LIQUID CRYSTALS, 2000, VOL. 27, NO. 12, 1683–1689

Improvement of LPS-based command surfaces: effect of inserting a flexible disiloxane segment into the azo side chain on photo-driven response

BIN KONG, LI CUI, PING XIE, RONGBEN ZHANG*
Polymer Chemistry Laboratory,
Chinese Academy of Sciences and China Petro-chemical Corporation (PCLCC),
Center for Molecular Science, Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100080, PR China

CHAOBIN HE and NEAL TAI-SHUNG CHUNG
Institute of Materials Research and Engineering of The National University of
Singapore, Singapore 119260

(*Received 15 March 2000; accepted 25 May 2000*)

A new synthetic route for azo grafted ladder-like polysilsesquioxanes (LPS) used for fabricating command surfaces has been developed. In comparison with previous work, the grafting ratio of azobenzene on the LPS backbone could be controlled more accurately and the low molar mass impurity, which might influence the concerted action of the azobenzene units as command moieties on the surrounding LC molecules, could be readily removed by repeated precipitation. The results of our measurements indicate that inserting a flexible disiloxane segment into the spacer of the side group can improve the photo-driven response. The response steepness of a LC cell is 20 times that of our previous result. However, the response speed also depends on the spacer length and the content of azo side groups. Using azo grafted LPS with a shorter spacer as the material for the command surface, the response speed is faster than with a longer spacer. Optimum response can be achieved at an azo content of 10 mol %.

1. Introduction

It is well known that the reversible change of the LC molecular alignment can be controlled by an electric field as in common LC displays or induced by photo-irradiation. In the latter case, the photo-driven process is achieved through the isomerization of azobenzene chromophores attached to the uppermost surface of the substrate plates or incorporated in polymer thin films covering the substrate plates. The photo-induced molecular information, i.e. the alteration of the chemical structure as well as of the orientational direction of the chromophores attached to the uppermost layers, can be dramatically amplified by realignment of the LC molecules surrounding the chromophores [1, 2]. Ichimura *et al.* first proposed the concept of the 'command surface' [3, 4]. The photo-responses induced by command surfaces have been attracting practical interest for the fabrication of versatile optical elements, optical memory media [5, 6], liquid crystal aligning layers for display devices, systems with molecular micro-assembly [7] and birefringent optical elements involving polarizers, light guides, light modulators, etc. [8, 9]. So far, three kinds of photo-driven modes have been reported. The first type involved the change in LC director from homeotropic to planar or the reverse controlled by the *trans-cis*-isomerization of azobenzene units upon exposure to UV or visible light [3, 10]. The second type concerned in-plane homogeneous alignments and azimuthal alterations of the LC molecules triggered by the interaction of linearly polarized light (LPL) with the chromophore molecule [7, 11–14]. The third type involved the three-dimensional orientation attained by irradiation of polymer films with azobenzene side groups with non-polarized light [15] directed at an angle.

The ladder-like polysilesquioxanes (LPS) prepared by a new route under the name of 'stepwise coupling polymerization' are a new type of glass-like film-forming material which possesses excellent all round properties such as good transparency, high oxidative and thermal

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*Author for correspondence;
e-mail: zhangrb@infoc3.icas.ac.cn

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
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stability and good resistance to irradiation [16]. In our previous study [16, 17, 18], we used an azo grafted ladder-like copolyhydrogenmethylsilsesquioxane (PHMSQ) to modify quartz surfaces, and investigated the photo-responsive behaviour of LCs sandwiched between two such quartz plates. Some promising results were obtained, but some problems still existed such as the relatively slow response, the difficulty of controlling the grafting ratio and the removal of the low molar mass impurity azo derivatives from the product in solution. Although a high response sensitivity can be achieved with the help of some enabling technological means discussed in [17], these would cause device fabrication complexity and increase cost. In this paper, a new grafting route using copolyallylmethylsilsesquioxane (PAMSQ), instead of PHMSQ, and Si–H terminated monomer as starting materials, and inserting a flexible disiloxane segment into the spacer chain in the side groups is described; the command surface prepared by this method is shown to have greatly improved photo-driven response.

2. Experimental

2.1. *Materials*

All the reagents and solvents were commercially available and of analytical purity. 4-Hexyloxy-4′-undecenyloxyazobenzene (6AZO11) and 4-hexyloxy-4′-allyloxyazobenzene (6AZO3) were prepared according to our previous report [16, 17, 18] and the nematic liquid crystal TEB-30 (T_{NI} = 65°C) was purchased from the Liquid Crystal Materials Company of Tsinghua University (Beijing, China).

The film-forming materials, azobenzene grafted LPS, were synthesized by a hydrosilylation reaction using copolyallylmethylsilsesquioxane (PAMSQ) and side group precursors 6AZO3-HMM and 6AZO11-HMM, derived from 6AZO3 or 6AZO11 with 1,1,3,3-tetramethyldisiloxane (HMM), as starting materials. The whole synthetic route is shown in figure 1. The details are described below.

2.2. *Synthesis of the ladder-like copolyallylmethylsilsesquioxane (PAMSQ)*

PAMSQ was synthesized in a similar manner to that described in [16, 19]. The acronym P-*r* is used to refer to the PAMSQ with *r* giving the molar ratio of allyl to methyl. For example the synthesis of P-10 is now described. A solution of 70 ml of THF containing 2.704 g (0.025 mol) of 1,4-phenylenediamine (PDA) was added dropwise to a solution of 70 ml of toluene containing 6.728 g (0.045 mol) of methyltrichlorosilane (MTCS), 0.877 g (0.005 mol) of allyltrichlorosilane (ATCS) and 6.9 ml (0.05 mol) of triethylamine at − 5°C. After the dropwise addition had finished, stirring was continued for 30 min. Then another 70 ml of a solution of THF containing 1.8 ml of water was added dropwise to the above mentioned solution and stirred overnight. After that, the solution was filtered with suction to remove the solid amine salt and the filtrate evaporated *in vacuo* to remove THF. It was then dried overnight with anhydrous sodium sulphate. Next, the polycondensation and equilibration reaction was carried out by stirring the solution at 30°C for one day in the presence of three drops of sulphuric acid as catalyst. Finally, the solution was washed at least three times with a saturated solution of sodium chloride until neutral. It was again dried with sodium sulphate, to give a transparent and colourless solution.

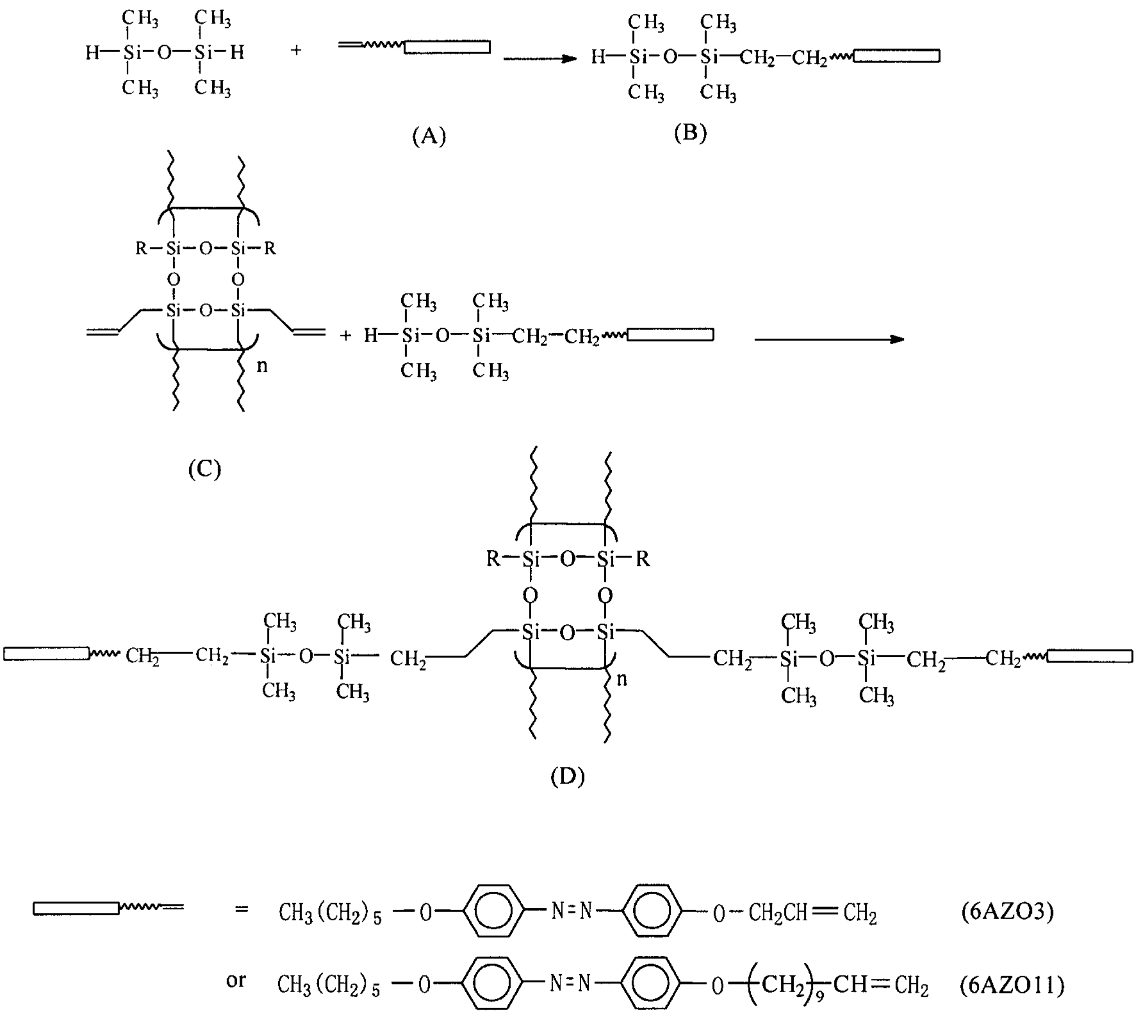
P-5 and P-30 were prepared in a similar way. The molar ratio of allyl/methyl was also calculated by means of ^{1}H NMR spectroscopy. The comparison between the determined and feed molar ratio is shown in table 1.

2.3. *Synthesis of 4-hexyloxy-4′-(3-(1,1,3,3-tetramethyldisiloxane)propyleneoxy)azobenzene (6AZO3-HMM) and 4-hexyloxy-4′-[11-(1,1,3,3-tetramethyldisiloxane)-undecyleneoxy]azobenzene (6AZO11-HMM)*

A Schlenk flask with 0.4085 g (1.2 mmol) of 6AZO3 was degassed three times with dry argon. Then 10 ml of methylthiophene-free toluene, 0.3 ml of dichloromethane solution containing 1 mg ml^{-1} of dicyclopentadienylplatinum dichloride (Cp_2PtCl_2) as catalyst, and 0.64 ml (3.6 mmol) of 1,1,3,3-tetramethyldisiloxane (HMM) in a much greater excess over stoichiometric ratio were injected. The solution was stirred at 80°C for 10 h. The completeness of the hydrosilylation reaction was confirmed by the disappearance of the absorption peak at 1640 cm^{-1} characteristic of the C=C bond in the IR spectra and the disappearance of the double bond with a chemical shift at 4.06 and 4.71 ppm in the ^{1}H NMR spectrum. Then the solvent and remaining HMM were removed *in vacuo* and the product was dissolved again in 10 ml of methylthiophene-free toluene. The solution was used in the subsequent grafting reactions without further purification. The crude product was purified by column chromatography on silica eluting with dichloromethane/light petroleum (1 : 1) to give pure 6AZO3-HMM as an orange solid.

Table 1. Comparison of the determined composition of copolyallylmethylsilsesquioxane (PAMSQ) and the feed stock ratio.

	Molar ratio of allyl/methyl		
Data origin	P-5	P-10	P-30
Feed stock	5 : 95	10 : 90	30 : 70
^{1}H NMR	4.6 : 95.4	10.15 : 89.85	28.5 : 71.5



R= $-CH_3$ or $-CH_2-CH=CH_2$

Figure 1. Synthetic route to azobenzene grafted LPS from a Si–H terminal monomer (B) and copolyallylmethylsilsesquioxane (PAMSQ) (C).

The synthesis of 6AZO11-HMM was carried out similarly to that of 6AZO3-HMM.

2.4. *Synthesis of 6AZO3-HMM grafted PAMSQ (PAZ3) and 6AZO11-HMM grafted PAMSQ (PAZ11)*

The acronym PAZ*n*-*r* is used to refer to the LPS in which *n* indicates the number of CH_2 groups in the spacer and *r* indicates the molar ratio of allyl to methyl groups. In the case of PAZ3-10, after flushing with dry argon three times, the Schlenk flask containing 0.01 mmol of P-10 (allyl = 0.001 mmol, methyl = 0.009 mmol) and excess 6AZO3-HMM dissolved in 10 ml of methylthiophene-free toluene was heated at 80°C under an argon atmosphere. Then 0.5 ml of a dichloromethane solution containing 1 mg × ml^{-1} of Cp_2PtCl_2 was added and the system stirred for 10 h. The completion of this reaction was confirmed by the disappearance of the absorption at 1640 cm^{-1} characteristic of the C=C bond in the IR spectrum and the disappearance of the proton of the double bond in the ^1H NMR spectrum. The reaction solution was cooled and the solvent removed *in vacuo* to give a solid which was then redissolved in toluene and precipitated with methanol more than three times, until the methanol solution was colourless and an orange product was obtained. The preparation procedure for PAZ11 is similar to that for PAZ3.

2.5. *Film fabrication and cell assembly*

A 0.5 wt % toluene solution of PAZ3 (or PAZ11) was spin coated onto a cleaned quartz glass plate at 1500 rpm to form a uniform thin film. The film was then annealed at 80°C for 1 h. A cell was then assembled using 8 μm-thick polyethylene film as a spacer between two plates covered with the film of PAZ3 (or PAZ11). The nematic liquid crystal TEB-30 was filled in by capillary action at 70–80°C.

2.6. *Measurement of photo-response*

A high pressure mercury lamp supplied 365 nm UV light as the driving source. The intensity of the UV light irradiated onto the film surface was 0.5 mw cm^{-2}. The light was nearly normal to the substrate plane. As described in a previous report [17], a computer-connected measuring system including a polarizing microscope, a photodiode and an amplifier was used to detect the photo-driven response of the cell. The sample cell was placed on a thermostat hot stage between two crossed polarizers. A laser diode (He-Ne laser, 633 nm) provided the light source for the detecting system. The intensity of the transmitted light passing through the sample and two polarizers was detected with the photodiode, which was connected to the computer through an amplifier. All data were program-controlled by the computer.

3. Results and discussion

In our previous study, copolyhydrogenmethylsilsesquioxane (PHMSQ) was used as the starting material to prepare azobenzene grafted LPS which was employed as the film forming material for the command surface. Although a high response sensitivity of the photo-driven cell was achieved with the aid of enabling technological methods, such as rubbing the command surface or applying a critical in-plane electric field, it was difficult to control accurately the content of grafted azo units and completely to remove the low molar mass impurity from the crude polymer solution. Because reactive Si–H groups remained on the LPS backbone, covered by bulky adjacent groups and the main chain, they could produce gelation in the precipitation treatments. It is obvious too that low molar mass impurity might affect the reorientation process of the LC molecules. Besides, it is difficult to control the ratio of hydrogen to methyl groups in the starting material PHMSQ because of the significant difference in reactivity between $HSiCl_3$ and $MeSiCl_3$.

Here an improved route is presented. Firstly, instead of PHMSQ, copolyallylmethylsilsesquioxane (PAMSQ) is used as the starting material in which the molar ratio of allyl to methyl can be controlled by the feed stock ratio of allyltrichlorosilane to methyltrichlorosilane. The composition of the copolymer was determined by ^{1}H NMR spectroscopy, and the results are very consistent with the feed stock ratio of allyl to methyl groups as shown in table 1. Secondly, the vinyl-terminated azo derivative (A) was reacted with an excess of HMM to obtain an active monomer (B) with a Si–H terminal group. Then, the PAMSQs react with the excess of monomer (B) by hydrosilylation to obtain the azobenzene grafted LPS (D), in which the grafted ratio was almost same as the content of allyl groups in the starting material. Finally, the additional advantage of this method is that the low molar mass impurity could be removed completely by repeat precipitation with methanol. Consequently, compared with the previous result, the photo-driven response of the title command surface is quicker as shown in table 2, figure 2 and figure 3.

The improvement in the photo-response can be attributed not only to the absence of low molar mass impurity, but also to the insertion of a flexible disiloxane segment in the spacer, which can remarkably increase the mobility of the side group [20]. Because the transmittance determined is dependent on the technical parameters of the LC cell and other factors, normalization is neccessarily made of the two curves determined in our previous report and presented here; these normalized curves are shown in figure 2.

In addition, we also investigated the effect of the spacer length and the azo content on the photo-driven response. LC molecules in all cells were homeotropically oriented before UV irradiation and the appearance was dark between crossed polarizers. Upon exposure to 365 nm UV light, the cell turned bright, indicating that the alignment of the LC had changed to homogeneous. A series of photo-response curves was recorded as shown in figure 3 and the calculated results are listed in table 2. The sharp change in the rate of transmittance increase took place at t_1 and t_2, which were determined from the zero of the Y ordinate in the 3rd order derivative curve as shown in figure 4 for PAZ3-10 as an example. t_1 is

Table 2. The effect of spacer length and azo content on the photo-optical response.

	Response time/s		
Film	t_1	t_2	$t_2 - t_1$
PAZ3-5	9.2	12.5	3.3
PAZ3-10	4.1	6.0	1.9
PAZ3-30	5.3	9.1	3.8
PAZ11-5	12.1	19.1	7.0
PAZ11-10	6.0	9.0	3.0
PAZ11-30	22.9	33.6	11.3
Ref [17]	8.0	45.6	37.6

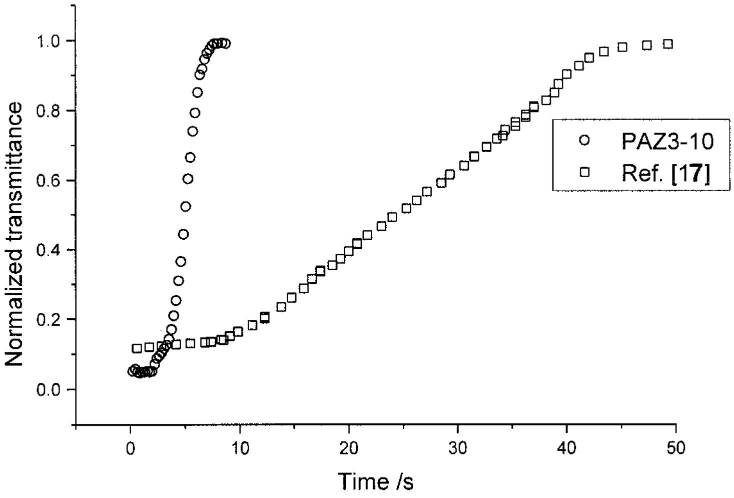
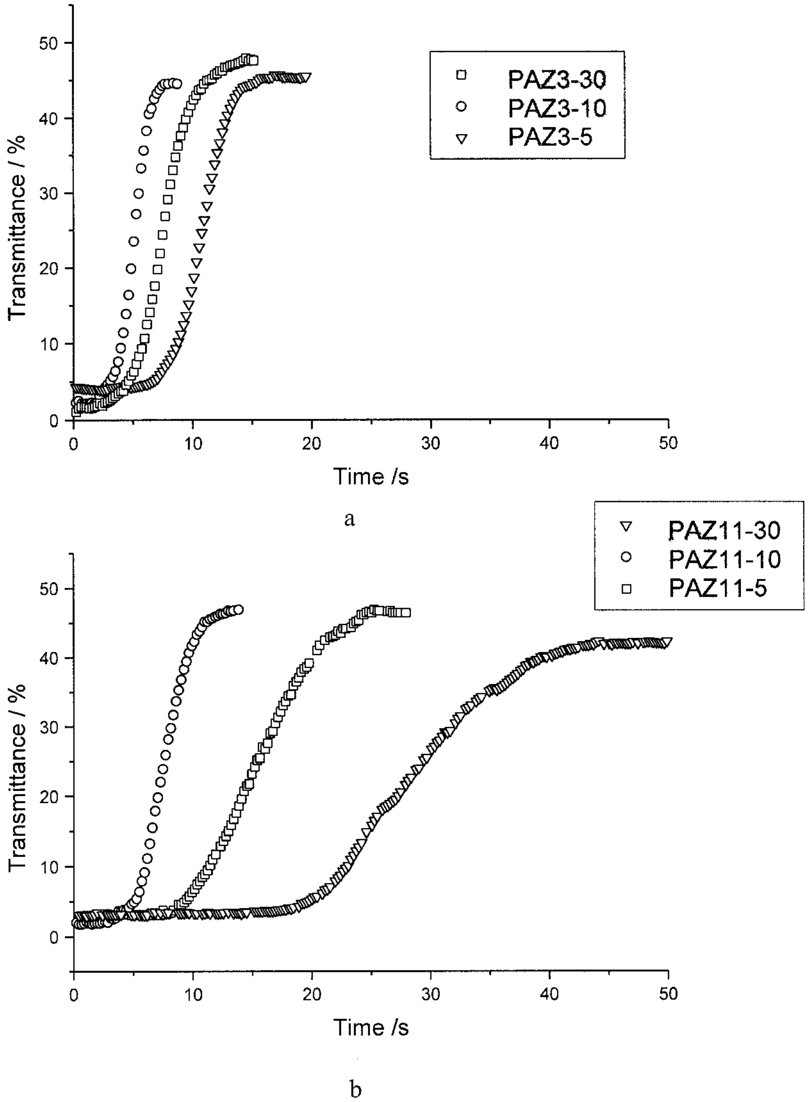


Figure 2. Normalized photo-optical response curves of cells based on PAZ3-10 under a UV intensity of 0.5 mW cm^{-2} and from a previous report [17] under a UV intensity of 1.0 mW cm^{-2} at room temperature.



a

b

Figure 3. The effect of spacer length and azo content on the photo-driven response: PAZ3-(5, 10, 30) (*a*) and PAZ11-(5, 10, 30) (*b*) under a UV intensity of 0.5 mW cm^{-2} at room temperature.

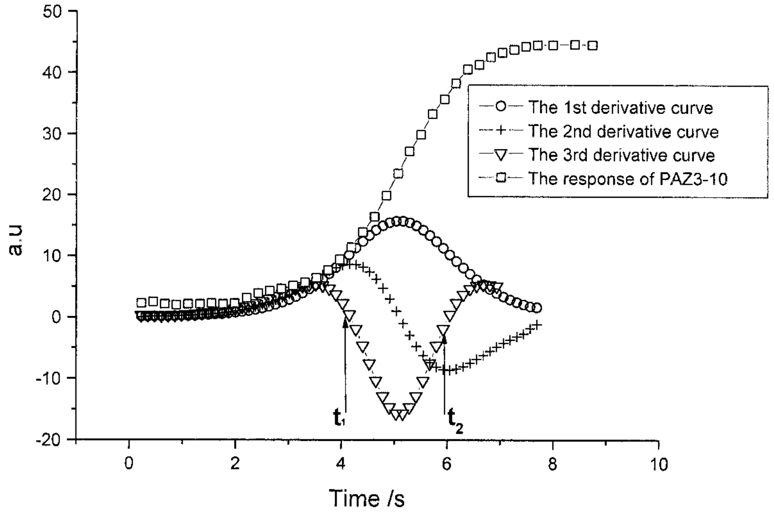


Figure 4. Definition of t_1 and t_2 from the 3rd order derivative curve of the experimental photo-response curve.

defined as the starting point of the photo-response and t_2 as the end of the photo-response. The period ($t_2 - t_1$) can be used to represent the response steepness, which is inversely proportional to the rate of change in the transmittance.

As shown in table 2, at the same azo content, the t_1 and ($t_2 - t_1$) values for LC cells based on PAZ3 are less than those for PAZ11; this means that the photo-response based on PAZ3 is faster than that for PAZ11. Comparing the photo-response speed at different azo contents for both PAZ3 and PAZ11, the optimal photo-response speed was achieved at 10 mol % of azo content, whereas the photo-response became slower at 5 and 30 mol %, respectively.

It has been suggested that the photo-driven response based on the command surface involves two processes: the first is the *trans*- to *cis*-photo-isomerization of the azo unit, which is the faster; the second is the induced reorientation of the LC molecules surrounding the azo units, which is slower.

It was found that the photo-induced response of the PAZ11-based command surface was slower than that of PAZ3 because the photo-induced configuration of the side groups with the longer spacer might become disoriented. In contrast, the relaxation effect in PAZ3 with the shorter spacer was much less.

With increasing content of azo units, it can be expected that reorientation of the LC molecules would be more easily induced, which corresponds to the increase in response speed with increase in azo content from 5 to 10 mol % as shown in figure 3. However, sufficient free volume around the azo moieties must be available [21]. When the azo content was excessively increased, the decrease of free volume around the azo moieties will cause reciprocal interference among them and influence the response speed, corresponding to the decrease in photo-response speed from 10 to 30 mol % of azo content.

4. Conclusion

A new grafting route for connecting azobenzene-containing side groups onto a ladderlike polysiloxane was developed. The photo-driven response of a LC cell fabricated using the new film-forming material for the command layer was remarkably improved because of insertion of a flexible disiloxane segment into the spacer of the azo side groups and removal of low molar mass impurity. The response steepness of the LC cell was 20 times better than the previous result.

This project is financially supported by the National Natural Science Foundation of China (No. 29874034 and 29974036).

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