Liquid crystal polymers copolymers and elastomers containing a laterally attached mesogenic unit

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The synthesis of a closely-coupled laterally attached side-chain liquid crystal polymer is described. The material exhibits liquid crystalline behaviour over a wide temperature range. Incorporation of non-mesogenic methyl acrylate as a comonomer with the potentially mesogenic monomer results in copolymers which are liquid crystalline, even when the non-mesogenic portion exceeds 60 mol%. Macroscopic alignment can be readily realised in both homopolymer and copolymer samples, either using a magnetic field or by pulling as fibres, and X-ray scattering shows the level of global orientation to be relatively high. Copolymerisation of the mesogenic unit with *ca.* 10 mol% of hydroxyethyl acrylate results in materials which can be cross-linked by reaction with a diisocyanate. The application of mechanical stress to liquid crystalline elastomers based on this closely coupled unit results in some global orientation of the mesogens, and the stress–strain-orientation behaviour of this cross-linked system is described. Both copolymers and elastomers are compared with liquid crystal polymers in which the mesogen is attached *via* a terminal linkage.

Typically, side-chain liquid crystal polymers are built up from a mesogenic unit, usually consisting of two or more aromatic units, and a polymer backbone, of which acrylate, methacrylate, and siloxane are the most commonly employed.^{1,2} The two components are connected *via* a coupling chain or flexible spacer, generally containing two or more methylene groups.³ In the majority of cases the mesogenic unit is attached to the coupling chain terminally (*i.e.* as a *para* substituent on one ring), but a number of variations to this geometry have yielded liquid crystalline polymers; for example, discotic systems,⁴ and lateral liquid crystalline polymers, where the mesogenic unit is linked through the mid-point rather than terminally,^{5–7} have been prepared. It is a material with this latter geometric arrangement which forms the basis for the investigations described in this presentation.

Most examples of lateral liquid crystal polymers retain the requirement for a flexible spacer to decouple the motion of the mesogen from the polymer backbone.^{5,6,8} An interesting variation on laterally attached polymers has been described, however, in which the mesogen is bonded very closely to the polymer backbone; *i.e.* the coupling chain is small. Such materials have been labelled by Zhou as 'mesogen jacketed' liquid crystal polymers.^{9–11} Of particular interest is the existence of a liquid crystal phase in a polymer where there is substantial coupling between the mesogen and the polymer backbone, such that the motion of the two units are strongly dependent. The mesogen jacketed model implies that the mesogenic moieties are not just the side-groups, but rather the polymer as a whole; such materials may be considered as intermediate between side-chain and main-chain liquid crystal polymers.¹²

As part of our continuing investigations of coupling in liquid crystal polymers and elastomers,^{3,13–16} it was decided to investigate further the mesogen jacketed model of Zhou. In the first part of this account we describe the effect of diluting the mesophase by the incorporation of non-mesogenic moieties along the polymer backbone, and compare the results with similar experiments for liquid crystal polymers with terminally attached mesogenic units.^{17,18} It was of particular interest to determine if the flexibility of the polymer backbone had a marked influence on the phase behaviour of such materials. In the case of the 'mesogen-jacketed' model of Zhou,^{9,10} it is clear that the formation of a liquid crystal phase requires that the polymer backbone adopts an extended chain conformation; presumably such a conformation relies on the rigidity imposed on the system by the extreme bulk of the side-groups. It might be expected that the addition of a high enough concentration of non-mesogenic comonomer units will provide the polymer backbone with sufficient flexibility to completely disrupt the liquid crystal phase.

In the second part of this account the behaviour of some liquid crystalline elastomers based on the closely-coupled, laterally-attached mesogen is described. These studies have focussed particularly on the phase behaviour and the mechanical behaviour of the materials. In this way it was intended to determine the influence of close coupling between the mesogenic unit and the polymer backbone on the magnitudes of the effects typical observed in such elastomers.¹⁹

Synthesis

Monomer synthesis was undertaken using a modification to the method given by Zhou:^{9,10} anisoyl chloride was reacted with 2,5-dihydroxybenzaldehyde to produce 2,5-bis(4-methoxybenzoyloxy)benzaldehyde I;



this was then reduced to 2,5-bis(4-methoxybenzoyloxy)benzyl alcohol II with BH_3 . THF followed by esterification to produce the monomer III. The modification was necessitated by the observation that the reported reduction of the aldehyde, using $NaBH_4$ in DMSO, was found to give an unexpected product. Spectroscopic analysis (see Experimental section) shows this is either IV or V,





Fig. 1 NMR spectra of (a) the expected product from the synthetic pathway described in the text, and (b) the product obtained on following the procedure listed in ref 10

In which complete reduction of the aldehyde to the methyl group has occurred, together with cleavage of one of the ester units, such a process is not untypical of reductions in DMSO and related media,²⁰ however, although the similarity in the predicted NMR spectra of these two isomers does not allow an unequivocal assignment to one or other, it would appear that one of the two isomers is formed exclusively, this suggests that electronic influences may be important. It should be noted here that the NMR spectrum quoted by Zhou for the appropriate intermediate^{9 10} is clearly not that of the alcohol claimed (Compound II), but rather that of either IV or V,[†] a similar spectrum for this unidentified compound was obtained in this work and this is shown together with the ¹H NMR of the alcohol II in Fig 1 Polymerisation of the acrylate of IV (V) gives a compound with no mesophase

In spite of the contradictory NMR evidence cited, the polymers described^{9 10} bear close similarity, in terms of their phase behaviour, to the liquid crystal polymers described below, furthermore it is clear that, more recently,²¹ Zhou has recognised over-reduction by sodium borohydride in DMSO to be a problem, and has found that this can be overcome by the complete removal of water from the solvent, unfortunately, this precludes the addition of the reducing agent as an aqueous solution. We believe the procedure described in this presentation to be superior, since it is both clean (with almost complete absence of any side-products) and relatively rapid, furthermore, as the starting material is only poorly soluble in tetrahydrofuran, the gradual disappearance of this material as the more soluble alcohol is produced provides a clear indication of the extent of reaction

In order to establish the most likely product of the sodium borohydride reduction, and in particular the site of ester cleavage, a small scale reduction in $(CD_3)_2SO$ was undertaken on the 4-methoxybenzoate esters of *ortho*- and *meta*-hydroxybenzaldehyde, and probed by ¹H NMR It was found that for the *meta* isomer, the aldehyde was reduced to the benzylic alcohol in good yield In contrast, for the *ortho* derivative, a mixture of products was obtained, most notably, 2-methylphenol These observations clearly support the exclusive cleavage of the ester unit *ortho* to the aldehyde, leading to the formation of **IV** rather than **V**

Polymers and copolymers were prepared by free radical polymerisation of the acrylate monomer III with varying proportions of the required comonomer In the first part of this account, copolymers with methyl acrylate were prepared (this being chosen such that the comonomer would disrupt the polymer backbone without introducing additional steric complications from the side-group), for the production of the elastomers described in the second part of this contribution, a small proportion of hydroxyethyl acrylate was added to allow subsequent cross-linking with a disocyanate (see Experimental section) The majority of the polymers were prepared in THF with 4 mol% AIBN, to maximize conversion Where higher molecular weights were required, chlorobenzene was used as a solvent (to minimise chain-transfer reactions) and the AIBN concentration was reduced to 1 mol%

Results and Discussion

Copolymers

Composition of copolymer systems. The final composition of polymers from the initial feedstock, determined from NMR spectroscopy, (together with the molecular weight data evaluated by GPC) are detailed in Table 1 From this, it can be seen that the uptake of the two monomers into the final polymer is as expected on the basis of their concentration in the initial feedstock. This is consistent with the monomers forming random copolymers,²² *i e* that both acrylates exhibit similar kinetic behaviour. This was confirmed by a series of experiments in which the composition of polymers of both L50 and L80 were monitored with time, it was found that the composition proceeded and at no stage was there any preference for one or other monomer

Molecular weight. The relatively low values for the molecular weight obtained from most samples reflect two factors, firstly the unusually high initiator concentration, and secondly, the influence of the polymerisation solvent, tetrahydrofuran is known to act efficiently as a chain transfer agent ²² However, this mode of termination is not responsible for the unusually narrow molecular weight distribution in these samples, it is likely that the rather narrow polydispersity arises from the removal of a substantial fraction of lower molecular weight material during the purification procedure

Phase behaviour. The phase behaviour of the copolymer samples was measured by DSC and optical microscopy The

Table 1 Composition of polymers synthesised

sample	feedstock methyl acrylate III (mol%) ^a	composition methyl acrylate III (mol%) ^b	$M_{\mathbf{w}}{}^{c}$	${M_{\mathbf{w}} / \over M_{\mathbf{n}}}$	D_{p}^{d}	yıeld (%)
L10	10 90	16 84	8.2×10^{3}	14	66	10
L20	20 80	23 77	9.0×10^{3}	13	56	20
L35	35 65	35 65	1.52×10^{4}	16	70	15
L40	40 60	39 61	9.9×10^{3}	12	42	40
L50	50 50	50 50	1.48×10^4	13	53	60
L60	60 40	60 40	1.18×10^4	11	38	70
L80	80 20	80 20	1.09×10^4	12	28	75
L100	100 0	100 0	4.57×10^4	15	28	75
HL100	100 0	100 0	$4~57\times10^4$	16	99	75

^{*a*} Initial feedstock added ^{*b*} Composition calculated from ¹H NMR ^{*c*} M_w determined from GPC ^{*d*} D_p =degree of polymerisation

 $[\]dagger$ The differences in the predicted NMR spectra of IV and V are minimal and it is not possible to distinguish these materials from the NMR data alone

behaviour observed was broadly in line with expectations on the basis of similar copolymer systems;¹⁷ the transition temperatures are shown in Fig. 2. As inspection of this figure shows, the glass transition temperature declines steadly as the concentration of methyl acrylate is increased, indicative of a rather more flexible polymer backbone. This increased flexibility is not accompanied by complete disruption of the mesophase except at relatively high methyl acrylate concentrations. The liquid crystal phase is able to tolerate a rather high concentration of non-mesogenic diluent. This possibly reflects the shear bulk of the mesogenic unit, and the wide temperature range over which a liquid crystalline phase can be observed for the homopolymer.

X-Ray scattering. Samples of the mesogenic material with a macroscopic director alignment could be readily prepared either using magnetic fields (typically a field of 0.6 T applied for 18 h was sufficient to induce alignment) or by pulling as fibres. X-Ray scattering measurements were made on aligned samples of these copolymer systems using procedures described elsewhere.¹³ In all cases the aligned samples gave scattering curves typical of an aligned nematic polymer. For the fibre samples, the long axis of the mesogenic units lay parallel to the draw direction in all cases. The X-ray scattering curves all showed two main peaks along the equatorial direction (i.e. normal to the alignment axis), with a maximum at ca. 1.25 Å⁻¹, arising from correlations within the mesogenic units, and a peak at ca. 2.8 Å⁻¹ which became more prominent as the mesognic concentration decreased. This latter peak is typical of simple polymer systems based on polyacrylates. The increased prominence reflects the greater concentration of chains per unit mass for these samples. However, it is clear that the packing of mesogenic units remains relatively unaffected, even by large changes in the polymer composition.

Fig. 3 shows the global orientation parameter,²³ measured at room temperature for a series of fibres prepared by drawing at temperatures in the liquid crystal phase followed by rapid cooling. Although pulling fibres was rather difficult owing to the unexpectedly high viscosity of the liquid crystal phase (particularly in view of the relatively low molecular weight of these materials), such samples gave consistently higher orientation parameters than observed for similar samples prepared using a magnetic field. The figure shows that relatively high degrees of macroscopic alignment are possible for all the samples which exhibited a liquid crystal phase. The slight decrease in the parameter $\langle P_2 \rangle$ at higher concentrations of methyl acrylate suggests less ordered structures, and such behaviour is typical of copolymer systems involving nonmesogenic monomers.^{17,18}

Elastomers

Cross-link density. Both swelling and mechanical measurements were used to estimate the cross-link density of the elastomeric samples using established procedures.²² For the



Fig. 2 Plot showing the phase behaviour of copolymers of III with methyl acrylate as a function of composition



Fig. 3 Measured global orientation parameter $\langle P_2 \rangle$ at s=1.25 Å⁻¹, for samples aligned as fibres, as a function of the mesogenic unit concentration

swelling measurements the cross-link density was obtained using the Flory–Huggins parameter for a similar system in which the same aromatic unit is connected to an acrylate backbone by a longer coupling-chain.²⁴ The data obtained are shown in Table 2. The HEA6 sample had rather poor mechanical properties and was found, from the swelling measurements, to have a rather high sol content (50% compared to 6% for the HEA10 sample) in keeping with the lower molecular weight of the precursor polymer. The discrepancy in the cross-link density for the HEA10 sample obtained from the two methods we believe to reflect inaccuracies in the procedures, which are particularly large for the swelling experiments (approximate errors being *ca*. 60% for swelling measurements and *ca*. 20% for the mechanical measurements).

Phase behaviour. In keeping with observations of other nematic elastomers, such as those based on the monomer VI,¹⁶ cross-links can be introduced into the system without substantial disruption of the nematic phase, although some changes in the phase transition temperatures are observed as shown in Table 2. The particular feature of interest in this data is the behaviour of the HEA10 sample, which showed a substantial decrease in the nematic–isotropic transition temperature when cross-linked in the liquid crystal phase. Theoretical studies,^{25,26} since bourn out by experiment,^{16,27} have shown that cross-linking a liquid crystalline polymer in the liquid crystalline phase should produce a stabilisation of that phase. Where deviations from this behaviour have been observed²⁸ they have been attributed to non-equilibrium behaviour.



In particular for systems based on VI where n is small, it is apparent that, because of the rather rigid polymer backbone, the cross-linking reaction occurs too rapidly to allow the polymer backbone to reach an equilibrium structure. It seems likely that the polymer system described here behaves in a similar way.

Mechanical behaviour. As with other liquid crystalline elastomers, the mechanical behaviour of these materials in the isotropic phase was similar to that expected for a conventional elastomer. Any effects arising from the proximity of the liquid

Table 2 Properties of copolymers of III with hydroxyethyl acrylate and elastomers formed from these poly
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$T_{g}^{a,b}$	$T_{\mathbf{N}-\mathbf{I}}^{b,c}$	M ^d	D e	${M_{\mathbf{w}}}/{M}$	М	XL-D ^f	$XL-E^{g}$
	, e	W		171 n	101 c	(70)	(70)
67	148	1.79×10^{4}	40	1.2			
74	151				6.37×10^{4} i	$1.4\%^{i}$	23 ⁱ
93	171	5.34×10^{4}	125	1.9			
85	158				$4.13 \times 10^{4 h}$	1.03 ^h	21 ^h
					7.06×10^{4i}	0.6^{i}	12 ^{<i>i</i>}
	<i>T</i> ^{<i>a,b</i>} / ^o ℃ 67 74 93 85	$\begin{array}{c c} T_{g}^{a,b} & T_{N-I}^{b,c} \\ /^{\circ}C & /^{\circ}C \\ \hline \\ 67 & 148 \\ 74 & 151 \\ 93 & 171 \\ 85 & 158 \\ \end{array}$	$\begin{array}{c cccc} T_{g}^{a,b} & T_{N-1}^{b,c} & & \\ & & & & \\ \hline C & & & & \\ \hline 67 & 148 & 1.79 \times 10^{4} \\ \hline 74 & 151 & & \\ 93 & 171 & 5.34 \times 10^{4} \\ 85 & 158 & & \\ \hline \end{array}$	$\begin{array}{c ccccc} T_{g}^{a,b} & T_{N-l}^{b,c} & & & \\ & & & & \\ & & & & \\ \hline C & & & & \\ \hline 67 & 148 & 1.79 \times 10^4 & 40 & & \\ \hline 74 & 151 & & & \\ 93 & 171 & 5.34 \times 10^4 & 125 & \\ \hline 85 & 158 & & \\ \hline \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

^{*a*} T_g measured at mid point. ^{*b*} Error of ± 1 °C. ^{*c*} T_{N-1} measured from peak maxima. ^{*d*} Weight average molecular weight measured using GPC. ^{*e*} D_p = degree of polymerisation. ^{*f*} XL-D = cross-link density. ^{*g*} XL-E = cross-link efficiency. ^{*h*} Determined from mechanical measurements.

^{*i*} Measured from swelling experiments.

crystalline phase²⁵ could not be observed due to the high temperatures and the poor mechanical properties of the samples at these temperatures. In the nematic phase a rather more complicated stress-strain curve was obtained. A typical example is shown in Fig. 4. Similar curves have been observed for other elastomer samples^{2,29,30} and the unusual behaviour arises as a consequence of global alignment of the mesogenic units,^{13,30} which may be considered to increase the effective sample length, as the stress is increased.²⁹

The stress-strain curves obtained from a liquid crystalline elastomer in the liquid crystalline phase reflect the relative ease with which alignment processes are possible. In order to gauge the extent of side-chain alignment, in situ X-ray scattering experiments were performed on samples extended in the liquid crystalline phase. The macroscopic orientation was measured after allowing sufficient time for its development (time dependence measurements of the level of orientation shows that the maximal orientation occurred after about 20 min; after this time at constant strain a slight decline was noted, presumably due to imperfections in the network). A typical plot of orientation as a function of extension is shown in Fig. 5. The plot correlates well with the stress-strain plot shown in Fig. 4 as discussed below (although these latter data were obtained from a dynamic experiment) and is in agreement with data obtained from terminally attached liquid crystalline polymers based on the acrylate VI.30

The orientation measurements shown in Fig. 4 provide a general picture of the processes occurring as the elastomer is extended. The rather high initial stress required reflects the energy needed to disrupt the local orientation of the mesogens in the polydomain structure. As the extension is increased less strain is required due to the global alignment of these mesogens; finally, any further extension requires the disruption, albeit temporarily, of the monodomain structure. The main difference between the behaviour of these samples and those of more loosely coupled systems is the rather low levels of orientation.



Fig. 4 The measured mechanical behaviour of 10% HEA-CL at 120 °C. Data obtained after sample was allowed to relax to an equilibrium stress value.



Fig. 5 Plot of orientation parameter $\langle P_2 \rangle$ as a function of extention for the sample 10% HEA-CL (at 105 °C). The data was obtained after allowing complete relaxation of the sample to provide an equilibrium orientation.

achieved, with orientation parameters only half those found for a terminally attached system,¹³ and furthermore, lower than when the samples were prepared with a magnetic field or as fibres (see above).

Summary

We have described an improved synthetic method for closely coupled laterally attached side-chain liquid crystalline polymers. Problems with the previously published method of Zhou arise because of the unusually strong reducing power of NaBH₄ in non-aqueous media. The homopolymer of III exhibits a reversible liquid crystal phase confirming the work of Zhou,^{9,10} although there is some confusion over the published NMR data. Copolymerization of III with methyl acrylate leads to a liquid crystal behaviour for copolymers containing up to 71 mol% methyl acrylate. This unusually high proportion of non-mesogenic diluent can be attributed both to the relative difference in bulk of the two monomers and the unusually broad temperature range over which a nematic phase is observed. Elastomeric materials can be prepared from these side-chain polymer systems, but there are some notable differences in the behaviour seen from these materials and that observed from less closely bound systems. In particular, the levels of orientation achieved on application of a stress field are unusually low. It is clear that the behaviour of elastomers prepared from this system is severely perturbed by dynamic constraints arising from the extreme proximity of the bulky mesogenic unit and the polymer backbone.

Experimental

Characterisation

The composition of the copolymers was calculated from the integration of the relevant peaks in the ¹H NMR; these were

the peak at $\delta = 5.2$ due to benzyl group derived from monomer III and the signal at $\delta = 3.6$ assigned to the methyl group in the methyl acrylate component.

Molecular weight data were obtained by GPC, using dichloromethane as an eluent except in the case of L100 for which chloroform was employed. The molecular weight data were obtained using a refractive index detector in conjunction with polystyrene standards; the data are included in Table 1, and are 'corrected' to compensate for the difference in molecular weight of the monomer repeat units.

The phase behaviour of the polymers was analysed using a Perkin Elmer DSC-2 calorimeter with approximately 10 mg samples and a scanning rate of $10 \,^{\circ}$ C min⁻¹. A polarizing microscope equipped with a variable temperature unit was used to confirm both the nature of the liquid crystalline phases and the liquid crystalline to isotropic phase transition temperatures.

Mechanical measurements were performed using a Rosand Precision Ltd. 'Microscope' tensile tested fitted with a 2 N transducer and a small oven to allow variable temperature measurements; the system has been described elsewhere.¹³

X-Ray scattering measurements utilized a Philips generator operating at 40 kV in conjunction with a pin-hole collimator and an incident beam monochromator to select the characteristic Cu-K α radiation (λ =1.542 Å). For measurements on the copolymer system, samples were analysed on a computer controlled 3-circle diffractometer operating in transmission mode. The X-ray scattering intensity was measured over the range s=0.2–6.2 Å⁻¹ in steps of 0.02 Å⁻¹ where |s|=4 $\pi \sin \theta/\lambda$. For samples with a preferential orientation direction, the azimuthal variation in the scattering intensity was measured from α =0–360 in 9° steps at constant s where α is the angle between the scattering vector |s| and the symmetry axis of the sample. The data obtained was then converted to an orientation parameter $\langle P_2 \rangle$ given by eqn. (1).

$$\langle P_2 \rangle = -2 \frac{\int I(\alpha) \sin \alpha (3 \cos^2 \alpha - 1)/2 d\alpha}{\int I(\alpha) \sin \alpha d\alpha}$$
 (1)

The orientation parameter $\langle P_2 \rangle$ relates to the average contribution of the mesogen, taking into account both the order parameter and the director distribution.

In situ X-ray scattering on mechanically deformed samples utilized the AXIS system, in which the scattering pattern is collected on an area detector and the image can be stored on video, with the data analysis being provided by a computer system. Full details of this apparatus are described elsewhere.³¹

Materials[‡]

2,5-Bis(4-methoxybenzoyloxy)benzaldehyde I. Compound I was prepared using the method of Zhou *et al.*^{9,10} The crude product, obtained from 2,5-dihydroxybenzaldehyde (14 g, 100 mmol), was dried under vacuum then recrystallised from toluene to give a compound which both TLC and NMR showed to be free of impurities (yield 70%); mp 189°C (nematic), 213°C (isotropic); m/z 406 (M⁺)(HRMS: Calc., 406.1052; measured, 406.1059); v_{max}/cm^{-1} 1722, 1690, 1604 and 1577; ¹H NMR [400 MHz, (CD₃)₂SO] $\delta_{\rm H}$: 3.8 [6H (OMe),

[‡] We have adopted a simple numbering system to describe the aromatic protons in the range of structurally similar materials described in this account. This is as indicated below:



This numbering system is also applied to the ¹³C NMR spectra.

s], 7.16(7) [2H (H^{5.6} or H^{5',6'}), d fine splitting, J_{ortho} 8.8], 7.17(2) [2H (H^{5.6} or H^{5',6'}), d fine splitting, J_{ortho} 8.8], 7.57 [1H (H²), d, J_{ortho} 8.8], 7.74 [1H (H³) dd, J_{meta} 2.9, J_{ortho} 8.8], 7.87 [1H (H¹), d, J_{meta} 2.9], 8.14(4) [2H (H^{4.7} or H^{4',7'}), d fine splitting, J_{ortho} 8.8], 8.15(7) [2H (H^{4.7} or H^{4',7'}), d fine splitting, J_{ortho} 8.8], 10.10 [1H (CHO), s].

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2-Methyl-4-(4-methoxybenzoyloxy)phenol. 2,5-Bis(4methoxybenzoyloxy)benzaldehyde (2.4 g, 6.0 mmol) was dissolved in dimethyl sulfoxide (DMSO) (120 ml). To this solution, NaBH₄ (1.2 g, 32 mmol) was added slowly at 10 °C. After addition of the NaBH₄ the reaction mixture was cooled to 0 °C and stirred for 4 h. Following this, the solution was poured into water (800 ml) with stirring to precipitate the product. This was then filtered, washed with water, dried under vacuum, then recrystallised from toluene to give a single product by TLC and NMR spectroscopy (yield ca. 40%); mp 158-160 °C; m/z 258 (M⁺)(HRMS: Calc. 258.08921; measured, 258.0896) v_{max}/cm⁻¹: 3457, 1714, 1611, 1585 and 1512; ¹H NMR (250 MHz, CDCl₃–CD₃OD) $\delta_{\rm H}$: 2.25 [3H (CH₃), s], 3.9 [3H (OMe), s], 6.78 [1H (H²), d, J_{ortho} 8.0], 6.85 [1H (H³), dd, J_{meta} 2.0, J_{ortho} 8.0], 6.94 [1H (H¹), d, J_{meta} 2.0], 7.00 [2H (H^{5.6}), d, J_{ortho} 8.5], 8.15 [2H (H^{4.7}), d, J_{ortho} 8.5]; ¹³C NMR (63 MHz) δ_{C} : 15.83 (CH₃), 55.34 (OMe), 113.71(C^{5.6}), 114.89, 122.54 [125.55] 119.27, 121.89, 123.50, 125.58, 132.04 (C^{4,7}), 143.34, 152.50, 163.76, 165.79.

2-Methyl-4-(4-methoxybenzoyloxy)phenyl acrylate. 2-Methyl-4-(4-methoxybenzoyloxy)phenol was reacted with acryloyl chloride in THF containing triethylamine according to established procedure.³² The crude product was filtered, dried and then recrystallised from ethanol to yield a single compound by TLC and NMR (yield ca. 60%); mp 109 °C; m/z312 (M⁺)(HRMS: Calc. 312.0997, measured, 312.1007) v_{max}/cm^{-1} 1725 and 1654; ¹H NMR (250 MHz,CDCl₃) δ_{H} : 2.21 [3H (Me), s] 3.90 [3H (OMe), s], 6.03 [1H (HCH=), dd, J_{gem} 1.3, J_{cis} 10.4], 6.35 [1H (HCCO₂), dd, J_{cis} 10.4, J_{trans} 17.3], 6.64 [1H (HCH=), dd, J_{gem} 1.3, J_{trans} 17.3], 6.98 [2H (H^{5.6}), d fine splitting, J 9.0], 7.14–7.04 [3H (H^{1,2,3}) m], 8.14 [2H (H^{4,7}), d fine splitting, J 9.0]; ¹³C NMR (63 MHz) $\delta_{\rm C}$: 16.29 (CH_3) , 55.48 (OCH_3) , 113.82 $(C^{5,6})$, 119.99, 121.76, 122.59, 124.09, 127.63, 131.49, 132.23 ($C^{4,7}$), 132.57 (= CH_2), 146.54, 148.48, 163.89, 164.10, 164.76.

2,5-Bis(4-methoxybenzoyloxy)benzyl alcohol. 2.5-Bis(4methoxybenzoyloxy)benzaldehyde (10.9 g, 27 mmol) was dissolved in THF (1.21). To this solution, $BH_3 \cdot THF$ complex (100 mmol) was added slowly under a nitrogen atmosphere, ensuring the temperature remained below 0 °C. After 2 h the reaction was quenched by the slow addition of air and water, until effervescence ceased. The solvent was then evaporated in vacuo and the remaining precipitate was filtered, washed with water then dried under vacuum and recrystallised from toluene to yield a single compound by TLC and NMR (yield >90%); mp 154–156 °C; m/z 408 (M⁺); v_{max}/cm^{-1} 1726; ¹H NMR (250 MHz, CDCl₃–CD₃OD) δ_{H} : 3.91 [6H (OMe), s], 4.63 [2H (CH₂), s], 7.00(0) [2H (H^{5,6} or H^{5',6'}), d fine splitting, J_{ortho} 8.8], 7.00(6) [2H (H^{5,6} or H^{5',6'}), d fine splitting, J_{ortho} 9.2], 7.17 [1H (H³), dd, J_{meta} 2.6, J_{ortho} 8.8], 7.21 [1H (H²), d, J_{ortho} 8.8], 7.43 [1H (H¹), d, J_{meta} 2.6], 8.14(7) [2H (H^{4.7} or H^{4/7}), d fine splitting, J_{ortho} 8.8], 8.15(3) [2H (H^{4,7} or H^{4'7'}), d fine splitting, J_{ortho} 9.2]; ¹³C NMR (63 MHz) $\delta_{\rm C}$: 55.31 (OCH₃), 58.85 (ArCH₂), 113.72 (C^{5,6} or C^{5',6'}), 113.81 (C^{5,6} or C^{5',6'}), 120.80, 121.16, 121.33, 122.92, 132.13, 132.19, 145.27, 148.54, 163.92, 164.03, 164.00, 165.24 (Found: C, 67.58; H, 4.97; O, 27.45. C₂₃H₂₀O₇ requires C, 67.64; H, 4.94; O, 27.42%).

2,5-Bis(4-methoxybenzoyloxy)benzyl acrylate III. 2,5-Bis(4-methoxybenzoyloxy)benzyl alcohol was reacted with acryloyl chloride in THF containing triethylamine and a small amount

of 3,5-di-*tert*-butyl-4-hydroxytoluene (to inhibit polymerisation) using a literature procedure ³² Purification of the crude material was carried out using column chromatography on neutral alumina with dichloromethane as the eluent and gave a single product by TLC and NMR (yield 60%), mp 119 °C, m/z 462 (M⁺)(HRMS Calc, 462 1314, measured, 462 1314), v_{max}/cm^{-1} 1727, 1632, 1584 and 1516, ¹H NMR (250 MHz, CDCl₃) $\delta_{\rm H}$ 39 [6H (OMe), s], 52 [2H (CH₂O), s], 5 30 [1H (HCH=), dd, J_{gem} 1 5, J_{cis} 11 5], 6 06 [1H (HCCO₂), dd, J_{trans} 17 5, J_{cis} 11 5], 6 48 [1H (HCH=), dd, J_{trans} 17 5, J_{gem} 1 5], 7 00(0) [4H (H^{5 6 5' 6'}), d fine splitting, J_{ortho} 7 6 (2 unresolved signals)], 7 27 [1H (H³), dd, J_{meta} 2 5, J_{ortho} 8 0], 7 30 [1H (H²), dd, J_{para} 0 5, J_{ortho} 8 0], 7 38 [1H (H¹) dd, J_{para} 0 5, J_{meta} 2 5], 8 13(6) [2H (H^{4 7} or H^{4'7'}), d fine splitting, J_{ortho} 7 6], 8 14(5) [2H (H^{4 7} or H^{4'7'}), d fine splitting, J_{ortho} 7 6], 13C NMR (63 MHz) $\delta_{\rm C}$ 55 50 (OCH₃), 61 35 (ArCH₂), 113 87 (C^{5 6} or C^{5 6'}), 113 93 (C^{5 6} or C^{5' 6'}), 121 26, 121 58, 122 64, 122 93, 123 67, 127 91, 129 43, 131 69 (=CH₂), 132 32 (C^{4 7 4' 7'}), 146 54, 148 47, 163 99, 164 09, 164 37, 164 62, 165 58 §

Polymerisation. All polymerisations were carried out in glass polymerisation tubes containing the comonomer and monomer **III** in the appropriate proportions as a 10% w/v solution in either THF or chlorobenzene AIBN (typically 4 mol%) was added to initiate polymerisation Polymerisation was carried out *in vacuo* at 55 °C for 24 h The reaction mixture was then precipitated into cold methanol The polymer was then filtered, dissolved in dichloromethane and reprecipitated twice The purified polymer was then dried overnight in a vacuum oven In all cases the absence of any detectable amount of solvent or unreacted monomer was confirmed by ¹H NMR The spectroscopic data for two selected samples are included below

Polymer sample L50 v_{max}/cm^{-1} 3079, 2954, 1731, 1605, 1581 and 1513, ¹H NMR (250 MHz, CDCl₃) $\delta_{\rm H}$ 24–11 [(CHXCH₂), broad], 36–32 [(OMe), s], 40–36 [(ArOMe), s], 52–47 [(CH₂O), s], 81–69 [(Ar-H), broad], ¹³ C NMR (63 MHz) $\delta_{\rm C}$ 314, 349 (broad), 413, 515, 554, 610, 1138, 1140, 1212, 1216, 1228, 1233, 1294, 1323, 1484, 1641, 173 (weak), 174 (weak)

Polymer sample L100 v_{max}/cm^{-1} 1730, 1605, 1581 and 1512, ¹H NMR (250 MHz, CDCl₃) $\delta_{\rm H}$ 2 4–1 1 [3H (CHXCH₂)O, broad], 5 2–4 7 [2H (CH₂O), s), 3 9–3 5 [6H (ArOMe), s], 8 2–6 9 [11H (Ar-H), broad m], ¹³C NMR (63 MHz) $\delta_{\rm C}$ 29 64, 31 12, 40 43, 41 19, 55 40, 60 87, 113 80, 113 92, 121 09, 121 54, 122 42, 123 33, 129 33, 129 63, 132 21, 146 14, 148 39, 163 88, 164 13, 172 03, 173 78

§ Interpretation of the ¹³C NMR spectrum for this compound (and its precursor) was somewhat complicated by the perturbation to the symmetry imposed by the presence of the polymerisable unit on the central aromatic ring The predicted ¹³C chemical shifts on the basis of the data tabulated in Williams and Flemming³³ are shown below Naturally this simple procedure is not sufficiently precise to predict any differences in the chemical shifts for the carbons of the 4-methoxybenzoyl substituents, however, by knowing the approximate position of the peaks it was possible to determine where the chemical shifts were too similar to allow resolution of the signals and where overlap occurred



Cross-linked samples of the copolymer of III and hydroxy ethyl acrylate were prepared by casting films of the polyme from a dichloromethane solution containing the polymer and the appropriate proportion of disocyanatohexane and triethyl amine (added to catalyse the reaction between the isocyanatunits and pendant hydroxy functionality on the polymer) Thsolution was then heated at the required temperature fo several days ¹⁵

3-(4-Methoxybenzoyloxy)benzaldehyde. The ester was pre pared by the reaction of 3-hydroxybenzaldehyde with p-anisoy chloride in THF (50 ml) containing triethylamine as described above The product was dried under vacuum before finally being purified by column chromatography (alumina with dichloromethane as the eluent) to yield a single product by TLC and NMR (yield ca 40%), v_{max}/cm^{-1} 1721, 1694, 160 and 1577, ¹H NMR [400 MHz, (CO₃)₂SO], $\delta_{\rm H}$ 699 [2H (H⁵⁶), d fine splitting, J 93], 749 [1H (H³), ddd, J_{ortho} 63 J_{meta} unresolved], 7 59 [1H (H²), t, J_{ortho} 7 8] 7 74 [1H (H₁) t, J_{meta} 1 5 (2 equivalent)], 7 79 [1H (H ortho to CHO, pare to O-CO), dm, J_{ortho} 6 3, J_{meta} 1, unresolved], 8 16 [2H (H^{4 7}) d fine splitting, Jortho 93], 1004 [1H (CHO), s], ¹³C NMF (100 MHz) $\delta_{\rm C}$ 55 5 (OMe), 113 90 (C^{5 6}), 121 25, 122 62, 127 18 128 01, 130 12, 132 43 (C^{4 7}), 137 76, 151 67, 164 15, 164 53 191 23 (CHO)

Reduction of 3-(4-methoxybenzoyloxy)benzaldehyde. 3-(4 Methoxybenzoyloxy)benzaldehyde (005 g, 0287 mmol) wa placed in a round bottom flask, a septum was fitted and $(CD_3)_2$ SO (2.5 ml) was added A solution of NaBH₄ (0.057 g 1 52 mmol) in D_2O (0 01 ml) was added via a syringe (over : period of a few minutes) to the round bottom flask and the reaction was then left at room temperature. The reaction was followed by ¹H NMR (60 MHz), after reaction was complete a small amount of D₂O was added and the reaction lef overnight High resolution NMR spectroscopy in conjunction with GC-MS was then used to ascertain the product(s) formed which were not isolated, GC-MS major peak at m/z 15. (M⁺), ¹H NMR [250 MHz, (CD₃)₂SO] $\delta_{\rm H}$ 37 [3H (OMe) s], 4 31 [2H (CH₂O), s], 4 40 [1H (OH), s], 6 45 [2H (H³ and H ortho to CH_2 and para to O-CO), d, J_{ortho} 78 (overlapping signals)], 654 [1H (H¹), broad], 685 [2H (H⁵⁶), d fine splitting, Jortho 87], 694 [1H (H²), t, Jortho 77], 720 [2H (H⁴⁷), d fine splitting, J_{ortho} 85]

2-(4-Methoxybenzoyloxy)benzaldehyde. The procedure user for 3-Hydroxybenzaldehyde (see above) was repeated for the 2-isomer The product was dried under vacuum before finally being purified by column chromatography (alumina with dichloromethane as the eluent) to give a single product by TLC and NMR (yield *ca* 30%) mp 82–84 °C, v_{max}/cm^{-1} 1725 1694, 1604 and 1577, ¹H NMR (400 MHz, CDCl₃) $\delta_{\rm H}$ 39([3H (OMe), s], 701 [2H (H⁵ 6), d fine structure, J 8 8], 73. [1H (H₂), dd, J_{ortho} 8 3, J_{meta} 10], 741 [1H (H meta to CHO para to ester), t, J_{ortho} 7 6] 7 67 [1H (H³), td, J_{ortho} 7 8, J_{met} 14), 795 [1H (H¹), dd, J_{ortho} 7 8, J_{meta} 19], 818 [2H (H⁴⁷) d fine splitting, J_{ortho} 8 8], 10 22 [1H (CHO) s], ¹³C NMF (100 MHz) $\delta_{\rm C}$ 555 (OMe), 114 35 (C5,6), 120 85, 123 66 126 33, 128 40, 129 82, 132 53 (C⁴⁷), 135 73, 152 65, 164 31 164 64, 188 51 (CHO)

Reduction of 2-(4-methoxybenzoyloxy)benzaldehyde. The procedure used for the reduction of 3-(4-methoxy benzoyloxy)benzaldehyde was repeated for 2-(4' methoxybenzoyloxy)benzaldehyde, GC-MS m/z 109 (M⁺) ¹H NMR [250 MHz, (CD₃)SO] $\delta_{\rm H}$ (from 2-methylphenol 202 [3H (CH₃), s], 6 64 [1H (H para to OH), t, J_{ortho} 7 3] 6 80 [1H (H²), d, J_{ortho} 7 3], 6 95 [1H (H³) td, J_{ortho} 7 3, J_{met} 17], 7 03[1H (H¹), d, J_{ortho} 7 3], (from 4-methoxybenzoic acid

3.77 [3H (CH³), s], 6.84 [2H (H^{5,6}), d, J_{ortho} 8.8], 7.81 [2H (H^{4,7}), d, J_{ortho} 8.8].

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