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Orientation effects in monodomain nematic liquid crystalline polysiloxane elastomers

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A series of monodomain liquid crystalline (LC) elastomers based on a polysiloxane were synthesised. These elastomers were prepared either with one or two cross-linking agents in the presence of a mechanical field. By using the real-time X-ray facility at the University of Reading (AXIS), we have shown that the nematic order parameter $\langle P_2 \rangle$ is dependent on both the extension λ value and the degree of cross-linking. We have also shown that the monodomain elastomers, exhibiting permanent alignment and $\langle P_2 \rangle$ values of about 0.5, can be prepared by using only one cross-linking agent making the synthesis of these monodomain LC elastomers much more simple and cost effective than that proposed by Küpfer.

Liquid crystalline polymers can be covalently cross-linked to form three dimensional networks, namely, LC elastomers. Since the synthesis of the first LC elastomer in 1981,[1] which was based on a polysiloxane backbone, a number of different types of elastomers have been reported. These have included elastomers containing polyacrylates and polymethacrylates[2–6] and work has been extended to slightly cross-linked main chain as well as combined main-chain–side-chain[3,7,8] materials. These networks are unique in their properties in that they exhibit rubber elasticity as well as properties associated with liquid crystals. Provided that the networks have a low cross-link density the motions of the chain segments are not impaired and the mesogenic moieties are still free to orientate. Only near to the cross-link points are the motions of the mesogens somewhat restricted. Due to cross-linking between chains, the translational diffusion of the polymer chains is prevented and therefore the elastomer exhibits shape retention. The field of LC elastomers has led to a number of ideas which combine the advantageous properties of LC low molecular mass and LC polymers as well as rubber elasticity and shape retention. Certain disadvantages of polymers, *e.g.* differing chain lengths leading to slight differences in physical properties amongst different polymer batches, are favourably lost on cross-linking. One of the major advantages of LC elastomers is the property of shape retention thereby allowing mesogenic alignment by mechanical deformation.[9,10]

The use of X-ray diffraction as a technique for studying and confirming phase types in LMMLC materials[11–14] and in LC polymers[15–20] has been well reviewed. X-Rays can also be used to define molecular ordering in samples and more quantitative studies such as the effect of temperature[21–23] or external fields, *e.g.* magnetic or mechanical,[24] on the orientational behaviour can also be carried out using this technique. The real-time X-ray equipment at the University of Reading (AXIS, area X-ray imaging system) allows *in situ* experiments on orientational behaviour in LC polymers, and of particular interest to this work, in LC elastomers, to be carried out and order parameters such as $\langle P_2 \rangle$ to be calculated.[19] X-Rays are scattered from the electrons within a molecule and therefore the scattering pattern reflects distribution of the regions of electron density. This method is restricted to the measurement of mesogenic anisotropy only and not to the polymer backbone anisotropy.

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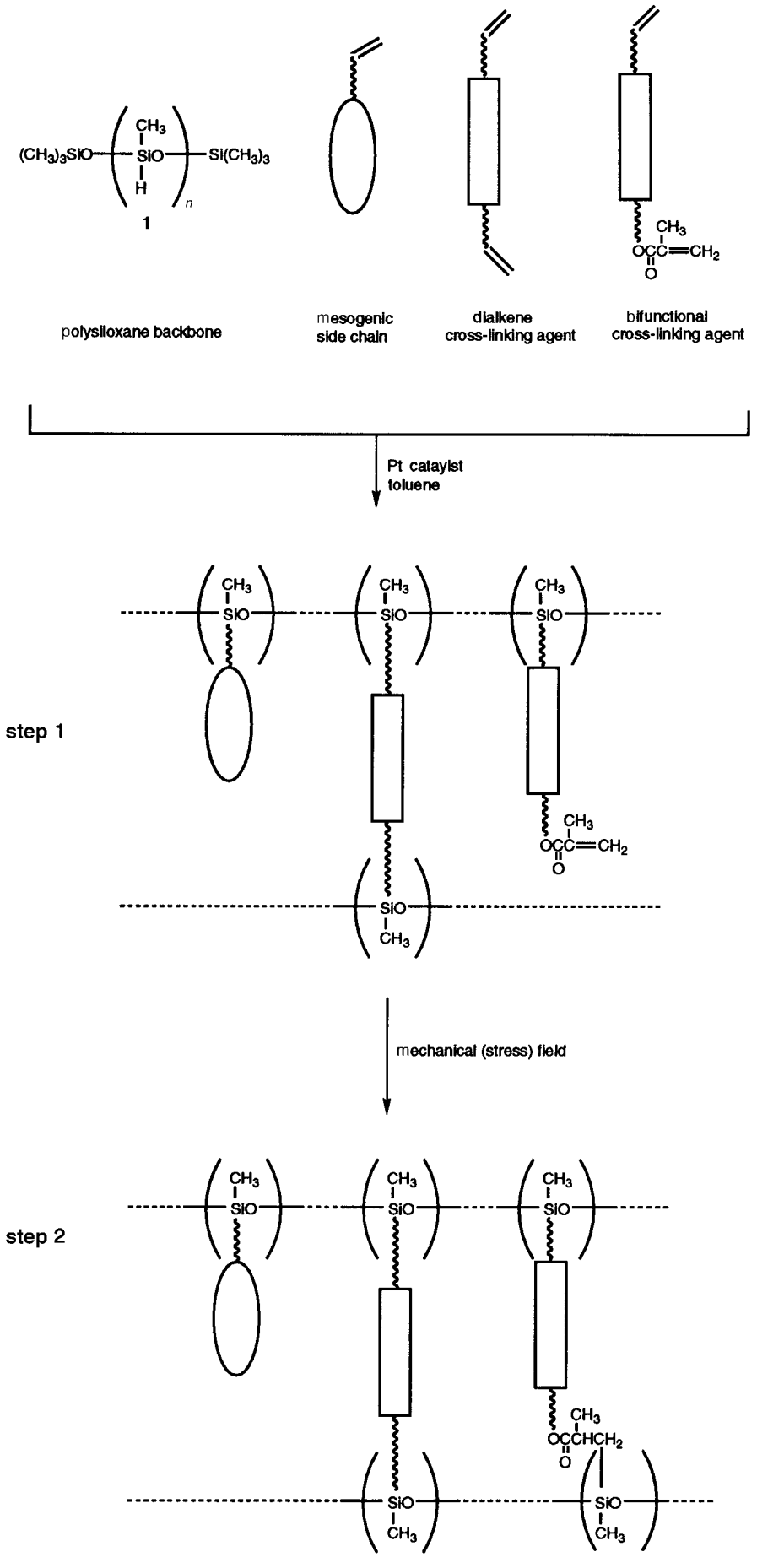
Results and Discussion

The first successful synthesis of a monodomain polysiloxane elastomer was achieved by Küpfer[25] in 1991 and a schematic representation of the route adopted by Küpfer is given in Scheme 1. The network was synthesised in two steps, with the second cross-linking step being carried out under the influence of a mechanical field. The different types of active sites on the two cross-linking agents gave rise to different rates of hydrosilylation of these active sites with the polysiloxane backbone. It was postulated that the alkene active site ($CH{=}CH_2$) would be of the order 100 times faster than that of the methacryloyloxy active site [$OCOC(CH_3){=}CH_2$] and therefore the formation of the monodomain could be carried out in two distinct steps. The first involves the formation of a polydomain elastomer involving the cross-linking agent containing the two alkene active sites. During this process, the second cross-linking agent would be attached to the polysiloxane backbone *via* the alkene active site only, leaving the methacryloyloxy active site untouched. The second cross-linking step involved only the methacryloyloxy active site (the bifunctional cross-linking agent), and because this was carried out under the influence of a mechanical (stress) field this will result in the formation of a monodomain elastomer.

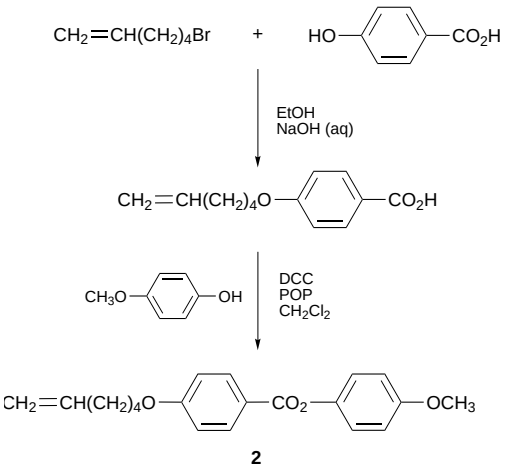
In our work presented in this paper we have used the real-time X-ray facility at the University of Reading to examine more closely the second cross-linking step in the route adopted by Küpfer *et al.* in the formation of monodomain polysiloxane elastomers. A number of elastomers were synthesised in which the structure of the mesogenic side chain was kept the same, but the number and structure of the cross-linking agents used to form the elastomer were varied. The synthesis of the cross-linking agents and the mesogenic side chain are given in Schemes 2–4. The formation of the monodomain polysiloxane elastomer involving both cross-linking agents are shown in Schemes 5 and 6 with step 2 in Scheme 5 being carried out under the influence of a mechanical (stress) field. The step shown in Scheme 6, which outlines the formation of the monodomains using only one cross-linking agent, involved initially the normal procedure for the formation of a polydomain elastomer, and then the elastomer was subjected to a mechanical (stress) field to manifest the monodomain elastomer.

Static X-ray diffraction

The X-ray diffraction pattern of an elastomer based on the mesogen **2** showed a diffuse outer ring characteristic of a


polysiloxane backbone
mesogenic side chain
dialkene cross-linking agent
bifunctional cross-linking agent
Pt catalyst toluene
step 1
mechanical (stress) field
step 2

Scheme 1



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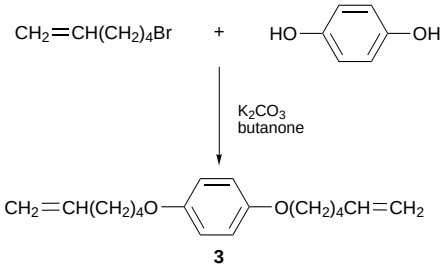
Scheme 2



3

Scheme 3

nematic phase. The corresponding polymer (g −0.4 N 95 I °C) was also nematic. In elastomeric samples of low cross-link density the state of the nematic phase remains unchanged on cross-linking.[1,5,26–28] All the elastomers presented in this paper exhibit a nematic phase at room temperature.

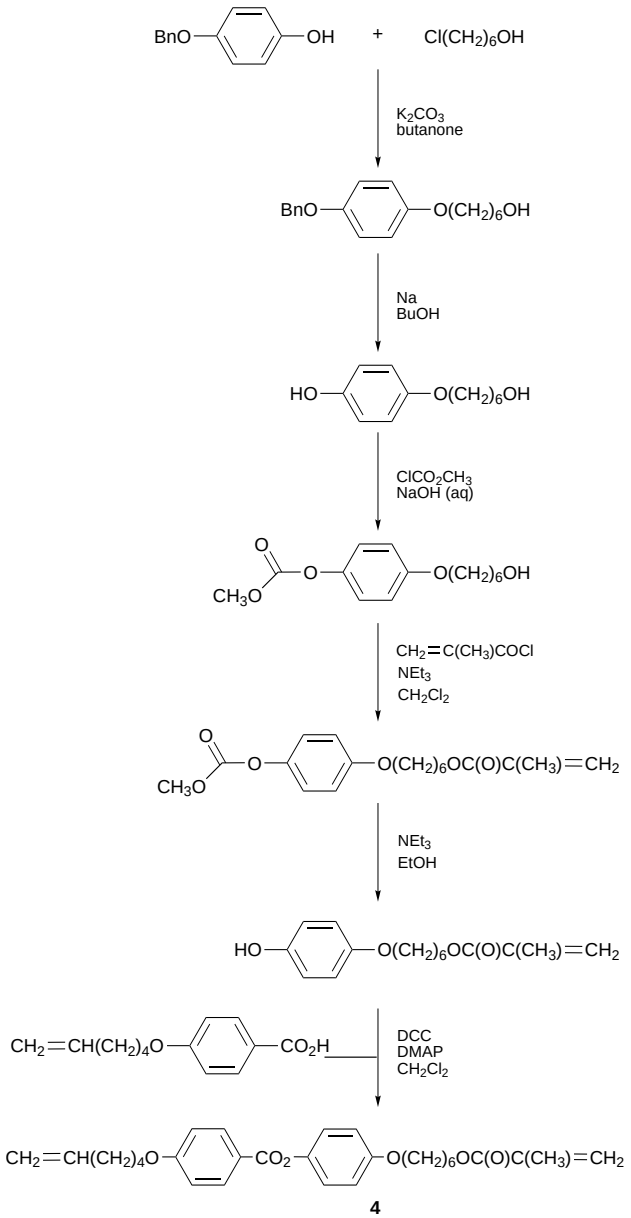
Cross-linking effects in elastomers

The data from AXIS for the elastomers, along with their extension values λ and phase behaviour are given in Table 1. The data from AXIS was used to measure the nematic order parameter $\langle P_2 \rangle$.[19]

Elastomers using both cross-linking agents **3** and **4** were synthesised (**a**, **b** and **c**) as well as elastomers using only cross-linking agent **3** (**d**), and cross-linking agent **4** (**e** and **f**). The maximum value of $\langle P_2 \rangle$ for these type of experiments obtained was 0.56 which corresponded to the elastomer which was extended the greatest amount.

Low values of $\langle P_2 \rangle$ are a consequence of the maximum extension not being attained. It must be pointed out that all the elastomers undergo an additional strain process which is extremely difficult to quantify. Initially, the elastomer is in a swollen state at the beginning of the stretching procedure. The toluene then evaporates out of the network and the sample shrinks exerting additional strain on the elastomer. Finally, the elastomer relaxes as the experiment proceeds releasing some of the strain. Elastomers with a much higher order parameter can be synthesised using a constant load rather than strain. Fig. 1 of sample (**b**) was recorded which shows a high degree of orientation of the mesogenic side chains.

A comparison between the elastomers which contain cross-linking agents **3** and **4** (**a**, **b** and **c**), showed that, on increasing the extension, the order parameter $\langle P_2 \rangle$ increased. Using only cross-linking agent **3** (elastomer **d**) and extending the elastomer during the synthesis to 30% ($\lambda = 1.30$) a $\langle P_2 \rangle$ value of 0.50 ± 0.03 was obtained which is comparable to elastomer **c**. For elastomer **f**, prepared with only cross-linking agent **4**, a $\langle P_2 \rangle$ value of 0.48 was obtained on extension of 38% ($\lambda = 1.38$), which is also



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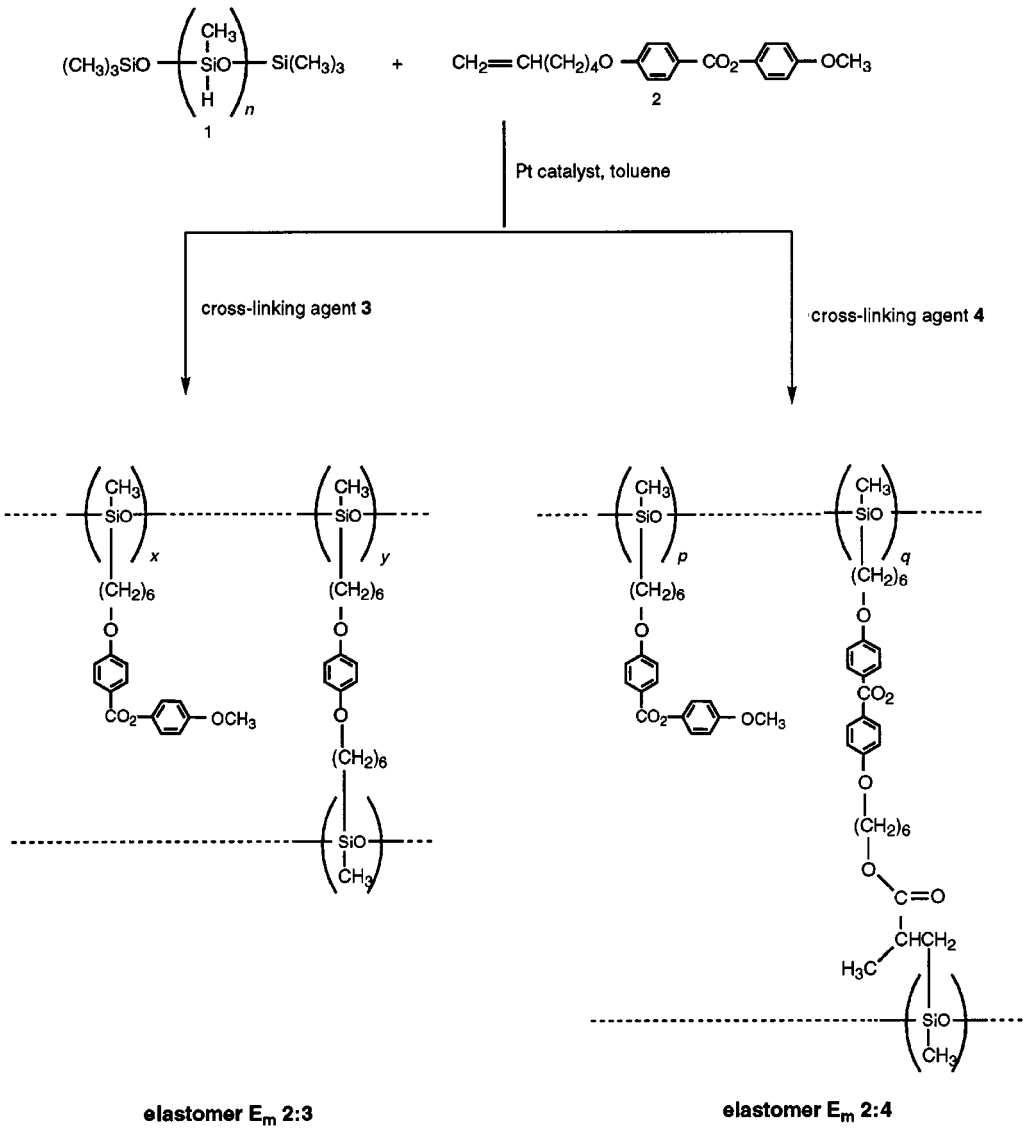
Scheme 4

comparable to elastomer **c**. Therefore it seems that the chemical structure of the elastomer has limited influence on the value of $\langle P_2 \rangle$ up to extensions of 38% ($\lambda = 1.38$) during the second step of the cross-linking reaction. The elastomer which was extended the most ($\lambda = 1.68$) gave the largest $\langle P_2 \rangle$ value (elastomer **b**, 0.56). Correspondingly the elastomer which was extended the least gave the smallest $\langle P_2 \rangle$ value (elastomer **e**, 0.40).

So that a direct comparison could be made between the different elastomers the time taken to reach 90% of the value of the maximum $\langle P_2 \rangle$ value for each elastomer was estimated from the plot of the orientation function coefficient against time. The shape of the plots of orientation function coefficient, *i.e.* $\langle P_2 \rangle$, *versus* time for elastomers **a**–**f** are all similar and the plot for elastomer **d** is given in Fig. 2 for illustration. Initially a large increase in order parameter is observed which eventually levels off to a plateau with time. The initial rate of change of orientation of elastomers is different which corresponds to the response of the network to strain. Initially the network is relatively lightly cross-linked and the gradient of the graph is steep. As the percentage of cross-linking agent increases within the network, the gradient of the graph decreases until eventually after 3 or 4 h there was virtually no more mesogenic alignment of the mesogenic side chains.



Scheme 5

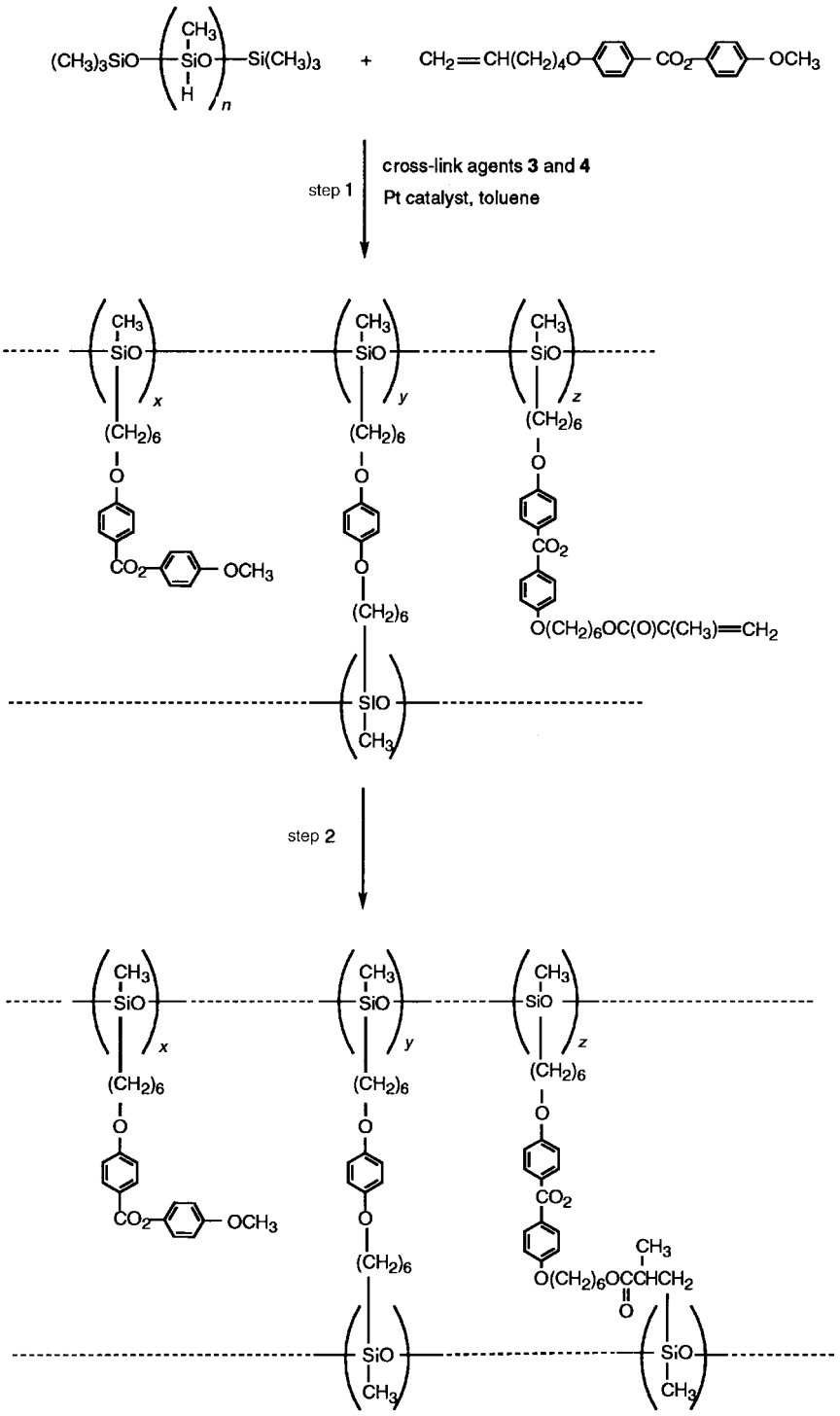
The three elastomers prepared using both cross-linking agents took the longest length of time to obtain 90% of their maximum $\langle P_2 \rangle$ value. It has been observed in similar previous experiments that the rate of evaporation of toluene from elastomers containing dissimilar cross-linking agents is different. The rate of evaporation, for example, from the elastomer containing cross-linking agent **4** (elastomers **e** and **f**) is much slower than that from the elastomer containing only cross-linking agent **3** (elastomer **d**). The rate of evaporation must also be taken into account when discussing the results from these experiments as it would seem likely that a rapid removal of solvent would swell the elastomer and therefore increase the rate of reaction of the second cross-linking agent.

Re-examination of the elastomers by AXIS was carried out after 4 to 5 days to check that the orientation of the mesogenic side chains had remained unchanged. Alignment of the mesogenic side chains is permanent in all of the elastomers prepared, showing that the second cross-linking process is effective.

Conclusions

The cross-linking effects and $\langle P_2 \rangle$ values of six different elastomers were compared (elastomers **a**–**f**) to find out how factors such as extension during the second step of the cross-linking reaction and chemical structure affected $\langle P_2 \rangle$ values. The cross-linking agents used and the extension ratios during the second step of the cross-linking process were varied, and the results were noted. The plots of orientation function coefficient ($\langle P_2 \rangle$) *vs.* time (see Fig. 2) are all of similar shape; the steepness of the curve corresponds to the response of the network to strain. Other factors such as rate of evaporation of solvent and cross-link density after the first step of the monodomain synthesis, must also be taken into account whilst discussing the results. A comparison of $\langle P_2 \rangle$ values was made and the values for these elastomers ranged from 0.40–0.56.

These experiments on cross-linking effects in polysiloxane elastomers show that the nematic order parameter $\langle P_2 \rangle$ is dependent on the extension, λ. This is as predicted by the Landau–de Gennes theory.[29–34] The value of the nematic order parameter $\langle P_2 \rangle$ also depends on the degree of cross-linking which has taken place prior to extension. A relatively high nematic order parameter $\langle P_2 \rangle$ value of about 0.5 was obtained using a modified and improved method of synthesis of monodomains developed by Küpfer *et al.*[1] From the data it can be clearly observed that the results for $\langle P_2 \rangle$ are the same within experimental error. Therefore it can also be concluded that there is little difference whether one cross-linking agent is used or two. It is possible to form a monodomain polysiloxane elastomer with permanent alignment by just using one cross-linking agent which makes the synthesis much more simple and cost effective. The time taken for the mesogenic side chains to align, during the second step of the cross-linking reaction,



Scheme 6

was found to be between 4 and 6 h. For all monodomain elastomers synthesised in the LC phase, during the second step of the reaction, the alignment was permanent.

Experimental

Physical techniques

^{1}H Nuclear magnetic resonance spectra (NMR) were obtained using a JMN GX270 FT spectrometer (270 MHz). Deuterated chloroform was used as the solvent and tetramethylsilane as the internal standard, unless otherwise stated. The multiplicities of absorptions are denoted by singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Infrared (IR) spectra were obtained using either a Perkin Elmer 983G or a Perkin Elmer 487G spectrometer. The samples were prepared as thin films in potassium bromide discs. Mass spectra were obtained on a Finnigan MAT 1020 GC–MS spectrometer: M^+ represents the molecular ion and the base peak is indicated by 100%. Optical microscopy was performed using an Olympus microscope BH2, in conjunction with a Mettler hot-stage FP52 and a Mettler controller FP5. Differential scanning calorimetry

Table 1[a]

elastomer	$\langle P_2 \rangle_{max}$	$\langle P_2 \rangle_{90\%}$	$t_{90\%}$/s	λ	phase behaviour/°C
(**a**)E_m.**2**:**3**,**4**	0.51	0.46	18 000	1.56	g −8.8 N 75 I
(**b**)E_m.**2**:**3**,**4**	0.56	0.50	12 000	1.68	g −7.7 N 80 I
(**c**)E_m.**2**:**3**,**4**	0.47	0.42	15 000	1.30	g −5.8 N 75 I
(**d**)E_m.**2**:**3**	0.50	0.45	10 000	1.30	g −6.1 N 83 I
(**e**)E_m.**2**:**4**	0.40	0.36	12 000	1.18	g −5.6 N 85 I
(**f**)E_m.**2**:**4**	0.48	0.43	8000	1.38	g −9.5 N 87 I

[a] $\langle P_2 \rangle_{max}$ and $\langle P_2 \rangle_{90\%}$ are the maximum $\langle P_2 \rangle$ value and 90% of the maximum $\langle P_2 \rangle$ value respectively, $t_{90\%}$ is the time taken to reach $\langle P_2 \rangle_{90\%}$ and λ is the extension where extension is defined as the final length of the elastomer divided by the initial length of the elastomer.

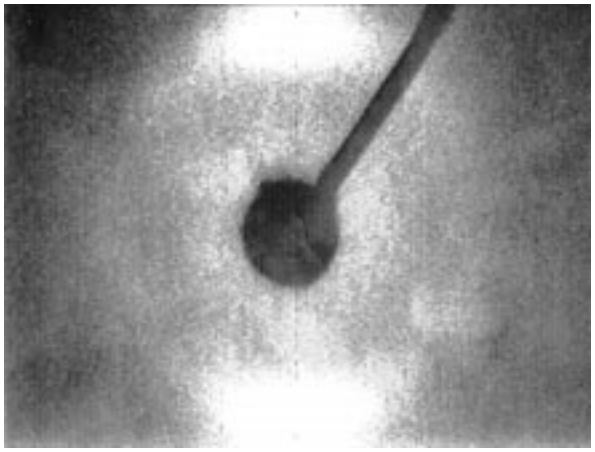


Fig. 1 High degree of orientation of mesogenic side groups in elastomer **b** as shown by AXIS

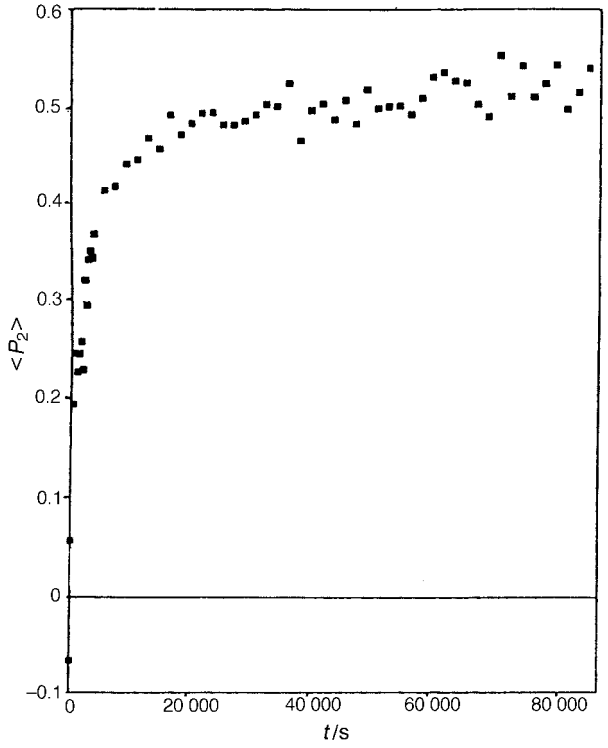


Fig. 2 Plot of the orientation function coefficient *vs.* time for elastomer **d**

(DSC) was carried out using a Perkin Elmer DSC 7, with TAC 7/PC instrument interface and controlled cooling accessory. Heating and cooling rates were usually 10 °C min^{-1} and a nitrogen atmosphere was maintained in the furnace. The reference sample used was gold and the calibration sample

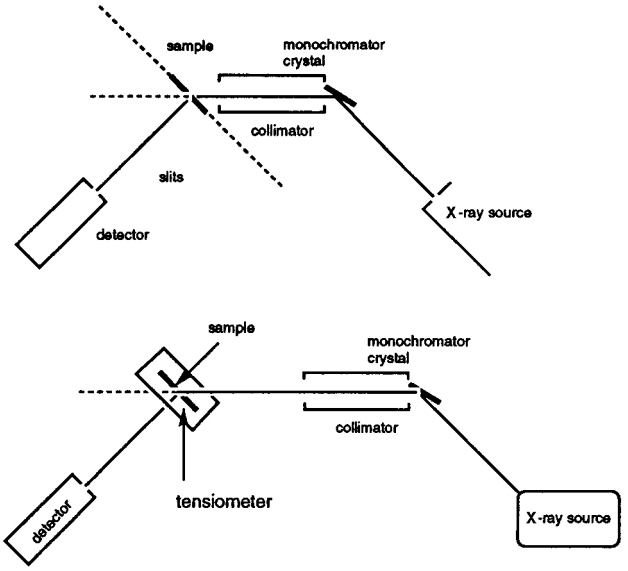


Fig. 3 Schematic representation of AXIS

was indium. Analytical thin layer chromatography (TLC) was performed on aluminium sheets coated in Kieselgel silica gel 60 F_{254}. All references to column chromatography signify flash column chromatography using Sorbsil C60 (40–60 μm) as the stationary phase. The column was put under pressure by the use of air or nitrogen from a laboratory line or a blowing ball. High performance liquid chromatography (HPLC) was used to measure the purity of samples by using reverse phase chromatography on a silica gel column (5 μm pore size, 25 × 0.46 cm, Dynamax Microsorb C18 column) and a Spectroflow 757 UV detector (λ = 254 nm) with data handling facilities. Melting points of the solids were measured using a Gallenkamp melting point apparatus with adjustable heating rates.

X-ray diffraction equipment (AXIS). The apparatus used at the University of Reading is shown in Fig. 3. The data collected for wide angle X-ray is on the scale of 1 to 100 Å and therefore of the order of a few repeat units of the polymer chain. In order to examine the orientational behaviour of samples on the application of a mechanical stress, the elastomers were mounted in a tensiometer (Rosand Precision Ltd.) which was placed in the path of the X-ray beam and extension ratios were measured. Cu-Kα radiation was used in conjunction with a graphite monochromator and a pinhole collimator was used to provide a 1 mm^2 collimated beam at a wavelength of 0.154 nm.

Fractionation of polysiloxane backbone. Preparative GPC was carried out at the University of York on a commercially available polysiloxane backbone (DC1107, Dow Corning) in order to fractionate the polydisperse polymer into relatively monodisperse fractions. The instrument at the University of York is fitted with two preparative columns 1.2 m long (from Waters Associates Ltd.), with an internal diameter of 0.06 m and each packed with Styragel (a polystyrene based gel). Column A is used for the fractionation of low molecular mass polymers up to 5×10^4 g mol^{-1}. It has a nominal porosity of 500 nm and is estimated to have a plate count of *ca.* 7000 plates m^{-1}. Column B is used for the fractionation of higher molecular mass polymers up to 1×10^6 g mol^{-1}. This Styragel column has a nominal porosity of 1000 nm. After the fractions were collected, the toluene was removed by distillation under reduced pressure and the polymer samples collected. The $\bar{M}_w$, $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were then determined using analytical GPC. For a more detailed account of the method used, see ref. 35.

The fraction 2 was used for this work which had a DP value of 234 and a DPI value of 1.1.

Preparation of mesogenic side chain 2 (Scheme 2)

4-(Hex-5-enyloxy)benzoic acid. 4-Hydroxybenzoic acid (0.5 mol) was dissolved in ethanol (300 ml). Sodium hydroxide (1 mol) and water (150 ml) were added and the solution was brought to reflux. 6-Bromohex-1-ene (0.6 mol) was added dropwise and the resulting solution was heated under reflux for 24 h. The ethanol was removed and the residue was diluted with water (300 ml). The cooled reaction mixture was acidified with concentrated hydrochloric acid and the crude product was filtered off and washed with water. The product was purified by recrystallisation (ethanol, 50% v/v aq.). The purity of the product was confirmed by TLC (dichloromethane, single spot). Yield, 92%, K 101 N 140 I °C. δ_H ($CDCl_3$), 8.05 (d, 2H), 6.9 (d, 2H), 5.85 (m, 1H), 5.0 (t, 2H), 4.05, (m, 2H), 2.15 (m, 2H), 1.85 (m, 2H), 1.62 (m, 2H); ν_{max} (KBr)/cm^{-1}, 3400, 3860–3980, 1690, 1610, 1510, 1430, 1260, 845; *m*/*z*, 220 (M^+), 138, 121, 82, 67, 55 (100%).

4-Methoxyphenyl 4-(hex-5-enyloxy)benzoate 2. 4-(Hex-5-enyloxy)benzoic acid (0.02 mol), 4-methoxyphenol (0.02 mol) and 4-pyrrolidin-1-ylpyridine (POP) (0.02 mol) were dissolved in dichloromethane (100 ml). Dicyclohexylcarbodiimide (DCC) (0.02 mol) was dissolved in dichloromethane (30 ml) and added to the mixture dropwise. The resulting solution was stirred at room temp. for 12 h. The resulting product was purified by column chromatography (dichloromethane) and by recrystallisation (acetonitrile). The purity of the product was confirmed by TLC (dichloromethane, single spot) and HPLC (acetonitrile), >99%. Yield, 70%, K 64.3 (N 58) I °C. δ_H ($CDCl_3$), 7.25 (d, 2H), 6.8 (d, 2H), 8.25 (d, 2H), 6.95 (d, 2H), 5.85 (m, 1H), 5.05 (m, 2H), 4.05 (t, 2H), 3.8 (s, 3H), 2.25 (m, 2H), 1.85 (m, 2H), 1.6 (m, 2H); ν_{max} (KBr)/cm^{-1}, 3060, 2930, 1740, 1165; *m*/*z*, 326 (M^+), 203, 196, 135, 121 (100%), 76.

Preparation of cross-linking agent 3 (Scheme 3)

1,4-Bis(hex-5-enyloxy)benzene 3. A stirred suspension of 6-bromohex-1-ene (0.06 mol), potassium carbonate (0.15 mol) and hydroquinone (0.03 mol) in dry butanone (100 ml) was heated under reflux for 24 h. When cooled, the potassium carbonate was filtered off and the butanone was removed by distillation under reduced pressure. The product was purified by column chromatography (dichloromethane), followed by recrystallisation (dichloromethane). The purity of the product was confirmed by TLC (dichloromethane, single spot) and HPLC (acetonitrile, >99%). Yield, 70%, mp 34–36 °C. δ_H ($CDCl_3$), 6.8–6.85 (s, 4H), 5.75–5.9 (m, 2H), 4.95–5.1 (t, 4H), 3.85–3.95 (t, 4H), 2.05–2.15 (m, 12H); ν_{max} (KBr)/cm^{-1}, 2860–2940, 1640, 1505, 1230, 1110, 1070, 1040, 995, 910, 830; *m*/*z*, 274 (M^+), 192, 110 (100%), 93, 81, 67.

Preparation of cross-linking agent 4 (Scheme 4)

1-Benzyloxy-4-(6-hydroxyhexyloxy)benzene. The method used to prepare 1-benzyloxy-4-(6-hydroxyhexyloxy)benzene was similar to that outlined for the preparation of 1,4-bis(hex-5-enyloxy)benzene (previous section), but using 6-chlorohexanol (0.05 mol), potassium carbonate (0.3 mol) and 4-(benzyloxy)phenol (0.05 mol) in dry butanone (130 ml). The product was purified by recrystallisation (ethanol) and the purity of the product was confirmed by TLC (dichloromethane, single spot). Yield, 50%, mp, 82–83 °C. δ_H ($CDCl_3$), 7.3–7.45 (m, 5H), 6.85–6.95 (m, 4H), 5.0–5.05 (s, 2H), 3.85–3.95 (t, 2H), 3.6–3.7 (t, 2H), 1.35–1.85 (m, 8H), 1.15 (s, 1H); ν_{max} (KBr)/cm^{-1}, 3290–3340, 2860–2940, 1605, 1380, 1240, 1120, 1080, 1040, 820, 740; *m*/*z*, 300 (M^+), 209, 122, 91 (100%), 55.

4-(6-Hydroxyhexyloxy)phenol. 1-Benzyloxy-4-(6-hydroxyhexyloxy)benzene (12 mmol) was dissolved in butanol (100 ml) and heated under reflux. Sodium (12 mmol) was added slowly. After all the sodium had completely reacted, water (15 ml) was added carefully followed by hydrochloric acid (15 ml, 20% v/v). The product was extracted into diethyl ether (100 ml) and the ether solution was washed with water (3 × 100 ml) and dried ($MgSO_4$). The product was purified by recrystallisation (ethanol). The purity of the compound was confirmed by TLC (dichloromethane, single spot). Yield, 55%, mp, 69–70 °C. δ_H ($CDCl_3$), 6.7–6.8 (s, 4H), 4.4–4.45 (s, 1H), 3.85–3.9 (t, 2H), 3.6–3.7 (m, 2H), 1.4–2.85 (m, 8H), 1.2–1.35 (s, 1H); ν_{max} (KBr)/cm^{-1}, 3350–3360, 2880–2940, 1510, 1470, 1450, 1370, 1290, 1230, 1100, 1040, 820, 730; *m*/*z*, 209 (M^+), 101, 91 (100%), 83, 65, 55.

1-(Methoxycarbonyloxy)-4-(6-hydroxyhexyloxy)benzene. 4-(6-Hydroxyhexyloxy)phenol (26 mmol) was added, with vigorous stirring, to a solution of sodium hydroxide (75 mmol) in water (250 ml), maintained at 0 °C. Methyl chloroformate (43 mmol) was added slowly to the resulting suspension, keeping the temperature at 0 °C. The resulting reaction mixture was allowed to stir at room temp. for a further 4 h. The reaction was adjusted to pH 5 (universal indicator paper) by the addition of a mixture of concentrated hydrochloric acid and water (1:1). The product was extracted into diethyl ether and the ether solution was washed with saturated sodium chloride solution and dried ($MgSO_4$). The product was purified by column chromatography (dichloromethane–ethyl acetate, 80:20). The purity of the product was confirmed by TLC (dichloromethane, single spot). Yield, 74%. δ_H ($CDCl_3$), 7.0–7.2 (d, 2H), 6.8–6.9 (d, 2H), 3.75–3.95 (m, 5H), 3.6–3.7 (m, 2H), 1.2–1.85 (m, 8H); ν_{max} (KBr)/cm^{-1}, 3260–3500, 2860–2980, 1760, 1595, 1505, 1440, 1200–1270, 1000–1060, 830, 730; *m*/*z*, 110 (100%), 93, 81, 65, 55.

1-Methoxycarbonyloxy-4-(6-methacryloyloxyhexyloxy)benzene. Methacryloyl chloride (19 mmol) was added to 1 - (methoxycarbonyloxy) - 4 - (6 - hydroxyhexyloxy) benzene (19 mmol), which was heated under reflux in dichloromethane (75 ml). Triethylamine (25 ml) was added dropwise into the stirred reaction mixture. After completion the reaction mixture was heated under reflux for a further 4 h. The reaction mixture was cooled and the organic phase washed with hydrochloric acid (10% v/v, 3 × 75 ml) and then with saturated sodium chloride solution until free of acid (universal indicator paper). The organic layer was dried over $MgSO_4$. The product was purified by column chromatography (dichloromethane–ethyl acetate, 80:20). The purity of the product was confirmed by TLC (dichloromethane, single spot). Yield, 76%. δ_H ($CDCl_3$), 7.0–7.1 (d, 2H), 6.8–6.9 (d, 2H), 6.05 (s, 1H), 5.5, (s, 1H), 4.05–4.35 (m, 2H), 3.8–3.95 (m, 5H), 1.2–2.35 (m, 11H); ν_{max} (KBr)/cm^{-1}, 2880–2940, 1760, 1710, 1630, 1500, 1440, 1250, 830; *m*/*z*, 336 (M^+), 168 (100%), 124, 109, 83, 69.

4-(6-Methacryloyloxyhexyloxy)phenol. 1-Methoxycarbonyloxy-4-(6-methacryloyloxyhexyloxy)benzene (14 mmol) was stirred at room temp. for 90 min in a mixture of ammonia and ethanol (1:3, 75 ml). The reaction was monitored by TLC (dichloromethane). The ammonia and ethanol were removed under reduced pressure and the product was washed with hydrochloric acid (10% v/v, 3 × 75 ml), followed by saturated sodium chloride solution (3 × 75 ml) until free of acid. The organic layer was dried over $MgSO_4$. The purity of the product was confirmed by TLC (dichloromethane, single spot). Yield, 77%. δ_H ($CDCl_3$), 6.7–6.8 (s, 4H), 6.1 (s, 1H), 5.05 (s, 1H), 5.2–5.3 (s, 1H), 4.05–4.3 (m, 2H), 3.8–3.9 (m, 2H), 1.45–2.35 (m, 11H); ν_{max} (KBr)/cm^{-1} 3380–3430, 2860–2940, 1710, 1505, 1450, 1230, 1155, 830, 750; *m*/*z*, 279 (M^+), 110 (100%), 83, 69, 65, 55.

4-(6-Methacryloyloxyhexyloxy)phenyl 4-(hex-5-enyloxy)benzoate. 4-(Hex-5-enyloxy)benzoic acid (15 mmol), 4-(6-methacryloyloxyhexyloxy)phenol (14 mmol) and 4-dimethylaminopyridine (DMAP) (2 mmol) were dissolved in dichloromethane (100 ml). Dicyclohexylcarbodiimide (DCC) (15 mmol) was dissolved in dichloromethane (30 ml) and added to the mixture dropwise. The resulting solution was allowed to stir at room temp. for 12 h. The resultant product was purified by column chromatography (dichloromethane) and recrystallisation (dichloromethane). The purity of the compound was confirmed by TLC (dichloromethane, single spot) and HPLC (acetonitrile, >99%). Yield, 29%, K (N 41) 48 I °C. δ_H ($CDCl_3$), 8.1–8.2 (d, 2H), 7.05–7.15 (d, 2H), 6.85–6.95 (d, 4H), 6.1 (s, 1H), 5.75–5.9 (m, 1H), 5.5–5.55 (s, 1H), 4.9–5.05, (t, 2H), 3.9–4.2 (3 × t, each 2H), 1.2–2.2 (m, 17H); ν_{max} (KBr)/cm^{-1}, 2840–2960, 1730, 1650, 1610, 1510, 1250, 1070, 830, 740; *m*/*z*, 480 (M^+), 203, 121 (100%), 93, 83, 69, 55.

Preparation of the elastomers (Schemes 5 and 6). The synthesis of the elastomers follows the well-known procedure of the hydrosilylation reaction with polysiloxanes in the presence of a Pt catalyst[36] and is based on the spin-cast technique developed by Finkelmann.[1] A solution of monomer **2** (0.8 mmol), cross-linking agent **3** and/or cross-linking agent **4**, polysiloxane backbone **1** (DP = 234, DPI = 1.1) [60 mg (1 mmol)] and Pt-catalyst SLM86003 (Wacker Chemie, Burgenhausen) (8 μl) in absolute toluene (1 ml). The reaction mixture was then filtered through a PTFE membrane filter (0.5 μm pore size) into the cylindrical vessel, with a diameter of 5 cm and a height of 1 cm, which was lined with Teflon film. The vessel was sealed and fitted onto the top of a specially adapted centrifuge, placed in an oven at 60 °C and spun at 4000 rpm for 4 h. After cooling the vessel, the swollen elastomer was removed and placed into a tensiometer. The sample was then extended (between 18 and 56%) and the second step of the cross-linking reaction was monitored *in situ* in the X-ray beam of AXIS (area X-ray imaging system). Data were collected continually over a period of 12 h. Finally graphs were plotted of orientation function coefficient ($\langle P_2 \rangle$) against time (s). The axis of orientation (°) *versus* time was also plotted for the corresponding experiments to observe the orientation process of the mesogenic side chains on application of a mechanical field. The axis of orientation is defined as the dissection line of the orientation arcs in the X-ray diffraction picture. In the equatorial sector the axis of orientation is equal to 0°. In the meridonal sector the axis of orientation is equal to 90°. The data from this work are summarised in Table 1.

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