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Effect of ionic aggregates of sulphonate groups on the liquid crystalline behaviours of liquid crystalline elastomers

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A series of siloxane-based liquid crystalline elastomers containing biphenyl benzoate mesogenic units and ionic Brilliant Yellow moieties was synthesized. The chemical structures and liquid crystalline properties of the samples were characterized by FTIR, ^{1}H NMR, DSC, POM and XRD. The effective crosslink density of the ionic elastomers was determined by swelling experiments in organic/buffer mixtures. All the polymers displayed a smectic mesophase. It was shown that the glass transition and melting point temperatures of the polymers increased slightly with increasing content of ionic and mesogenic groups in the polymers, while the liquid crystal mesophase region decrease slightly.

1. Introduction

Liquid crystalline elastomers (LCEs) are being actively studied because of their technological potential and scientific challenges. The polymer elastomer structures of LCEs are usually produced by the introduction of crosslinking into liquid crystalline polymer systems. LCEs combine the properties of a liquid crystalline (LC) phase (the combination of order and mobility) with rubber-like elasticity. This combination results in materials with a number of unique optical, mechanical and piezoelectric properties [1].

Some recent work has been devoted to the functionalization of LCPs with ionic groups [2]. Ionic aggregates can play a role in physical crosslinking and provide a useful and characteristic viscoelastic behaviour of ionomers. Strong ionic interactions between polymer molecules are known significantly to enhance mechanical properties such as compressive strength [3]. They also dramatically improve the compatibility between different polymers in polymer blends [4]. The incorporation of a small concentration of ions into organic polymers has been shown to lead to microphase-separated ionic domains that greatly influence the properties of the polymers [5].

The most outstanding characteristic of slightly crosslinked LCEs is their good mechanical orientability [6, 7]. On the other hand, it is known that strong ionic interactions between polymer chains can significantly enhance mechanical properties. An ion-containing LCE displaying liquid crystalline phases is obviously of great interest for both basic and applied studies. Ionic LCEs would combine the mechanical properties of ionic polymers with the mechanical orientability of conventional LCEs, resulting in new technological applications.

In the present study, we prepared a series of siloxane-based LCEs using a divinyl monomer that contains biphenyl benzoate mesogenic units and ionic Brilliant Yellow moieties. The elastomers may be readily prepared in a one-step reaction by graft copolymerization, their general structure is shown in the scheme.

2. Experimental

2.1. *Characterization*

Fourier transform infrared spectroscopy (FTIR) of the synthesized polymers and monomers in the solid state were obtained by the KBr method performed on a Nicolet 510P FTIR spectrometer. ^{1}H NMR (300 MHz) spectra were obtained with a Varian WH-90 NMR spectrometer with Fourier transform, with dimethyl sulphoxide-d$_6$ (DMSO-d$_6$) or CDCl$_3$ as a solvent and tetramethylsilane (TMS) as an internal standard. Thermal transition properties were measured using a differential scanning calorimeter (DSC), model DSC204 from Netzsch, under nitrogen at a heating rate of $10^\circ\mathrm{C\,min^{-1}}$. Visual observation of liquid crystalline transitions under crossed polarizers was made with a Leits Laborlux S polarizing optical microscope (POM) equipped with a Mettler FP82 hot stage. X-ray measurements were performed using an Rigaku DMAX-3A X-ray diffractometer. Nickel-filtered CuKα (λ=1.542 Å) radiation was used as the incident

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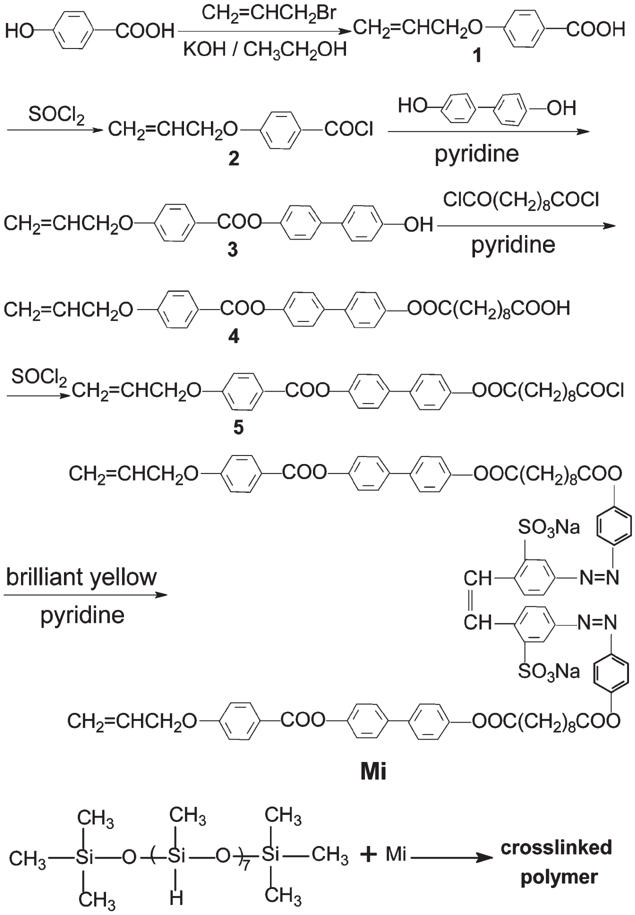


Scheme 1. Synthesis route for the monomer and polymers.

X-ray beam. Sodium ion was characterized by an atomic absorption spectrophotometer A-1800 from Hitachi, using air/acetylene as flame at wavelength 589 nm.

2.2. *Materials*

3-Bromopropene, p-hydroxybenzoic acid, potassium hydroxide, sodium bicarbonate, 4,4′-biphenyldiol, hexachloroplatinic acid and poly(methylhydrogeno)siloxane (PMHS) (M_n=700–800) were obtained from Jilin Chemical Industry Company and used without any further purification. Pyridine, thionyl chloride, toluene, ethanol, chloroform, tetrahydrofuran (THF) and methanol were purchased from Shenyang Chemical Co. Brilliant yellow (Eastman Kodak Chemical Co.) and sebacoyl dichloride (Aldrich) were used as received. All solvents were purified by standard procedures.

2.3. *Monomer synthesis*

The ionic liquid crystalline monomer was prepared by an esterification reaction, as shown in the scheme 1.

2.3.1. 4′-Hydroxybiphenyl-4-yl 4-allyloxybenzoate, 3. 4-Allyloxybenzoic acid (**1**) was synthesized according to a reported procedure [8]. 4-Allyloxybenzoyl chloride (**2**) was obtained from **1** by reaction with thionyl chloride. 4′-Hydroxybiphenyl-4-yl 4-allyloxybenzoate (**3**) was synthesized from the reaction of excess 4,4′-biphenyldiol with **2**. 4,4′-Biphenyldiol (89.3 g, 0.48 mol) was dissolved in 300 ml pyridine. This solution was added dropwise to a pyridine solution of **2** (15.8 g, 0.08 mol) at room temperature. The reaction mixture was stirred at 100°C for 14 h in a dry atmosphere. After cooling to room temperature, the mixture was poured into 500 ml cold water and acidified with 6N hydrochloric acid. The precipitate was isolated by filtration and dried in a vacuum oven. Recrystallization from 95% ethanol gave white crystals of **3**; yield 71%, m.p. 205–206°C. IR (KBr, cm^{-1}): 3421 (–OH), 3028, 2933 ($-CH_2$), 1710 (C=O), 1605, 1507, 1268 (C–O–C), 1208, 1178, 1088, 1024 (C–O–C), 805. ^1H NMR (DMSO-d_6, δ/ppm): 5.08 (d, 2H), 5.70 (m, 1H), 5.83 (s, 1H), 6.12 (d, 2H), 6.81–6.91 (m, 4H), 7.17 (m, 2H), 7.47–7.64 (m, 6H).

2.3.2. Mono[4′-(4-allyloxybenzoyloxy)biphenyl-4-yl] decanedioate, 4. Compound **3** (3.0 g, 0.01 mol) was added to a solution of sebacoyl dichloride (19.1 g, 0.08 mol) in 230 ml pyridine. The mixture was heated and stirred at 80°C for 12 h in a dry atmosphere. The reaction solution was poured into a large excess of cold water and acidified with 6 N sulphuric acid. The resulting precipitates was isolated by filtration, washed with water and ethanol, and then recrystallized twice from acetic acid to give 3.0 g of mono[4′-(4-allyloxybenzoyloxy)biphenyl-4-yl] decanedioate (**4**); yield 62%. IR (KBr, cm^{-1}): 3029, 2930, 2853 ($-CH_2-$), 2690–2510 (–OH in –COOH), 1760–1700 (C=O in ester and carboxylic acid modes) 1605, 1504, 1269 (C–O–C), 1207, 1179, 1089, 1024, 902. ^1H NMR (DMSO-d_6, δ/ppm): 1.23–1.35 (m, 10H), 1.69 (m, 2H), 2.11 (m, 2H), 3.06 (m, 2H), 5.01 (d, 2H), 5.70 (m, 1H), 5.82 (s, 1H), 6.11 (m, 2H), 6.81–7.17 (m, 4H), 7.47–7.64 (m, 8H).

2.3.3. Sodium 2,2′-(1,2-ethenediyl)bis{5-{4-{9-{[4′-(4-allyloxybenzoyl)oxybiphenyl-4-yl]oxycarbonyl}nonanoyloxy}phenyl}azo}benzenesulphonate (Mi). A mixture of compound **4** (4.8 g, 0.01 mol) and 15 ml thionyl chloride was heated under reflux with stirring for 3 h. Excess thionyl chloride was removed by evaporation under reduced pressure. The crude 4′-(9-chlorocarbonylnonanoyloxy)biphenyl-4-yl 4-allyloxybenzoate (**5**) was added with stirring to 20 ml anhydrous THF, cooled in an ice bath and containing brilliant yellow (3.1 g, 5 mmol) and pyridine (15 ml). The mixture was then heated under reflux with stirring for 12 h. After completion of the reaction, the solution was poured into 400 ml cold water and acidified with 6 N hydrochloric acid. The resulting brown solid was filtered off, washed with water, and recrystallized from benzyl alcohol to give 4.6 g (61%) of ionic liquid crystalline monomer Mi. IR (KBr, cm^{-1}): 3051, 2931, 2853 ($-CH_2-$), 1760–1708, 1604, 1505, 1268, 1206, 1178, 1078, 1026, 815. ^1H NMR ($CDCl_3$-d_1, δ/ppm): 1.10–1.40 (m, 24H), 1.59–1.80 (t, 8H), 4.92–5.10 (d, 4H), 5.50–5.79 (m, 2H), 6.01–6.19 (m, 4H), 6.70–6.89 (d, 6H), 7.15–7.21 (d, 4H), 7.35–7.69 (m, 20H), 7.81–8.09 (d, 10H).

2.4. *Polymer synthesis*

For the synthesis of ionic LCEs P1, P2 and P3, the same method was adopted. The polymerization experiments are summarized in table 1. The synthesis of polymer P2 is given as an example. Monomer Mi (1.50 g, 1.0 mmol) was dissolved in 120 ml of dry toluene/THF (v/v=1/1). To the stirred solution, poly(methylhydrogeno)siloxane (PMHS, 0.47 g, 0.80 mmol) and 2 ml of H_2PtCl_6/THF (0.5 g hexachloroplatinic acid hydrate dissolved in 100 ml THF) were added, and the mixture used heated underding nitrogen at 65°C for 48 h. After filtration, the product was dried at 80°C for 2 h under vacuum to obtain 1.45 g of polymer. P2: IR (KBr, cm^{-1}): 2932, 2853 ($-CH_2-$), 2160 (Si–H), 1762–1707 (C=O in different ester modes), 1605, 1504, 1268, 1212, 1180, 1112, 1079, 1013, 805, 782.

3. Results and discussion

3.1. *FTIR spectra*

Evidence for the formation of the target polymer structures is found by comparing the IR spectra of polymers with corresponding monomers Mi. For P2, for example, the appearance of the peak at 2160 cm^{-1} for Si–H stretching indicates excess PMHS in the hydrosilylation reaction. Compared with Mi, polymer P2 shows strong overlapping peaks in the range 1000–1300 cm^{-1}. This is due to overlap found for stretching bands of O=S=O with C–O and Si–O stretching bands (see figure 1).

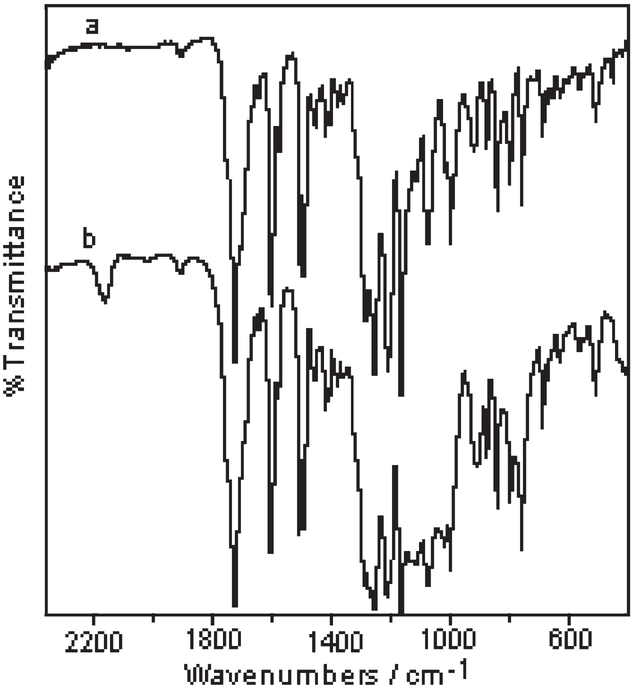


Figure 1. IR spectra in the range of 400–2300 cm^{-1} for (*a*) monomer Mi, (*b*) polymer P2.

3.2. *Swelling behaviour*

There are several ways to determine the effective crosslink density (or the molecular mass between the crosslink points M_c) of a polymer elastomer. Most commonly used are the methods of measuring the rubber elasticity or the swelling characteristics. We have studied these elastomers with the help of swelling experiments. Amphiphilic elastomers exhibit both hydrophilic and hydrophobic properties, so organic/water mixtures were chosen as swelling solvent. Because of the nature of the pH-sensitive ionic elastomers, an organic/buffer mixture was used as solvent. For ionic elastomers containing sulphonate groups, it has been shown that the swelling ratio is large in dimethyl sulphoxide (DMSO)/buffer, so our swelling measurements were made in this DMSO/buffer solvent [9].

Table 1. Polymerization and phase transition temperatures of the polymers.

	Feed			Thermal transitions[b]/°C			
Polymer	PMHS/mmol	Mi/mmol	Ion content[a]/%	T_g	T_m	T_c	ΔH/J g^{-1}
P1	1.0	1.0	2.2	62	157	238	13.67
P2	0.8	1.0	2.4	118	173	234	32.91
P3	0.6	1.0	2.5	109	175	238	41.72

[a]Mass content of ionic group Na^+ in the polymers obtained by atomic absorption spectrophotometry. [b]DSC data from the second heating curve, heating rate 10°C min^{-1}. T_m=melting point; T_c=clear point.

Swelling measurements were made in 10 ml of DMSO/buffer mixtures (volume ratio 1/1) with samples of about 0.2 g in initial weight. A buffer solution of desired pH and ionic strength I (0.1M) was used as a function of solvent composition. Buffer solutions of different pH values were made by the Britton–Pobinson method. Swelling was accomplished in several days at room temperature. Swollen elastomers removed from the solvent at regular intervals were dried superficially with filter paper, weighed and returned to the same conditions. Measurements were continued until a constant weight was reached for each sample.

The equilibrium/swelling ratio of elastomers was determined gravimetrically through the following equation:

$$Q = 1 + (W_2/W_1 - 1)\rho_p/\rho_s \tag{1}$$

where Q is the elastomer swelling ratio by volume; W_1 is the weight of the elastomer before swelling; W_2 is the weight of the elastomer at equilibrium swelling; ρ_p and ρ_s are the densities of elastomer and solvent, respectively. The volume fraction of elastomers $V_{2\mathrm{S}}$ was calculated as

$$V_{2S} = 1/Q \tag{2}$$

The density of the elastomers was determined in absolute ethyl alcohol by measuring the exact volume of the sample (~1 g).

Ionic elastomers in aqueous solutions present a more complicated situation than that of neutral polymers. When the elastomers contain ionizable groups, the forces that influence swelling may be greatly increased. The Flory–Rehner models which describe the molecular mass between crosslinks can only be applied to homogeneous elastomers [10]. Ionic elastomers do not fall in this category. Brannon–Peppas derived an equation to describe the ionic contribution term for both anionic and cationic systems [11]:

$$\begin{gathered} V_1\left[K_a/(10^{-pH}+K_a)\right]^2(V_{2S}/V)^2\Big/4I = \left[\ln(1-V_{2\mathrm{S}}) + V_{2S} + \chi V_{2S}^2\right] + \\ \left[V_1/(VM_c)\right](1-2M_c/M_n)\times V_{2r}\left[(V_{2S}/V_{2r})^{1/3} - (V_{2S}/V_{2r})/2\right] \end{gathered} \tag{3}$$

where M_c is the number average molecular mass between crosslinks; χ is the Flory polymer–swelling agent interaction parameter; V_1 is the molar volume of the swelling agent; I is the ionic strength of the swelling medium; K_a is the dissociation constant of ionizable groups on the polymer; V is the specific volume of dry polymer; M_n is the number-average molecular mass of the linear macromolecules before crosslinking; and $V_{2\mathrm{r}}$ is the polymer volume fraction after crosslinking but before swelling.

Using equation (3), we can obtain a linear relationship with χ and M_c values as the intercept and inverse slope, respectively, as expressed by equation (4):

$$A = \chi + B/M_c \tag{4}$$

where A and B are defined as

$$\begin{gathered} A = \Big\{V_1\left[K_a/(10^{-pH}+K_a)\right]^2(V_{2\mathrm{S}}/V)^2\Big/4I - \ln(1-V_{2\mathrm{S}}) - V_{2\mathrm{S}} + \\ 2\ V_1\ V_{2\mathrm{r}}\left[(V_{2\mathrm{S}}/V_{2\mathrm{r}})^{1/3} - (V_{2\mathrm{S}}/V_{2\mathrm{r}})\Big/2\right]\Big/(V\ M_\mathrm{n})\Big\}\Big/V_{2\mathrm{S}}^2 \end{gathered} \tag{5}$$

$$B = V_1\ V_{2r}\left[(V_{2S}/V_{2r})^{1/3} - (V_{2S}/V_{2r})/2\right]\Big/\left(V\ V_{2S}^2\right). \tag{6}$$

The relevant experimental parameters to be used are: I=0.1M; V_1=28.7 cm^3 mol^{-1}; M_n=800; pK_a=6.5. The parameter V is calculated by using density values of the polymers. Information about the structural properties of the elastomers is collected in table 2. By using both the experimentally measured polymer volume fractions $V_{2\mathrm{S}}$ of the elastomers in their eqilibrium-swollen state and the above-mentioned data, we can calculate the values of A and B; using the values of A and B, it is possible to establish the corresponding linear relationships involving χ and $1/M_\mathrm{c}$, as shown in figure 2. The χ and M_c values were determined via linear regression analysis of the lines given in figure 2, which are listed in table 2. From the results listed in table 2 it can be seen that for the ionic elastomer with the largest of PMHS content, relatively high values of M_c are found.

3.3. *Phase behaviour*

The LC phases of the polymers under investigation were characterized by POM, DSC and XRD. The results are collected in table 1. Figure 3 shows the DSC thermograms of all the polymers synthesized. The polymers P1,

Table 2. Some swelling properties of the Polymers.

				$V_{2\mathrm{S}}$					
Polymer	Density/g cm^{-3}	V/cm^3 g^{-1}	$V_{2\mathrm{r}}$	pH2.4	pH3.5	pH4.0	pH4.5	χ	M_c/g mol^{-1}
$\mathrm{P_1}$	1.26	0.79	0.79	0.42	0.38	0.35	0.33	0.81	1250
$\mathrm{P_2}$	1.31	0.76	0.76	0.50	0.44	0.34	0.30	0.85	1100
$\mathrm{P_3}$	1.35	0.74	0.74	0.55	0.47	0.38	0.27	0.88	920

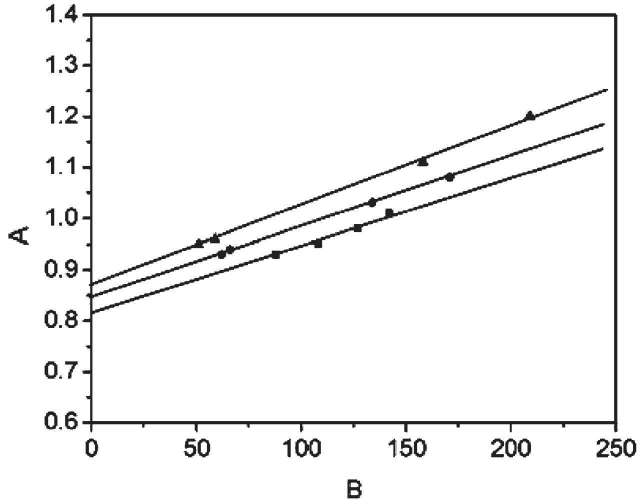


Figure 2. Determination of χ and M_c values of polymers from swelling data: (-■-) for P_1; (-•-) for P_2; (-▲-) for P_3.

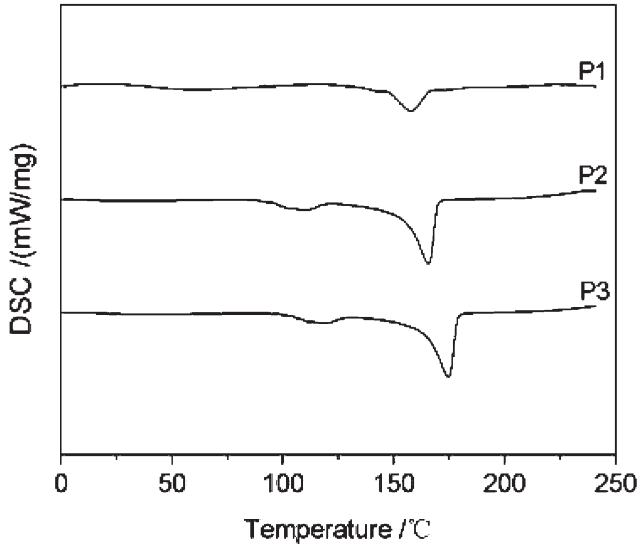


Figure 3. DSC thermograms of the polymers on second heating (10°C min^{-1}).

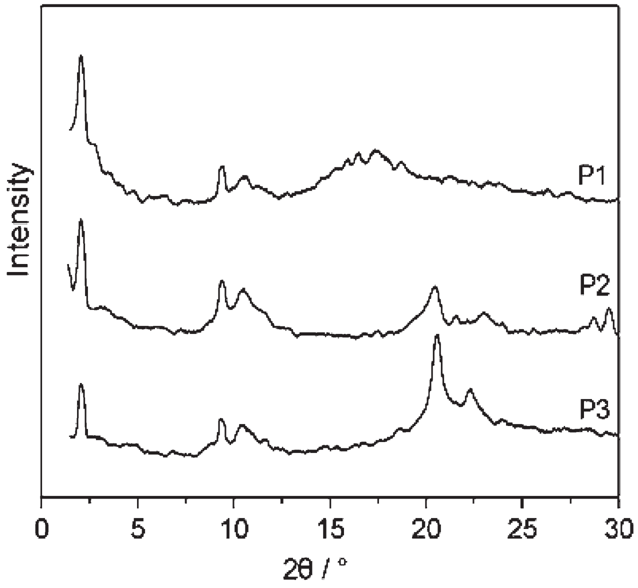
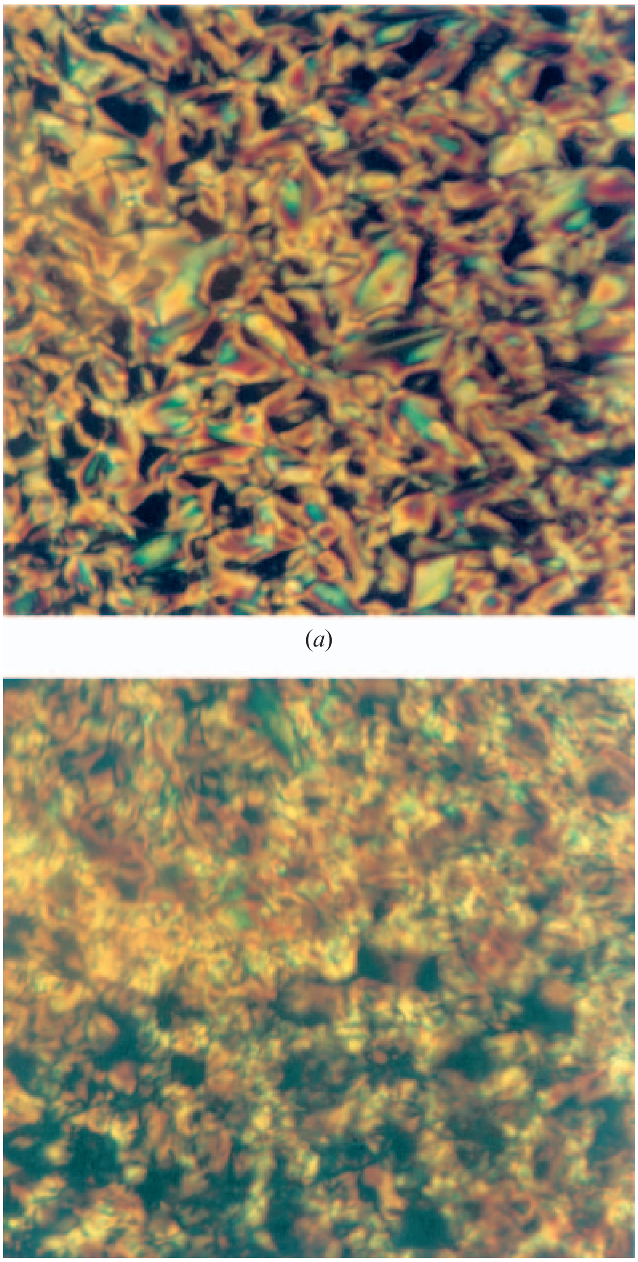


Figure 4. X-ray profiles of the polymers.

P2 and P3 displayed smectic mesophases. The samples were placed on glass plates, covered with a glass slide, and observed by POM using the hot stage, for their liquid crystalline behaviour and thermo-optical properties. For P1, P2 and P3, the smectic nature of the LC phase is characterized by the presence of sharp small angle reflections in the X-ray profile as shown in figure 4, clearly revealing the lamellar structure of the sample. Polymer P1 shows a mesomorphic sequence of G-Cr–SmA-I; the focal-conic fan-shaped texture of the SmA phase is observed at 187°C, as shown in figure 5(*a*) on heating. For P3, a focal-conic texture is seen at 178°C, see figure 5(*b*). On moving from P1 to P3, it was shown that the glass transition and melting point temperatures of the polymers increase slightly with the decrease of PMHS content in the polymers. In addition, the clearing points of the polymers were not all readily observed. The liquid crystal mesophase region decreases slightly with increasing crosslinking content from P1 to P3.

Both ionic groups and chemical crosslinking may influence the liquid crystalline behaviour of the ionic elastomers. Chemical crosslinking imposes additional constrains on the segmental motion of polymer chains, and might be expected to raise the glass transition temperatures. Liquid crystalline polymers are most commonly composed of flexible and rigid moieties. Therefore, self-assembly and nanophase separation into specific microstructures (often lamellar for side chain architecture) frequently occur due to geometric and chemical dissimilarity of the two moieties. The majority of side chain liquid crystalline polymers such as siloxane polymers are atactic; for such disordered systems low temperatures induce vitrification rather than crystallization. For polymer of this type, the glass transition temperature may be considered as a measure of the backbone flexibility.

For ionomers, ionic side chain polymers lead to nanophase-separated morphologies [12]. For ionomers with a relatively low proportion of ionic units, two-phase behaviour is frequently observed due to ionic aggregation in a relatively non-polar matrix, with consequent reduction in mobility of neighbouring non-polar regions. As a result, the incorporation of ionic groups leads to an elevated glass transition


(*a*)

(*b*)

Figure 5. Optical polarizing micrographs for (*a*) P1 at 187°C and (*b*) P3 at 178°C (200 ×).

temperature for ionomers based on amorphous, flexible polymers [13].

In the ionomer literature, cluster aggregation in which the ion clusters are completely surrounded by the organic material and actual microseparation of the ionic phase from the siloxane matrix takes place. For LC ionomers, it has been shown that ionic clusters are compatible with LC phases [14]. Competition between the formation of ionic cluster phases and the LC phase depends on the chemical structure. On the other hand, polymethylsiloxane has a low glass transition temperature; the phase separation process should thus be rapid because the siloxane matrix has a high mobility [15]. Obviously the organization of the longer hard segments is easer, resulting in a higher degree of crystallinity of the hard phase. These results demonstrate the behaviour of the siloxane soft segment glass transition (T_g), and the melting temperature corresponds to crystallization. Therefore a large variation in glass transition and melting point for P3 is seen, as compared with P1.

For the polymers P1, P2 and P3 which contain fewer ionic crosslinking groups, the formation of the LC phase is dependent on the competition between ionic cluster phases and LC phases. As a result, the polymers exhibit behaviours analogous to that of conventional LC elastomers. These results are confirmed by X-ray measurement. Diffraction peaks were observed in the X-ray profiles of as-cast films of P1, P2 and P3 as illustrated in figure 4; the data are listed in table 3. All the polymers show a sharp diffraction peak around $2\theta=2.1°$, and the derived Bragg spacing (*d*) is 42 Å in the profiles. The presence of these peaks at small angles suggests the layered packing of the mesogenic groups. However, there are some differences among polymer P1, P2 and P3. For P1, there is diffuse X-ray peak around 18° suggesting unordered structure between molecules. For P2 and P3, some sharp peaks are seen in the region around 20.4°, corresponding to the lateral distance between molecules, which is due to an increasing of crystallinity with increasing content of ionic and mesogenic groups. Also, P3 shows a stronger diffraction peak at $2\theta=20.6°$ than the small angle diffraction peak intensity. This indicates that it possesses a higher ordered smectic phase.

Table 3. X-ray data for the series of polymers.

Peak number	P1			P2			P3		
	$2\theta/°$	Intensity	d/Å	$2\theta/°$	Intensity	d/Å	$2\theta/°$	Intensity	d/Å
1	2.1	100	42.6	2.1	100	41.8	2.2	70	41.9
2	16.4	60	5.4	20.4	34	4.3	20.6	100	4.3
3	17.4	64	5.1	29.5	25	3.0	22.2	38	4.0

4. Conclusions

We have synthesized a series of liquid crystalline elastomers containing biphenyl benzoate mesogenic units and brilliant yellow moieties, which are siloxane-based materials. An ionic divinyl monomer, sodium 2,2′-(1,2-ethenediyl)bis{5-{4-{9-{[4′-(4-allyloxybenzoyl)-oxybiphenyl-4-yl]oxycarbonyl}nonanoyloxy}phenyl}azo}-benzenesulphonate, was used as liquid crystalline monomer and chemical crosslinking agent. The polymers were prepared in a one-step reaction with ionic groups Na^+ content of around 3% (mass content). Their chemical structures were determined by various experimental techniques including FTIR and ^{1}H NMR. The liquid crystalline properties were characterized by DSC, POM, and XRD. The effective crosslink density of the ionic elastomers was determined by swelling experiments in organic/buffer mixtures. All the polymers displayed a smectic mesophase. It was shown that the glass transition temperatures and melting points of the polymers increased slightly with increasing content of ionic and mesogenic groups in the polymers, while the liquid crystal mesophase region of stability decreased slightly from P1 to P3.

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