861 (C–H), 16079 1508 (C=C), 1242 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.40–7.20 (14 H, C_6H_5, C_6H_4 *meta* to –OR), 6.75 (*d*, J = 8.8 Hz, 4 H, C_6H_4 *ortho* to –OR), 4.60 (*s*, 5 H, C_5H_5), 3.95 (*br*, 4 H, $-OCH_2-$), 1.79–1.36 (8 H, $-CH_2-$).

3d-C$_6$: yield, 87%; i.r. (neat, cm^{-1}) 2924, 2855 (C–H), 1607, 1514 (C=C), 1242 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.36 (*d*, J = 9.0 Hz, 8 H, C_6H_4 *meta* to –OR), 6.74 (*d*, J = 8.6 Hz, 8 H, C_6H_4 *ortho* to –OR), 4.57 (*s*, 5 H, C_5H_5), 3.95 (*t*, J = 6.3 Hz, 8 H, $-OCH_2-$), 1.78–1.27 (56 H, $-CH_2-$), 0.88 (*t*, J = 5.6 Hz, 6 H, $-CH_3$).

4d-C$_6$: yield, 87%; i.r. (neat, cm^{-1}) 2924, 28S5 (C–H), 1607, 1514 (C=C), 1244 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.34 (*d*, J = 7.2 Hz, 8 H, C_6H_4 *meta* to –OR), 6.73 (*d*, J = 8.0 Hz, 8 H, C_6H_4 *ortho* to –OR), 4.56 (*s*, 5 H, C_5H_5), 3.94 (*br*, 8 H, $-OCH_2-$), 1.72–1.27 (56 H, $-CH_2-$), 0.88 (*t*, J = 5.6 Hz, 6 H, $-CH_3$).

3d-C$_9$: yield, 77%; i.r. (KBr, cm^{-1}) 2924, 2853 (C–H), 1607, 1514 (C=C 1242 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.35 (*d*, J = 8.8 Hz, 8 H, C_6H_4 *meta* to –OR), 6.74 (*d*, J = 8.6 Hz, 8 H, C_6H_4 *ortho* to –OR), 4.57 (*s*, 5 H, C_5H_5), 3.95 (*br*, 8 H, $-OCH_2-$), 1.78–1.27 (62 H, $-CH_2-$), 0.88 (*t*, J = 5.6 Hz, 6 H, $-CH_3$).

4d-C$_9$: yield, 70%; i.r. (KBr, cm^{-1}) 2924, 2853 (C–H), 1607, 1514 (C=C), 1242 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.35 (*d*, J = 8.8 Hz, 8 H, C_6H_4 *meta* to –OR), 6.74 (*d*, J = 8.4 Hz, 8 H, C_6H_4 *ortho* to –OR), 4.57 (*s*, 5 H, C_5H_5), 3.95 (*br*, 8 H, $-OCH_2-$), 1.74–1.27 (62 H, $-CH_2-$), 0.88 (*br*, 6 H, $-CH_3$).

3d-C$_{10}$: yield, 87%; i.r. (KBr, cm^{-1}) 2924, 2853 (C–H), 1607, 1514 (C=C), 1242 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.35 (*d*, J = 8.6 Hz, 8 H, C_6H_4 *meta* to –OR), 6.74 (*d*, J = 8.6 Hz, 8 H, C_6H_4 *ortho* to –OR), 4.57 (*s*, 5 H, C_5H_5), 3.95 (*br*, 8 H, $-OCH_2-$), 1.78–1.27 (64 H, $-CH_2-$), 0.88 (*br*, 6 H, $-CH_3$).

4d-C$_{10}$: yield, 80%; i.r. (KBr, cm^{-1}) 2924, 2855 (C–H), 1607, 1514 (C=C), 1244 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.35 (*d*, J = 8.8 Hz, 8 H, C_6H_4 *meta* to –OR), 6.74 (*d*, J = 8.8 Hz, 8 H, C_6H_4 *ortho* to –OR), 4.57 (*s*, 5 H, C_5H_5), 3.95 (*br*, 8 H, $-OCH_2-$), 1.74–1.27 (64 H, $-CH_2-$), 0.88 (*br*, 6 H, $-CH_3$).

4.2.4. Polyesters **5**–**8** *(Typical procedure for* **5d-C$_4$***)*

Solutions of triethylbenzylammonium chloride (0.2 g, 0.88 mmol) and NaOH (1.0 g, 25 mmol) in water (25 ml) (Solution I) and **9d** (50 mg, 0.053 mmol) in 1,4-dioxane (0.5 ml) (Solution II) were prepared in separate vessels. An aliquot of Solution I (1.0 ml) was added to Solution II, and the resulting emulsion was stirred at room temperature for several minutes. After turning to a homogeneous brown solution, a solution of adipoyl chloride (10 mg, 0.053 mmol) in dichloromethane (0.80 ml) was added in one portion. The heterogeneous reaction mixture was stirred vigorously for 20 min and was poured into methanol (50 ml). The precipitate was filtered off, washed repeatedly with water, and then with methanol, and dried *in vacuo* to afford **5d-C$_4$** (39 mg, 70%) as a yellow powder. i.r. (KBr, cm^{-1}) 2924, 2853 (C–H), 1759 (COO), 1607, 1512 (C=C), 1244 (=C–O–); ^{1}H n.m.r. (400 MHz, $CDCl_3$) δ 7.41–7.33 (8 H, C_6H_4 *meta* to –OOC and –OR), 6.91 (*d*, J = 8.8 Hz. 4 H, C_6H_4 *ortho* to –OOC), 6.77 (*d*, J = 8.8 Hz. 4 H, C_6H_4 *ortho* to –OR), 4.59 (*s*, 5 H, C_5H_5), 3.95 (*t*, J = 6.6 Hz, 4 H, $-OCH_2-$), 2.65 (*br*, 4 H, OOC–CH_2), 1.90–1.26 (52 H, $-CH_2-$),0.88 (*t*, J = 6.8 Hz, 6 H, $-CH_3$).

6d-C$_4$: yield, 45%; i.r. (KBr, cm^{-1}) 2924, 2853 (C–H), 1759 (COO), 1607, 1512 (C=C), 1244 (=C–0–); ^{1}H n.m.r. (400 MHz, $CDCl_3$) δ 7.43 (*d*, J = 8.0 Hz, 4 H, C_6H_4 *meta* to –OOC), 7.33 (*d*, J = 8.4 Hz, 4 H, C_6H_4 *meta* to –OR), 6.93 (*d*, J = 8.4 Hz, 4 H, C_6H_4 *ortho* to –OOC), 6.74 (*d*, J = 8.0 Hz, 4 H, C_6H_4 *ortho* to –OR), 4.59 (*s*, 5 H, C_5H_5), 3.94 (*br*, 4 H, $-OCH_2-$), 2.65 (*br*, 4 H, OOC–CH_2), 1.90–1.26 (52 H, $-CH_2-$), 0.88 (*t*, J = 6.0 Hz, 6 H, $-CH_3$).

5d-C$_7$: yield, 62%; i.r. (KBr, cm^{-1}) 2924, 2853 (C–H), 1759 (COO), 1607, 1512 (C=C), 1244 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.36 (*br*, 8 H, C_6H_4 *meta* to –OOC and –OR), 6.91–6.75 (8 H, C_6H_4 *ortho* to –OOC and –OR), 4.58 (*s*, 5 H, C_5H_5), 3.94 (*br*, 4 H, $-OCH_2-$), 2.57 (*br*, 4 H, OOC–CH_2), 1.95–1.27 (58 H, $-CH_2-$), 0.88 (*br*, 6 H, $-CH_3$).

6d-C$_7$: yield, 45%; i.r. (KBr, cm^{-1}) 2924, 2853 (C–H), 1759 (COO), 1607, 1512 (C=C), 1244 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.28 (*br*, 8 H, C_6H_4 *meta* to –OOC and –OR), 6.93–6.70 (8 H, C_6H_4 *ortho* to –OOC and –OR), 4.57 (*s*, 5 H, C_5H_5), 3.88 (*br*, 4 H, –OCH_2–), 2.51 (*br*, 4 H, OOC–CH_2), 1.80–1.26 (58 H, –CH_2–),0.88 (*br*, 6 H, –CH_3).

5d-C$_8$: yield, 32%; i.r. (KBr, cm^{-1}) 2924, 2855 (C–H), 1759 (COO), 1607, 1512 (C=C), 1244 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.34 (*br*, 8 H, C_6H_4 *meta* to –OOC and –OR), 6.95–6.70 (8 H, C_6H_4 *ortho* to –OOC and –OR), 4.58 (*s*, 5 H, C_5H_5), 3.94 (*br*, 4 H, –OCH_2–), 2.55 (*br*, 4 H, OOC–CH_2), 1.95–1.27 (60 H, –CH_2–), 0.88 (*br*, 6 H, –CH_3).

6d-C$_8$: yield, 59%; i.r. (KBr, cm^{-1}) 2924, 2853 (C–H), 1759 (COO), 1607, 1512 (C=C) 1244 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 7.43–7.29 (8 H, C_6H_4 *meta* to –OOC and –OR), 6.95–6.69 (8 H, C_6H_4 *ortho* to –OOC and –OR), 4.58 (*s*, 5 H, C_5H_5), 3.94 (*br*, 4 H, –OCH_2–), 2.57 (*br*, 4 H, OOC–CH_2–), 1.71–1.26 (60 H, –CH_2–),0.88 (*br*, 6 H, –CH_3).

7a-Biph: yield, 77%; i.r. (KBr, cm^{-1}) 3057 (C–H), 1736 (COO), 1605, 1505 (C=C), 1260 (=C–O–); ^{1}H n.m.r. spectrum was not registered because of insufficient solubility of this polymer in available n.m.r. solvents. An authenticity of **7a-Biph** was confirmed by its i.r. spectrum, which was nearly identical to that of **8a-Biph**. See also Fig. 4 for g.p.c. traces.

8a-Biph: yield, 67%; i.r. (KBr, cm^{-1}) 3055 (C–H), 1738 (COO), 1605, 1508 (C=C), 1260 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 8.34 (*d*, J = 7.9 Hz, 4 H, C_6H_4 from Biph), 8.17 (*d*, J = 8.5 Hz, C_6H_4 from Biph, end group), 7.81 (*d*, J = 7.9 Hz, C_6H_4 from Biph), 7.68–7.40 (8 H, C_6H_4 *meta* to –OOC and C_6H_5, 2,6-positions), 7.28–7.08 (10 H, C_6H_4 *ortho* to –OOC and C_6H_5, 3,4,5-positions), 4.68 (*s*, 5 H, C_5H_5), 4.63 (shoulder, C_5H_5, end group).

7b-Biph: yield, 75%; i.r. (KBr, cm^{-1}) 2928, 2859 (C–H), 1738 (COO), 1607, 1512 (C=C), 1244 (=C–O–); ^{1}H n.m.r. (400 MHz, $CDCl_3$) δ 8.33 (*d*, J = 7.6 Hz, 4 H, C_6H_4 from Biph), 8.15 (*d*, J = 7.9 Hz, 0.67 H, C_6H_4 from Biph, end group), 7.82 (*d*, J = 7.4 Hz, 4 H, C_6H_4 from Biph), 7.50 (*d*, J = 7.6 Hz, 4 H, C_6H_4 *meta* to –OOC), 7.44 (*d*, J = 8.4 Hz, 4 H, C_6H_4 *meta* to –OR), 7.09 (*d*, J = 8.0 Hz, 4 H, C_6H_4 *ortho* to –OOC), 6.82 (*d*, J = 8.8 Hz, 4 H, C_6H_4 *ortho* to –OR), 6.67 (*d*, J = 8.2 Hz, 0.64 H, C_6H_4 *ortho* to –OH, end group), 4.65 (*s*, 5 H, C_5H_5), 4.51 (*s*, 0.82 H, C_5H_5, end group), 3.99 (*t*, J = 5.8 Hz, 4 H, –OCH_2–), 1.81–1.36 (16 H, –CH_2–), 0.93 (*br*, 6 H, –CH_3).

8b-Biph: yield, 67%; i.r. (KBr, cm^{-1}) 2928, 2857 (C–H), 1738 (COO), 1607, 1512 (C=C), 1244 (=C–O–); ^{1}H n.m.r. (400 MHz, $CDCl_3$) δ 8.33 (*d*, J = 7.6 Hz, 4 H, C_6H_4 from Biph), 8.15 (*d*, J = 7.9 Hz, 0.53 H, C_6H_4 from Biph, end group), 7.82 (*d*, J = 7.6 Hz, 4 H, C_6H_4 from Biph), 7.55 (*d*, J = 8.4 Hz, 4 H, C_6H_4 *meta* to –OOC), 7.39 (*d*, J = 8.0 Hz, 4 H, C_6H_4 *meta* to –OR), 7.12 (*d*, J = 8.0 Hz, 4 H C_6H_4 *ortho* to –OOC), 6.78 (*d*, J = 8.0 Hz, C_6H_4 *ortho* to –OR), 4.64 (*s*, 5 H, C_5H_5), 4.51 (*s*, 0.66 H, C_5H_5, end group), 3.97 (*t*, J = 5.2 Hz, 4 H, –OCH_2–), 1.81–1.36 (16 H, –CH_2–), 0.93 (*br*, 6 H, –CH_3).

7c-Biph: yield, 77%; i.r. (KBr, cm^{-1}) 2924, 2855 (C–H), 1738 (COO), 1607, 1512 (C=C), 1246 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 8.33 (*d*, J = 7.3 Hz, 4 H, C_6H_4 from Biph), 7.81 (*d*, J = 8.4 Hz, 4 H, C_6H_4 from Biph), 7.55–7.34 (8 H, C_6H_4 *meta* to –OOC and –OR), 7.09 (*d*, J = 7.9 Hz, 4 H C_6H_4 *ortho* to –OOC), 6.81 (*d*, J = 8.9 Hz, C_6H_4 *ortho* to –OR), 4.65 (*s*, 5 H, C_5H_5), 4.61 (shoulder, C_5H_5, end group), 3.98 (*t*, J = 6.0 Hz, 4 H, –OCH_2–), 1.74–1.29 (32 H, –CH_2–), 0.89 (*t*, J = 5.5 Hz, 6 H, –CH_3).

8c-Biph: yield, 51%; i.r. (KBr, cm^{-1}) 2924, 2855 (C–H), 1738 (COO), 1607, 1512 (C=C), 1244 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 8.34 (*d*, J = 8.2 Hz, 4 H, C_6H_4 from Biph), 7.81 (*d*, J = 8.8 Hz, 4 H, C_6H_4 from Biph), 7.60–7.34 (8 H, C_6H_4 *meta* to –OOC and –OR), 7.11 (*d*, J = 8.6 Hz, 4 H C_6H_4 *ortho* to –OOC), 6.78 (*d*, J = 8.9 Hz, C_6H_4 *ortho* to –OR), 4.64 (*s*, 5 H, C_5H_5), 3.96 (*t*, J = 5.5 Hz, 4 H, –OCH_2–), 1.80–1.28 (32 H, –CH_2–), 0.88 (*t*, J = 6.0 Hz, 6 H, –CH_3).

7d-Biph: yield, 89%; i.r. (KBr, cm^{-1}) 2924, 2853 (C–H), 1738 (COO), 1607, 1512 (C=C), 1244 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 8.34 (*d*, J = 8.6 Hz, 4 H, C_6H_4 from Biph), 7.82 (*d*, J = 7.5 Hz, 4 H, C_6H_4 from Biph), 7.46 (*br*, 8 H, C_6H_4 *meta* to –OOC and –OR), 7.09 (*d*, J = 8.5 Hz, 4 H C_6H_4 *ortho* to –OOC), 6.81 (*d*, J = 8.6 Hz, C_6H_4 *ortho* to –OR), 4.65 (*s*, 5 H, C_5H_5), 4.61 (shoulder, C_5H_5, end group), 3.97 (*br*, 4 H, –OCH_2–), 1.75–1.27 (48 H, –CH_2–), 0.87 (*t*, J = 5.3 Hz, 6 H, –CH_3).

8d-Biph: yield, 79%; i.r. (KBr, cm^{-1}) 2924, 2853 (C–H), 1740 (COO), 1607, 1512 (C=C) 1246 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 8.34 (*d*, J = 8.2 Hz, 4 H, C_6H_4 from Biph), 7.80 (*d*, J = 8.2 Hz, 4 H, C_6H_4 from Biph), 7.66–7.35 (8 H, C_6H_4 *meta* to –OOC and –OR), 7.11 (*d*, J = 8.4 Hz, 4 H C_6H_4 *ortho* to –OOC), 6.78 (*d*, J = 8.4 Hz, C_6H_4 *ortho* to –OR), 4.64 (*s*, 5 H, C_5H_5), 3.96 (*t*, J = 5.0 Hz, 4 H, –OCH_2–), 1.84–1.26 (48 H, –CH_2–), 0.88 (*br*, 6 H, –CH_3).

7c-Phen: yield, 62%; i.r. (KBr, cm^{-1}) 2924, 2855 (C–H), 1742 (COO), 1607, 1512 (C=C) 1244 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 8.35 (*s*, 4 H, C_6H_4 from Phen), 8.24 (shoulder, C_6H_4 from Phen, end group), 7.55–7.40 (8 H, C_6H_4 *meta* to –OOC and –OR), 7.09 (*d*, J = 8.6 Hz, 4 H, C_6H_4 *ortho* to –OOC), 6.81 (*d*, J = 9.1 Hz, C_6H_4 *ortho* to –OR), 4.65 (*s*, 5 H, C_5H_5), 4.61 (shoulder, C_5H_5, end group), 3.98 (*t*, J = 5.3 Hz, 4 H, –OCH_2–), 1.81–1.29 (32 H, –CH_2–), 0.89 (*t*, J = 5.3 Hz, 6 H, –CH_3).

8c-Phen: yield, 66%; i.r. (KBr, cm^{-1}) 2926, 2855 (C–H), 1742 (COO), 1609, 1512 (C=C), 1244 (=C–O–); ^{1}H n.m.r. (90 MHz, $CDCl_3$) δ 8.36 (*s*, 4 H, C_6H_4 from Phen), 8.25–8.22 (shoulder, C_6H_4 from Phen, end group), 7.60–7.34 (8 H, C_6H_4 *meta* to –OOC and –OR), 7.12 (*d*, J = 8.4 Hz, 4 H, C_6H_4 *ortho* to –OOC), 6.78 (*d*, J = 8.6 Hz, 4 H, C_6H_4 *ortho* to –OR), 4.64 (*s*, 5 H, C_5H_5), 3.97 (*t*, J = 6.0 Hz, 4 H, –OCH_2–), 1.78–1.28 (32 H, –CH_2–), 0.88 (*br*, 6 H, –CH_3).

7d-Phen: yield, 69%; i.r. (KBr, cm^{-1}) 2924, 2853 (C–H), 1742 (COO), 1607, 1512 (C=C), 1244 (=C–O–); ^1H n.m.r. (90 MHz, $CDCl_3$) δ 8.35 (*s*, 4 H, C_6H_4 from Phen), 8.20 (shoulder, C_6H_4 from Phen, end group), 7.40 (*br*, 8 H, C_6H_4 *meta* to –OOC and –OR), 7.09 (*d*, $J = 8.2$ Hz, 4 H, C_6H_4 *ortho* to –OOC), 6.81 (*d*, $J = 8.2$ Hz, C_6H_4 *ortho* to –OR), 4.65 (*s*, 5 H, C_5H_5), 3.98 (*t*, $J = 5.8$ Hz, 4 H, $-OCH_2-$), 1.79–1.27 (48 H, $-CH_2-$), 0.88 (*t*, $J = 5.4$ Hz, 6 H, $-CH_3$).

8d-Phen: yield, 84%; i.r. (KBr, cm^{-1}) 2924, 2853 (C–H), 1742 (COO), 1607, 1512 (C=C), 1246 (=C–O–), 1200; ^1H n.m.r. (90 MHz, $CDCl_3$) δ 8.36 (*s*, 4 H, C_6H_4 from Phen), 8.25–8.22 (shoulder, C_6H_4 from Phen, end group), 7.60–7.34 (8 H, C_6H_4 *meta* to –OOC and –OR), 7.12 (*d*, $J =$ 8.6 Hz, 4 H C_6H_4 *ortho* to –OOC), 6.78 (*d*, $J = 8.4$ Hz, C_6H_4 *ortho* to –OR), 4.64 (*s*, 5 H, C_5H_5), 3.98 (*t*, $J =$ 5.0 Hz, 4 H, $-OCH_2-$), 1.79–1.27 (48 H, $-CH_2-$), 0.88 (*t*, $J = 5.4$ Hz, 6 H, $-CH_3$).

7c-Naph: yield, 48%; i.r. (KBr, cm^{-1}) 2924, 2855 (C–H), 1738 (COO), 1607, 1512 (C=C), 1246 (=C–O–); ^1H n.m.r. (90 MHz, $CDCl_3$) δ 8.87 (*s*, 2 H, Naph, 1,5-positions), 8.23 (*br*, 4 H, Naph, 3,4,7,8-positions), 7.47 (*br*, 8 H, C_6H_4 *meta* to –OOC and –OR), 7.17 (*br*, 4 H C_6H_4 *ortho* to –OOC), 6.80 (*br*, C_6H_4 *ortho* to –OR), 4.66 (*s*, 5 H, C_5H_5), 3.99 (*br*, 4 H, $-OCH_2-$), 1.81–1.29 (32 H, $-CH_2-$),0.89 (*br*, 6 H, $-CH_3$).

8c-Naph: yield, 51%; i.r. (KBr, cm^{-1}) 2926, 2855 (C–H), 1738 (COO), 1607, 1512 (C=C), 1246 (=C–O–); ^1H n.m.r. (90 MHz, $CDCl_3$) δ 8.81 (*br*, 2 H, Naph, 1,5-positions), 8.11 (*br*, 4 H, Naph, 3,4,7,8-positions), 7.45–7.15 (12 H, C_6H_4 *meta* to –OOC and –OR, and *ortho* to –OOC), 6.75 (*br*, 4 H, C_6H_4 *ortho* to –OR), 4.64 (*s*, 5 H, C_5H_5), 3.96 (*br*, 4 H, $-OCH_2-$), 1.71–1.27 (32 H, $-CH_2-$), 0.88 (*br*, 6 H, $-CH_3$).

7d-Naph: yield, 77%; i.r. (KBr, cm^{-1}) 2924, 2853 (C–H), 1738 (COO), 1607, 1512 (C=C), 1246 (=C–O–); ^1H n.m.r. (90 MHz, $CDCl_3$) δ 8.84 (*s*, 2 H, Naph 1,5-positions), 8.35–8.19 (4 H, Naph 3,4,7,8-positions), 7.42 (*br*, 8 H, C_6H_4 *meta* to –OOC and –OR), 7.13 (*d*, $J = 8.2$ Hz, 4 H, C_6H_4 *ortho* to –OOC), 6.83 (*d*, $J = 8.4$ Hz, C_6H_4 *ortho* to –OR), 4.67 (*s*, 5 H, C_5H_5), 4.62 (shoulder, C_5H_5, end group), 3.99 (*br*, 4 H, $-OCH_2-$), 1.79–1.27 (48 H, $-CH_2-$ 0.87 (*t*, $J = 5.8$ Hz, 6 H, $-CH_3$).

8d-Naph: yield, 77%; i.r. (KBr, cm^{-1}) 2924, 2853 (C–H), 1738 (COO), 1609, 1512 (C=C), 1246 (=C–O–); ^1H n.m.r. (90 MHz, $CDCl_3$) δ 8.83 (*s*, 2 H, Naph 1,5-positions), 8.35–8.19 (4 H, Naph 3,4,7,8-positions), 7.60–7.33 (8 H, C_6H_4 *meta* to –OOC and –OR), 7.10 (*br*, 4 H, C_6H_4 *ortho* to –OOC), 6.78 (*br*, C_6H_4 *ortho* to –OR), 4.67 (*s*, 5 H, C_5H_5), 3.97 (*br*, 4 H, $-OCH_2-$), 1.79–1.27 (48 H, $-CH_2-$), 0.87 (*br*, 6 H, $-CH_3$).

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References

[1] Rozhanskii IL, Tomita I, Endo T. Macromolecules 1997;30:1222.
[2] Allcock HR. Adv Mater 1994;6:106.
[3] Biswas M, Mukherjee A. Adv Polym Sci 1994;115:89.
[4] Oriol L, Serrano JL. Adv Mater 1995;7:348.
[5] Manners I. Angew Chem Int Ed Engl 1996;35:1603.
[6] Tomita L, Nishio A, Igarashi T, Endo T. Polym Bull 1993;30:179.
[7] Tomita L, Nishio A, Endo T. Macromolecules 1994;27:7009.
[8] Rozhanskii IL, Tomita I, Endo T. Macromolecules 1996;29:1934.
[9] Rozhanskii IL, Tomita I, Endo T. Chem Lett 1997;0:477.
[10] Altmann M, Bunz UHF. Macromol Rapid Comm 1994;15:785.
[11] Altmann M, Bunz UHF. Angew Chem Int Ed Engl 1995;34:569.
[12] Lee JC, Nishio A, Tomita I, Endo T. Macromolecules 1997;30:5205.
[13] Rausch MD, Westover GF, Mintz E, Reisner GM, Bernal L, Clearfield A, Troup JM. Inorg Chem 1979;18:2605.
[14] Rozhanskii IL, Tomita I, Endo T. Liq Crystallogr 1996;21:631.
[15] Demus D. Liq Crystallogr 1989;5:75. and references therein.
[16] Ballauff M. Angew Chem Int Ed Engl 1989;28:253.
[17] Yarnazaki H, Wakatsuki Y. Inorg Synth 1989;26:195.