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Synthesis of side chain liquid-crystalline polysiloxane containing *trans*-cyclohexane-based mesogenic side groups

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The synthesis and characterization of nine new side chain liquid-crystalline polysiloxanes containing one cyclohexyl ring and another 2–4 aromatic rings in their mesogenic side groups are described. All synthesized polymers displayed nematic mesomorphism. Most of the polymers showed a very wide mesomorphic temperature range. The mesogenic core length has profound influence on the phase transitions of the polymers. The mesomorphic temperature range increased with increasing mesogenic core length.

1. Introduction

Side chain liquid-crystalline polymers are of both theoretical and practical interest because they combine the anisotropic properties of liquid crystals with polymeric properties and have the potential of being used for some electro-optical applications [1–3]. Recently, high temperature mesomorphic polysiloxane solvents have demonstrated an excellent application as high resolution gas chromatographic (GC) stationary phases [4–9]. Basically, there are two important requirements for a side chain liquid-crystalline polymer to be used as a GC stationary phase with better column efficiency and separation properties. Firstly, the side chain polymer should have a very wide mesophase range and second, it should exhibit high thermal stability. To date, as far as homopolymer nematic GC solvents are concerned, polysiloxane containing 4-propanyloxybenzoyl-4′-methoxybiphenyl side groups, which gives a crystal–nematic transition at 91°C and a nematic–isotropic clearing point of 317°C, the broadest nematic range yet produced, has been found to be most useful [5].

Since 1973, when Demus *et al.* [10] reported the nematic cyclohexane carboxylate, several kinds of low molar mass liquid crystals containing a *trans*-cyclohexane ring have been synthesized [11–16]. Most of the 1,4-disubstituted cyclohexane derivatives showed lower melting points and wider mesophase ranges than those of their corresponding benzene derivatives [13–16]. The goal of this study is to present the synthesis and characterization of a series of side chain liquid-crystalline polysiloxanes containing a *trans*-cyclohexyl ring and 2–4 aromatic rings in the mesogenic side groups. The prepared polymers are expected to exhibit a very wide mesomorphic temperature range and have potential applications as GC stationary phases.

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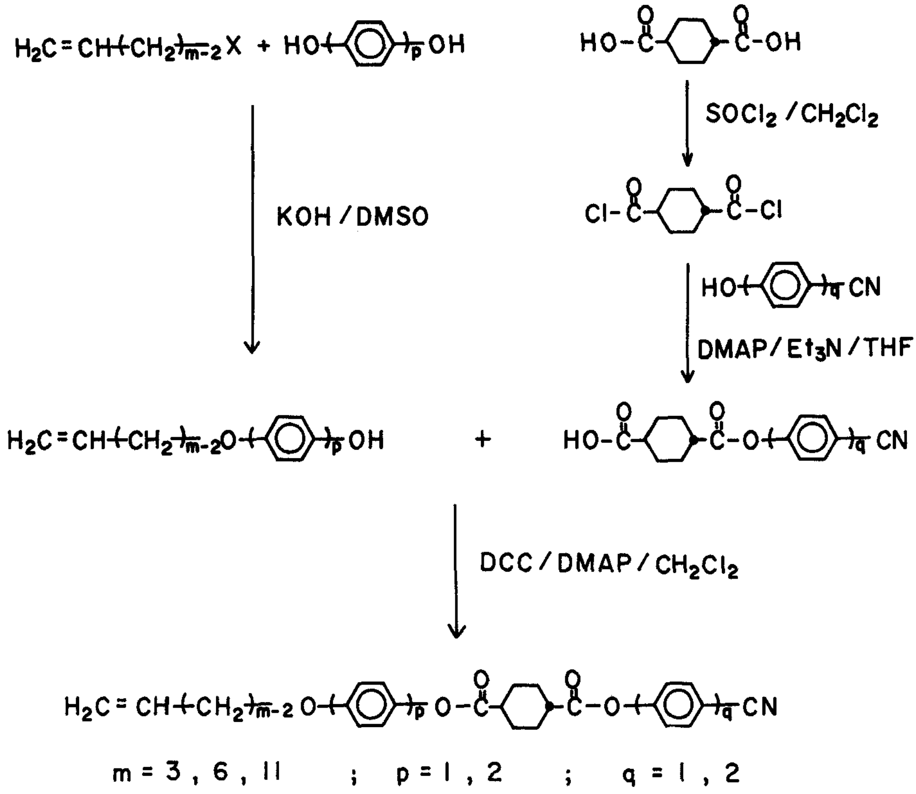
2. Synthesis

The synthesis of *trans*-cyclohexane-based monomers 1M–9M is outlined in scheme 1. Monomers were synthesized by etherification and esterification reactions. Therefore, most of the reactions were accomplished with high yields. The monomers were purified by column chromatography to achieve high purity, then their structure and purity were determined by high performance liquid chromatography and ^1H NMR spectroscopy. The synthetic route used to prepare the side chain liquid-crystalline polysiloxanes 1P–9P is outlined in scheme 2.

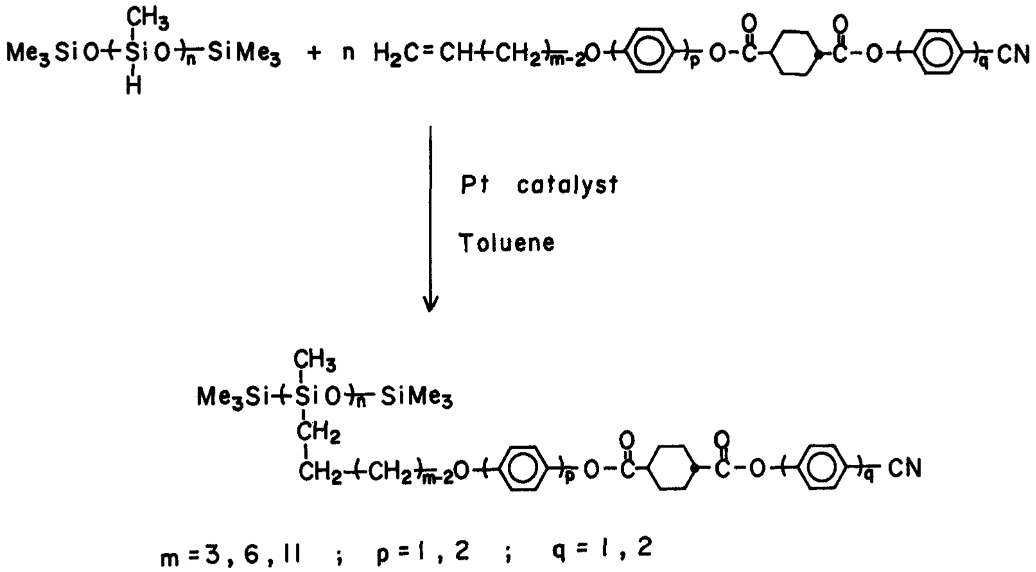
Synthetic details of the above reactions are described in Experimental.



Scheme 1. Synthesis of *trans*-cyclohexane-based monomers 1M–9M.

3. Results and discussion

The thermal transitions and their corresponding enthalpy changes of the monomers 1M–9M are summarized in table 1. All monomers exhibited a very wide nematic mesophase. Monomers 1M–3M whose mesogens possess two phenyl rings linked on both sides of the *trans*-cyclohexane ring through an ester linkage, contain different alkenyloxy end groups. The influence of the length of the alkenyloxy group on their phase transitions is illustrated by figure 1. Both the crystalline to nematic and nematic to isotropic phase transition temperatures are decreased by increasing the length of the alkenyloxy groups. The temperature ranges of the nematic mesophase of three monomers are larger than 87°C. Monomers 4M–6M containing a biphenyl, a phenyl



Scheme 2. Synthesis of side chain liquid-crystalline polysiloxanes 1P–9P.

Table 1. Phase transition and temperatures (°C) enthalpies in brackets of (kJ mol^{-1}) monomers 1M–9M.

Monomer	*m*‡	*p*	*q*	Phase transition data‡						
1M	3	1	1	C	116	(36·40)	N	230	(1·34)	I
2M	6	1	1	C	83	(32·73)	N	198	(1·05)	I
3M	11	1	1	C	86	(44·77)	N	173	(0·71)	I
4M	3	2	1	C	126	(21·21)	N	300	(dec.)	
5M	6	2	1	C	109	(13·89)	N	300	(dec.)	
6M	11	2	1	C	103	(17·87)	N	280	(0·88)	I
7M	11	0	2	C	63	(35·56)	N	140	(0·67)	I
8M	11	1	2	C	96	(40·12)	N	288	(0·84)	I
9M	11	2	2	C	168	(45·61)	N	300	(dec.)	

† *m*, *p*, *q*, according to scheme 1.

‡ C: crystalline; N: nematic: I: isotropic, dec.: decomposed.

and a cyclohexyl ring in their mesogens, respectively have different terminal alkenyloxy groups. The effect of the length of the alkenyloxy groups on their phase transitions show a very similar tendency as those of monomers 1M–3M. However, the temperature ranges of their nematic phase are wider than 174°C. This result should be due to their longer mesogenic core length. Monomer 6M presents a nematic to isotropic temperature at 280°C while both monomers 4M and 5M show a decomposition temperature at 300°C. The thermogravimetric thermogram of monomer 5M is shown in figure 2. Monomers 7M–9M containing the same undecenyloxy end groups have differences in their mesogenic core length. Their phase transitions reveal that both melting and isotropization temperatures increase dramatically as the mesogenic core

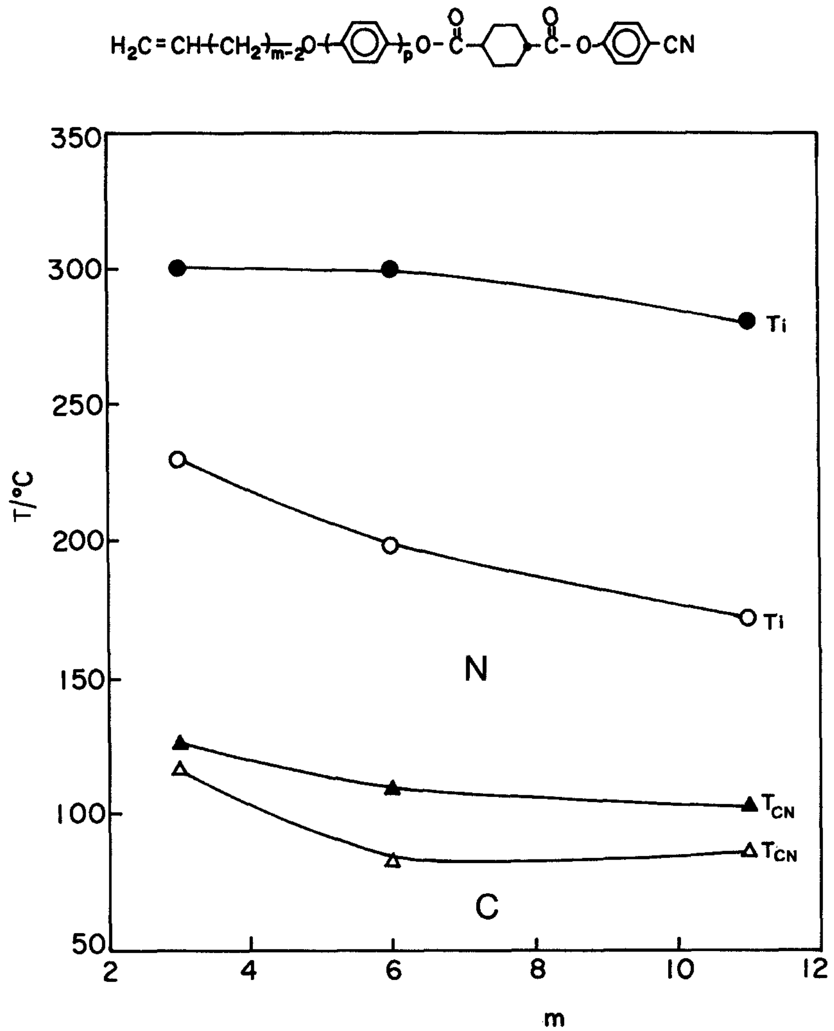


Figure 1. The effect of spacer length, *m*, on phase transition temperatures of monomers 1M–6M. △, ○ $p=1$, ▲, ● $p=2$.

length increases. Monomer 8M shows the widest nematic temperature range (192°C) among all synthesized monomers.

The thermal transitions and thermal transition enthalpy changes of all synthesized polymers 1P–9P are recorded in table 2. Figure 3 shows DSC thermograms of polymers 1P–3P which contain the same mesogenic side groups, but different spacers. Curve A belongs to DSC traces of polymers 1P. It reveals a glass transition temperature (T_g) at 24°C, followed by a nematic to isotropic transition at 275°C. Curves B and C are DSC traces of polymers 2P and 3P. Both polymers show a glass transition, a melting transition and an isotropization transition. As the spacer length increases, the glass transition temperature decreases, while the isotropization temperature first decreases and then increases. A longer spacer also enhances the tendency of the polymer to crystallize.

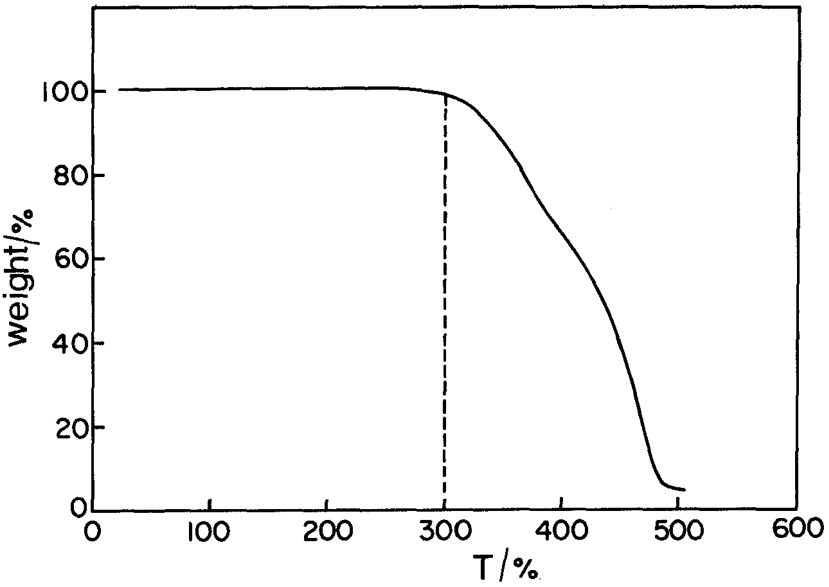


Figure 2. Thermogravimetric thermogram of monomer 5M.

Table 2. Phase transition temperatures (°C) and enthalpies in brackets of (kJ min^{-1}) polymers 1P–9P.

Polymer	m‡	p	q	Phase transition data									$\bar{M}$n × 10^{-3}§	$\bar{M}$w/$\bar{M}$n
1P	3	1	1	g	24	N	275	(1·51)	I				27·5	2·27
2P	6	1	1	g	10	C	62	(3·89)	N	238	(1·72)	I	30·4	2·03
3P	11	1	1	g	8	C	66	(5·61)	N	266	(3·52)	I	37·4	1·93
4P	3	2	1	g	25	N	300	(dec.)					24·9	2·32
5P	6	2	1	g	12	C	58	(25·02)	N	300	(dec.)		28·7	2·24
6P	11	2	1	g	11	C	87	(3·77)	N	300	(dec.)		30·1	1·97
7P	11	0	2	g	−11	C	41	(6·82)	N	219	(3·26)	I	35·4	2·18
8P	11	1	2	g	10	C	81	(4·69)	N	300	(dec.)		29·8	2·27
9P	11	2	2	g	17	C	81	(3·89)	N	300	(dec.)		25·2	2·32

† mru: mole repeated unit; g: glass; C: crystalline; N: nematic; I: isotropic; dec.: decomposed.
‡ *m*, *p*, *q*, according to scheme 2.
§ The molecular weight was determined by GPC.

In table 2, polymers 4P–6P show a very wide nematic mesophase. All of them decompose at about 300°C. Figure 4 presents the thermogravimetric thermogram of polymer 4P. A typical nematic texture displayed by 4P at 200°C is shown in figure 5. Polymers 7P–9P contain the same spacer, but different mesogenic cores. Both glass transition and melting transition temperatures increase with increasing mesogenic core length. Polymer 7P shows a transition from nematic to isotropic at 219°C while both polymers 8P and 9P exhibit a nematic phase until they decompose at 300°C.

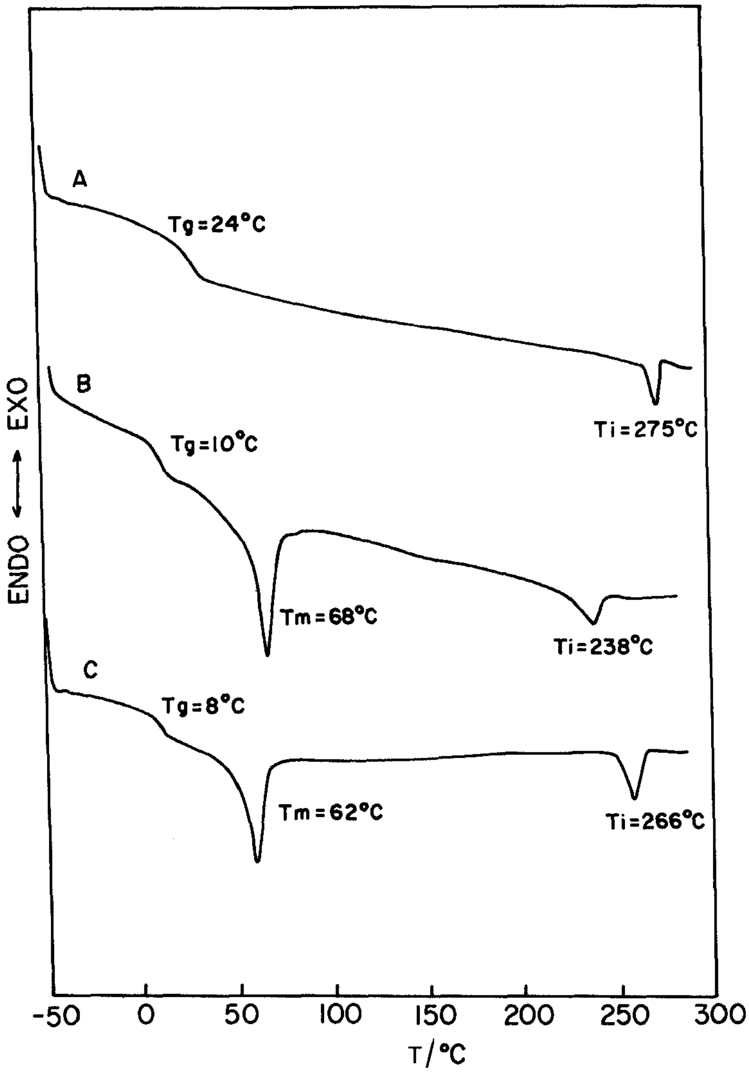


Figure 3. DSC thermograms of polymers: (A) 1P, (B) 2P and (C) 3P.

4. Conclusion

A series of side chain liquid-crystalline polysiloxanes containing one cyclohexane ring and 2–4 aromatic rings in their mesogenic side groups were prepared. All obtained momomers and polymers display only a nematic mesophase. An increase in the mesogenic core length leads to an enhancement of the thermal stability of the mesophase. Therefore, most of the polymers show a very wide mesomorphic temperature range. The polymers which display very low glass transition temperatures and very wide nematic mesomorphic ranges have potential applications as high resolution GC stationary phases.

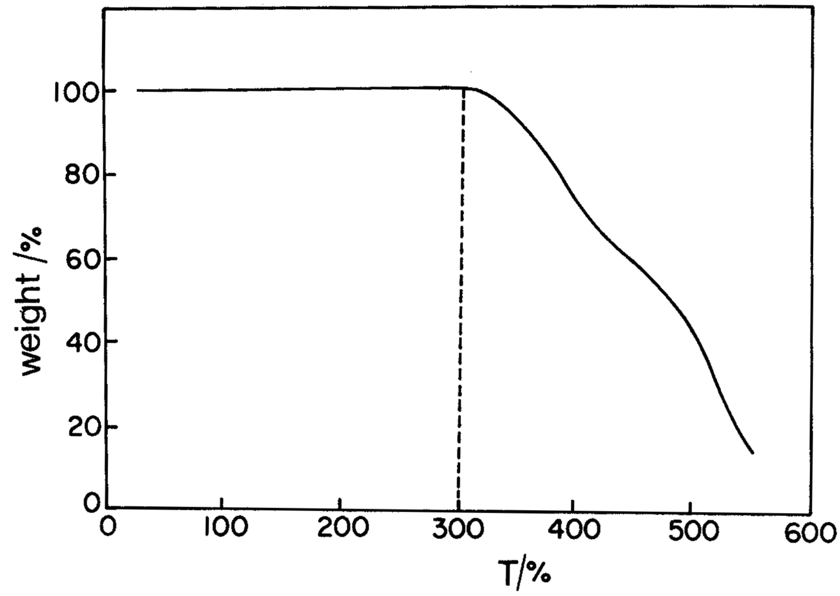


Figure 4. Thermogravimetric thermogram of polymer 4P.

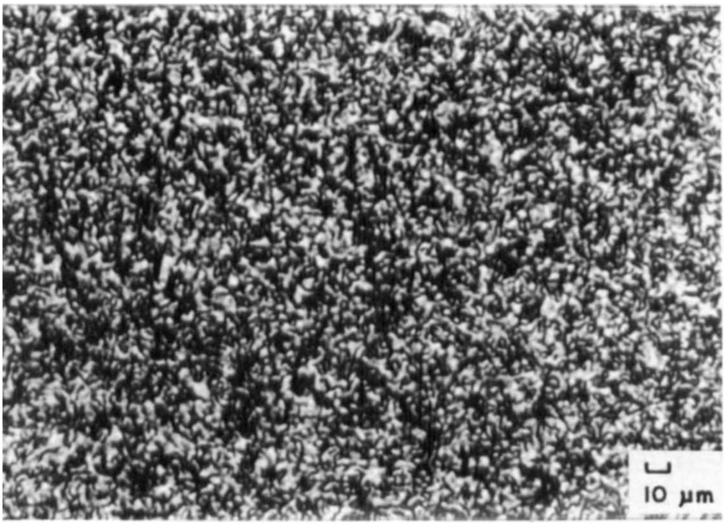


Figure 5. Optical polarizing micrograph displayed by polymer 4P: typical texture obtained at 200°.

5. Experimental

5.1. *Materials*

Poly(methylhydrogensiloxane) ($\bar{M}n = 4500$–5000) was obtained from Petrarch Systems, Inc. and was used as received. *Trans*-cyclohexanedicarboxylic acid and other reagents (from Merck) were used as received. Toluene used in the hydrosilylation reaction was first refluxed over sodium and then distilled under nitrogen.

5.2. *Measurements*

^1H NMR spectra were obtained with a Jeol JNM-FX100 spectrometer. All spectra were recorded in $CDCl_3$ with TMS as the internal standard unless otherwise noted. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a Viscotek 200 system equipped with a differential refractometer and a viscometer. A set of four Ultrastyragel linear columns was employed with tetrahydrofuran as solvent at a flow rate of 1 ml min^{-1}. The number and weight average molecular weights ($\bar{M}n$ and $\bar{M}w$, respectively) were determined relative to polystyrene standards. A DuPont 910 differential scanning calorimeter (DSC) equipped with a 9900 computer system was used to determine the thermal transitions that were read at the maximum of their endothermic or exothermic peaks. In all cases, heating and cooling rates were 10°C min^{-1}, unless otherwise specified. Glass transition temperatures (T_g) were read at the middle of the change in heat capacity. After the first heating scan, the sample was annealed at 10°C above the isotropization temperature for 5–10 min. Under these conditions, beginning with the second heating and cooling scans, all recorded DSC scans gave reproducible data. The transitions reported were read during the second or third heating scan and cooling scan unless otherwise specified. Thermogravimetry (TG) was measured by a DuPont 951 Thermogravimetric analyser. A Nikon Microphot-FX optical polarized microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used in observing thermal transitions and anisotropic textures.

5.3. *Synthesis of the monomers*

All of the monomers were synthesized by similar methods. A typical procedure is shown below with monomer 3M.

5.3.1. *4-Benzyloxyphenyl-10-undecenyl ether* I

A mixture of 4-benzyloxyphenol (12·0 g, 0·058 mol), potassium hydroxide (3·3 g, 0·058 mol) and dry dimethyl sulphoxide (150 ml) was heated at 65°C for several minutes. Then 10-undecene-1-chloride (10·0 g, 0·053 mol) was added dropwise and the temperature kept at 65°C for 18 h. The cooled reaction mixture was poured into water (500 ml). The raw product was filtered and washed with dilute potassium hydroxide, then recrystallized from ethanol. The yield of colourless crystals was 14·0 g (75 per cent). MS: 352 (M^+). ^1H NMR ($CDCl_3$, TMS) δ 1·21–2·27 (m, 16 H, $\leftarrow CH_2 \rightarrow_8$), 4·13 (t, 2 H, $-CH_2-\underline{CH_2}-O-$), 4·93 (m, 4 H, $\underline{H_2}C{=}CH-$ and $-O-CH_2-Ph$), 5·81 (m, 1 H, $H_2C{=}C\underline{H}-$), 6·82–7·85 ppm (m, 9 H, aromatic protons).

5.3.2. *4-Hydroxyphenyloxy-10-undecene* II

Sodium (2·1 g, 0·091 mol) was added rapidly but in small pieces, to a hot solution of 4-benzyloxyphenyl 10-undecenyl ether, I (5 g, 0·014 mol) in anhydrous *tert*-butanol (50 ml) [17]. After the sodium had all reacted, the cooled mixture was then poured into water (500 ml). The filtered solution was acidified with dilute hydrochloric acid. The resultant precipitate was filtered, washed with portions of water, and finally recrystallized from ethanol. The yield of colourless crystals was 3·27 g (88 per cent). MS: 262 (M^+). ^{1}H NMR ($CDCl_3$, TMS) δ 1·22–2·26 (m, 16 H, $(C\underline{H}_2)_8$), 4·14 (t, 2 H, $-C\underline{H}_2-O-$), 4·92 (m, 4H, $\underline{H}_2C{=}CH-$), 5·82 (m, 1 H, $H_2C{=}C\underline{H}-$), 6·80 ppm (s, 4 H, aromatic protons).

5.3.3. *4-Hydroxybiphenyloxy-10-undecene* III

The reaction was performed as described for compound I. The cooled mixture was poured into water. The filtered solution was acidified with dilute hydrochloric acid. The resultant precipitate was filtered, and washed with portions of water. The residual powder was purified by column chromatography on silica gel with 50 : 1 chloroform/tetrahydrofuran and subsequent recrystallization from ethanol gave a pure product (42 per cent). MS: 338 (M^+). ^{1}H NMR ($CDCl_3$, TMS) δ 1·21–2·28 (m, 16 H, $(C\underline{H}_2)_8$), (t, 2 H, $-CH_t-O-$), 4·95 (m, 4 H, $\underline{H}_2C{=}CH-$), 5·85 (m, 1 H, $H_2C{=}C\underline{H}-$), 6·91–7·78 ppm (4d, 8 H, aromatic protons).

5.3.4. *trans-Cyclohexanedicarboxylic acid 4-cyanophenyl ester* IV

trans-1,4-Cyclohexanedicarboxylic acid (5·0 g, 0·029 mol) was dissolved in anhydrous dichloromethane (30 ml). Then a solution of cyanophenyl (3·8 g, 0·032 mol), triethylamine (4·43 ml, 0·032 mol) and 4-(dimethylamino) pyridine (0·14 g, 0·0016 mol) and anhydrous dichloromethane (20 ml) was added dropwise cooled via an ice water bath. The resulting mixture was allowed to reach room temperature and stirred overnight. The mixture was acidified with dilute hydrochloric acid, poured into water and shaken with dichloromethane. The extracts were washed with water and then dried. The filtered solution was evaporated under reduced pressure and the residue purified by column chromatography on silica gel with 30 : 1 chlorform/tetrahydrofuran and subsequent recrystallization from ethanol. The yield of the pure acid 3·25 g (41 per cent). MS: 273 (M^+). ^{1}H NMR ($CDCl_3$, TMS) δ 1·51–2·73 (m, 10 H, cyclohexane protons), 7·25–7·84 ppm (2d, 4 H, aromatic protons).

5.3.5. *trans-Cylohexanedicarboxylic acid 4′-cyanophenyl undecene-4-phenyloxy diester* (monomer 3M)

4-Hydroxyphenyloxy-10-undecene, II, (2 g, 0·0076 mol), *trans*-cyclohexanedicarboxylic acid 4-cyanophenyl ester, IV (2·13 g, 0·0078 mol) and 4-(dimethylamino) pyridine (0·05 g, 0·00041 mol) were dissolved in anhydrous dichloromethane (30 ml). Dicyclohexylcarbodiimide (1·81 g, 0·0088 mol) was added and the solution was stirred at room temperature overnight. After filtration to remove precipitated material, the filtered solution was evaporated to dryness under reduced pressure. The residual dry powder was purified by column chromatography on silica gel with 50 : 1 toluene/tetrahydrofuran, and then recrystallized from ethanol. The yield of colourless crystals was 2·5 g (65 per cent). MS: 517 (M^+). ^{1}H NMR ($CDCl_3$, TMS) δ 1·21–2·72 (m, 26 H, cyclohexane protons and $(CH_2)_8$), 3·91 (t, 2 H, $-CH_2-O-$), 4·93 (m, 2 H, $\underline{H}_2C{=}CH-$), 5·81 (m, 1 H, $H_2C{=}C\underline{H}-$), 6·82–7·83 ppm (4d, 8 H, aromatic protons).

$C_{32}H_{39}O_5$: calculated C, 74·24 per cent; H, 7·59 per cent; N, 2·70 per cent; found C, 74·10 per cent; H, 7·58 per cent; N, 2·67 per cent.

5.4. *Synthesis of polysiloxanes*

A general synthetic procedure is described: 1·0 g (10 mol% excess versus the Si-H groups present in polysiloxane) of the olefinic derivative was dissolved in 100 ml of dry, freshly distilled toluene together with the proper amount of poly(methylhydrogensiloxane). The reaction mixture was heated to 110°C under nitrogen and then 100 μg of dicyclopentadienylplatinum (II) chloride catalyst was injected with a syringe as a methylene chloride solution (1 mg mL^{-1}). The reaction mixture was refluxed (110°C) under nitrogen for 24 h. After this reaction time, FT–IR analysis showed that hydrosilation reaction was complete. The polymers were separated and purified by several reprecipitations from tetrahydrofuran solution in methanol, and further purified by preparative GPC, and then dried under vaccum.

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