RSC Advances

PDLC films with graft copolymer matrix exhibited slow rise times and fast decay times.

Response times of polymer dispersed liquid crystals with linear or graft copolymer matrix prepared by controlled living polymerization

Tian Lan, Wenjie Yang, Hao Huang, Yinghan Wang[*]

ABSTRACT: Response time, an important property of polymer dispersed liquid crystals (PDLCs), was reported to be affected by the structures of polymer matrix. In this study, reversible addition fragmentation chain transfer (RAFT) polymerization and atom transfer radical polymerization (ATRP) were used to synthesize well-defined copolymer matrix. A kind of graft macroinitiator with both controlled main chain and branched chains was employed to prepare PDLCs with graft copolymer matrix; meanwhile a linear macroinitiator was also synthesized to prepare PDLCs with linear copolymer matrix. The effect of different matrix structures on response times was investigated. It was found that the introduction of branched chains made a big difference to response times, and a possible mechanism was proposed.

KEYWORDS: PDLC; graft copolymer matrix; response times; RAFT; ATRP.

1. Introduction

[*] Corresponding author. Tel./fax: +86 28 8546 0823.

State Key Laboratory of Polymer Materials Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu 610065, PR China

E-mail address: wang_yh@scu.edu.cn.

Polymer dispersed liquid crystals (PDLCs), a kind of novel materials, have intensively attracted researcher's interests for their particular properties.[1-5] Under a suitable electric field, a PDLC film can be switched from a light-scattering opaque state (OFF state) to an optical transparent state (ON state) without polarizer and alignment layers because of the refractive index (RI) matching between liquid crystals (LCs) and polymer matrix.[6] Generally speaking, many methods have been reported to prepare PDLCs, such as thermally induced phase separation (TIPS), solvent induced phase separation (SIPS) and polymerization induced phase separation (PIPS).[7] Among them, the most convenient method is PIPS because of its industrialization prospect, in which a homogeneous solution of monomer/prepolymer and liquid crystal was initiated (usually by UV light) and polymerized until the polymer and liquid crystal were well separated. Due to PDLC's unique properties, they find applications such as light shutters, smart windows and large-scale flexible displays in a range of optical devices.[8] For practical applications, PDLC films with fast response times, including rise time and decay time is of great importance.

It is reported that the response times of PDLC films are dependent on several parameters. Many researchers discovered that the shape of LC droplets was an important factor to affect the response times of PDLCs.[9] Drzaic reported that PDLC films with large droplets had faster rise time than those with small droplets.[18] Beyond that, the structure of polymer matrix is obviously an important factor to control the response times of PDLCs.[13, 19] Thus, a clear study of the size of LC droplets[9-12] and the properties of polymer matrix[13-17] on the boundary surface[13] is necessary. There can

be no doubt that all of these factors can affect the anchoring force between LC

droplets and polymer matrix. In general, this anchoring force is the most important

factor to affect the response times of PDLCs.

In our previous work, living polymerization played an important role in the

preparation of PDLC films for its good properties in synthesizing well-defined

polymers.[20-27] But these researches were mainly focused on the electro-optical

properties of PDLCs, such as driving voltage, transmittance and memory effect,

seldom on the response times. On one hand, it was reported that the size of the LC

droplets and the molecular weight of polymer matrix had great influence on the

response times of PDLCs,[9] and the different structures between linear and graft

copolymer matrixes had enormous impact on the two factors.[27] On the other hand, the

anchoring force on the boundary surface is a factor to influence the response times,[13]

and the different structures between linear and graft copolymer matrixes precisely

affect the anchoring force on the boundary surface. Thus, it is essential to require a

better understanding of the effect of different structures between linear and graft

copolymer matrixes on the response times of PDLC films.

In this article, reversible additional fragmental chain transfer (RAFT)

polymerization and atom transfer radical polymerization (ATRP) were employed to

prepare PDLCs with well-defined copolymer matrix. Therefore, the graft

macroinitiator (RAFT-PS-co-PCMS-g-PMMA) was synthesized via RAFT

polymerization and ATRP. CMS was short for 4-Chloromethyl styrene. Meanwhile, a

linear macroinitiator (RAFT-PS) was also synthesized by RAFT polymerization,

whose degree of polymerization was similar to that of the main chain of graft macroinitiator.

Based on the experimental results performed by us,[27] we used Kruss DSA100 goniometer system to calculate the surface energy on the boundary surface quantificationally. The influence of different structures between linear and graft copolymer matrixes on the response times of PDLC films was investigated.

2. Experimental

2.1 Materials

A positive dielectric anisotropy nematic liquid crystal E7 (n_o = 1.521, Δn = 0.22, T_{N-I} = 60 °C) was obtained from Yantai Xian Hua Chem-Tech. Co., Ltd. Styrene (St), methyl acrylate (MA) and methyl methacrylate (MMA) (98.0%, analytical grade, from Tianjing Chemical Reagent Co., China) were passed through a column of silica to remove inhibitors. Photoinitiator (1104, from Changzhou LanDing Sci-Tech. Co., Ltd.), tetrahydrofuran (THF) (99.0%, analytical grade, from Tianjing Chemical Reagent Co., China), 2,2'-Azobis(isobutyronitrile) (AIBN), N,N-Dimethylformamide (DMF) (99.5%, analytical grade, from Tianjing Chemical Reagent Co., China), N,N,N',N'',N'''-Pentamethyldiethylenetriamine (PMDETA) (99.0%, analytical grade, from Aladdin Industrial Inc.), CuBr (99.0%, analytical grade, from Aladdin Industrial Inc.), 4-Chloromethyl styrene (CMS) (99.0%, analytical grade, from WDL Chemical Reagent Co., Jiangsu) and other reagents were used as received. Trithiocarbonate (the structure was shown in Fig. 1) was synthesized according to the literature.[27, 28]

2.2 Preparations of RAFT-PS, RAFT-PS-co-PCMS and RAFT-PS-co-PCMS-g-PMMA

The RAFT-PS and RAFT-PS-co-PCMS were synthesized according to the literature.[27] The samples were analyzed by GPC shown in Table 1.

The RAFT-PS-co-PCMS-g-PMMA was synthesized according to the literature.[27] (The same to the g-PMMA-1 in the literature[27]). The Table 1 showed the molecular weights of these macroinitiators measured by GPC. The structures of macroinitiators were shown in Fig. 2.

The synthesis was shown in Fig. 4.

2.3 Preparation of PDLCs[26, 27]

The obtained macroinitiator (RAFT-PS or RAFT-PS-co-PCMS-g-PMMA) was dissolved in MA with predetermined ratio, and a photoactive solution was obtained. PDLCs were prepared by PIPS from a homogeneous mixture of photoactive solution, LC E7 and photoinitiator in a predetermined ratio as shown in Table 2. The reactive mixture was sandwiched between glass substrates covered with indium tin oxide (ITO). Glass spheres were used to make the thickness of the cells to be about 20 μm. Then, cells were exposed to a UV light (100 W) for 1 h. The distance was 20 cm and the temperature was about 30 °C. The wavelength of the UV light is in the range of 300 ~ 400 nm and peaked at 365 nm.

Fig. 3 showed the structures of RAFT-PS-b-PMA (linear copolymer matrix) and

(RAFT-PS-co-PCMS-g-PMMA)-b-PMA (graft copolymer matrix). Simple models for the structures of theirs were also shown in Fig. 3. The synthesis was shown in Fig. 4.

2.5 Measurements

Molecular weights of macroinitiators (RAFT-PS and RAFT-PS-co-PCMS-g-PMMA) and copolymer matrixes were measured by gel permeation chromatography (GPC) on an Agilent1100 column using polystyrene standards as the calibration without any purification (flow rate: 0.6 mL/min; temperature: 40 ℃; solvent: THF; detector: RI). The contact angles of deionized water on the surface of copolymer matrixes in PDLC films were measured using a Kruss DSA100 goniometer system (Kruss GmbH, Germany). Each sample was tested five times, then the mean value of contact angle was recorded, and the surface energy of each sample was calculated.

The response times of these PDLC films were measured by a LCD parameter tester (ZKY-LCDEO-2, from Chengdu Shiji Zhongke Instrument Co., Ltd). The response of the sample was monitored by a digital storage oscilloscope. Rise time and decay time were defined as the time for the optical response (transmittance) to reach 90% and to drop 10% of the maximum transmittance, respectively.

3. Results and discussion

Fig. 5 showed the rise times of the samples with applied electric fields. It was evident that the rise time of every sample decreased with the increase of applied voltage from 30 V to 70 V. Under the same voltage, the PDLC with graft copolymer matrix

exhibited slower rise time than linear one. It was concluded that the introduction of graft macroinitiator resulted in higher rise times. Meanwhile, decay times shown in Fig. 6 increased as the applied voltage increased from 30 V to 70 V. Under the same voltage, the PDLC with graft copolymer matrix exhibited faster decay time than linear sample. The higher the applied voltage was, the stronger external force would be, which meant rising quickly and decaying slowly. In conclusion, it was obvious that the response times of PDLCs with graft copolymer matrix were much different from linear samples. All PDLCs with graft copolymer matrixes exhibited slower rise times but faster decay times.

Why the introduction of graft macroinitiator could make so big difference in response times of PDLC films. We discussed carefully from the following aspects.

It was reported that the size of LC droplets,[18] the anchoring energy on the boundary surface[13] and the properties of polymer matrix[27] were important factors to affect the anchoring force between LC droplets and polymer matrix, and therefore also the response times of PDLCs. On one hand, large LC droplets meant fast rise times but slow decay times.[18] Based on the experimental results performed by us,[27] graft copolymer matrix led to smaller LC droplets than linear one. Since the glass transition temperature (T_g) of branched chains (PMMA) was much higher than room temperature, these branched chains could prevent the LC droplets from gathering together during PIPS process, so smaller LC droplets were exhibited in graft macroinitiator dependent PDLCs. Munekazu Date has reported that the decrease of droplet size would result in higher anchoring force in the PDLC films because the

ratio of the surface to volume was higher.[29] Thus, PDLCs with graft copolymer matrixes showed higher rise times but lower decay times.

On the other hand, the variation of the molecular weights of copolymer matrix was also an important factor to affect the anchoring force. According to the literature, in RAFT polymerization, the calculated M_n could be predicted by eq 1.[20]

$$Culculated\ M_n = \frac{[monomer]_0 \times M_m \times conversion}{[macroinitiator]_0} + M_{macroinitiator} \quad (1)$$

Where M_n was the molecular weight of polymer matrix; $[monomer]_0$ and $[macroinitiator]_0$ were the initial concentration of the monomer and macroinitiator, respectively; M_m and $M_{macroinitiator}$ were the molecular weight of the monomer and macroinitiator, respectively. Since the graft macroinitiator was employed to prepare PDLCs, its high molecular weight had led to a huge growth in the molecular weight of copolymer matrix. As shown in Table 1 and Fig. 7, the molecular weight of graft copolymer matrix was much higher than that of linear one, which led to stronger anchoring force between copolymer matrix and LC droplets. This made the graft copolymer matrix PDLC exhibit higher rise times but lower decay times. As illustrated in Fig. 8 and 9, high molecular weight resulted in high rise time but low decay time under a certain voltage.

Regarding the anchoring energy on the boundary surface, in order to characterize it quantificationally, we calculated the surface energy by using Kruss DSA100 goniometer system, and the results were shown in Table 3. It was found that when the copolymer matrix was replaced from the linear to graft, however, the surface energy was decreased from 21.92 to 9.79 mN/m. It was presumed that since the branched

chains of graft copolymer matrix were not locomotive enough, this might restrict the movement of the polar end group to the boundary surface. So the anchoring energy on the boundary surface of the graft copolymer matrix was smaller than that of the linear one.

Based on the several points above, we proposed a possible explanation to this phenomenon. When copolymer matrix was replaced from the linear to the graft, the decrease of the radius of LC droplets and the increase of the molecular weight of copolymer matrix were the keys for the increase of the anchoring force, although the anchoring energy on the boundary surface was reduced in certain degree. Under the consequence of synthetic functioning of various factors, the anchoring force between LC droplets and the graft copolymer matrixes became much stronger and PDLCs with this polymer matrix exhibited higher rise time and lower decay time.

Furthermore, from another point of view, the change of driving voltage (the threshold voltage V_{th} and the saturation voltage V_{sat}) was in rather good agreement with the variation of anchoring force mentioned above. It was well known that there was a classical relationship between anchoring force and V_{sat}.[30]

$$A = \frac{V_{sat}\sqrt{\varepsilon_0 \Delta \varepsilon K_3}}{d} \tanh\left[\frac{V_{sat}}{2}\sqrt{\frac{\varepsilon_0 \Delta \varepsilon}{K_3}}\right] \quad (2)$$

Where A, ε_0, $\Delta\varepsilon$, K_3 and d were the anchoring force, permittivity of vacuum, the dielectric anisotropy of liquid crystal, the elastic constant and the thickness of the liquid crystal cells, respectively. From the results reported by us,[27] when graft macroinitiators were employed to synthesize copolymer matrix, PDLCs exhibited high V_{sat}, although the memory effect was rather small. According to the eq 2,

anchoring force was positively correlated with V_{sat}, the high V_{sat} could also reflect the strong interaction between LC droplets and copolymer matrix. Thus, the PDLC with graft copolymer matrix took more time to align with the applied field and less time to return to the original state under a certain voltage.

4. Conclusion

In conclusion, we discussed the effect of graft copolymer matrix on the response times of PDLCs by introducing branched chains on linear copolymer matrix. It was found that when the graft macroinitiator was employed to prepare copolymer matrix, PDLCs exhibited slow rise times but fast decay times. By introducing branched chains on linear copolymer matrix, on one hand, the gathering of LC droplets was prevented to a large extent, the LC droplets were very small; on the other hand, with the increase of molecular weight of copolymer matrix, the interaction between LC droplets and copolymer matrix became much stronger. These were the key factors which led to the variation of response times. This explanation corresponded well to the experimental results.

20071108-18-12).

Notes and references

1 G. D. Filpo, F. P. Nicoletta and G. Chidichimo, *Adv. Mater.*, 2005, **17**, 1150.

2 M. Macchione, G. D. Filpo, F. P. Nicoletta and G. Chidichimo, *Chem. Mater.*, 2004, **16**, 1400.

3 M. Mucha, *Prog. Polym. Sci.*, 2003, **28**, 837.

4 M. W. P. L. Baars, M. C. W. van Boxtel, C. W. M. Bastiaansen, D. J. Borer, S. H. M. Söntjens and E. W. Meijer, *Adv. Mater.*, 2000, **12**, 715.

5 D. A. Higgins, *Adv. Mater.*, 2000, **12**, 251.

6 J. H. Ryu, Y. H. Choi and K. D. Suh, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2006, **275**, 126.

7 L. Bouteiller and L. P. Barny, *Liq. Cryst.*, 1996, **21**, 157.

8 G. H. Springer and D. A. Higgins, *J. Am. Chem. Soc.*, 2000, **122**, 6801.

9 J. W. Doane, N. A. Vaz, B. G. Wu and S. Zumer, *Appl. Phys. Lett.*, 1986, **48**, 269.

10 J. Erdmann, J. W. Doane, S. Zumer and G. Chidichimo, *Proc. SPIE.*, 1989, **1080**, 32.

11 B. G. Wu, *Liq. Cryst.*, 2006, **33**, 1315.

12 P. S. Drzaic, *Liq. Cryst.*, 2006, **33**, 1286.

13 D. Cupelli, F. P. Nicoletta, G. D. Filpo, G. Chidichimo, A. Fazio, B. Gabriele and G. Salerno, *Appl. Phys. Lett.*, 2004, **85**, 3292.

14 P. Song, H. Cao, F. Wang, M. Ellahi and H. Yang, *Liq. Cryst.*, 2012, **39**, 903.

15 P. Song, H. Cao, F. Wang, F. Liu, J. Wang, M. Ellahi, F. Li and H. Yang, *Liq. Cryst.*, 2012, **39**, 1131.

16 Y. W. Jin, S. J. Im, J. H. Sung, C. H. Noh and D. S. Sakong, *Liq. Cryst.*, 1995, **19**, 755.

17 W.-J. Yang, T. Lan, S.-L. Xia, L.-P. Ma and Y.-H. Wang, *Liq. Cryst.*, 2014, **41**, 202.

18 J. L. West, K. Jewell, J. Francl, Y. M. Ji and J. R. Kelly, *Proc. SPIE.*, 1992, **1665**, 8.

19 L. Y. Ljungberg, *Mater. Design.*, 2003, **24**, 383.

20 J. He, B. Yan, S.-L. Wang, B.-Y. Yu, X.-A. Wang and Y.-H. Wang, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 4144.

21 J. He, B. Yan, B.-Y. Yu, S.-L. Wang, Y. Zeng and Y.-H. Wang, *Eur. Polym. J.*, 2007, **43**, 2745.

22 B. Yan, J. He, Y.-Q. Fang, X. Du, Q. Zhang, S.-L. Wang, C.-H. Pan and Y.-H. Wang, *Eur. Polym. J.*, 2009, **45**, 1936.

23 X. Du, B. Yan, J.-L. Yao, S. Chen, M.-K. Li and Y.-H. Wang, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 5557.

24 X. Du, B. Yan, M.-K. Li, S. Chen, J.-L. Yao and Y.-H. Wang, *Polym. Int.*, 2011, **60**, 971.

25 L.-S. Shao, Y.-L. Zhang, C.-H. Liu, J.-J. Li, A.-L. Qin and Y.-H. Wang, *Liq. Cryst.*, 2012, **39**, 1458.

26 T. Lan, W.-J. Yang, J. Peng, M.-K. Li and Y.-H. Wang, *Polym. Eng. Sci.*, DOI: 10.1002/pen.23857.

27 T. Lan, W.-J. Yang, J. Peng, M.-K. Li and Y.-H. Wang, *Polym. Int.*, DOI: 10.1002/pi.4693.

28 J. Skey and R. K. O'Reilly, *Chem. Commun*., 2008, 4183.

29 M. Date, Y. Takeuchi and K. J. Kato, *Phys. D*., 1999, **32**, 3164.

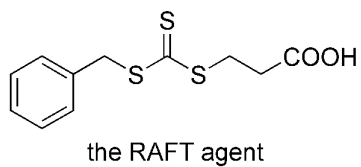30 A. Sugimura and D. Ishino, *Thin Solid Films*, 2003, **433**, 438.

the RAFT agent

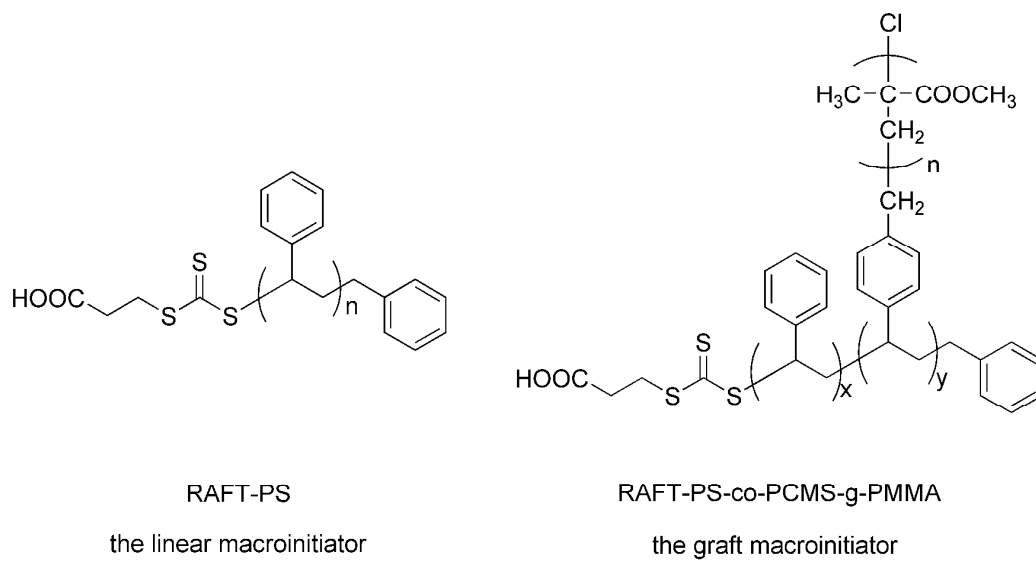**Fig. 1** The structure of trithiocarbonate.

RAFT-PS

the linear macroinitiator

RAFT-PS-co-PCMS-g-PMMA

the graft macroinitiator

Fig. 2 The structures of macroinitiators.
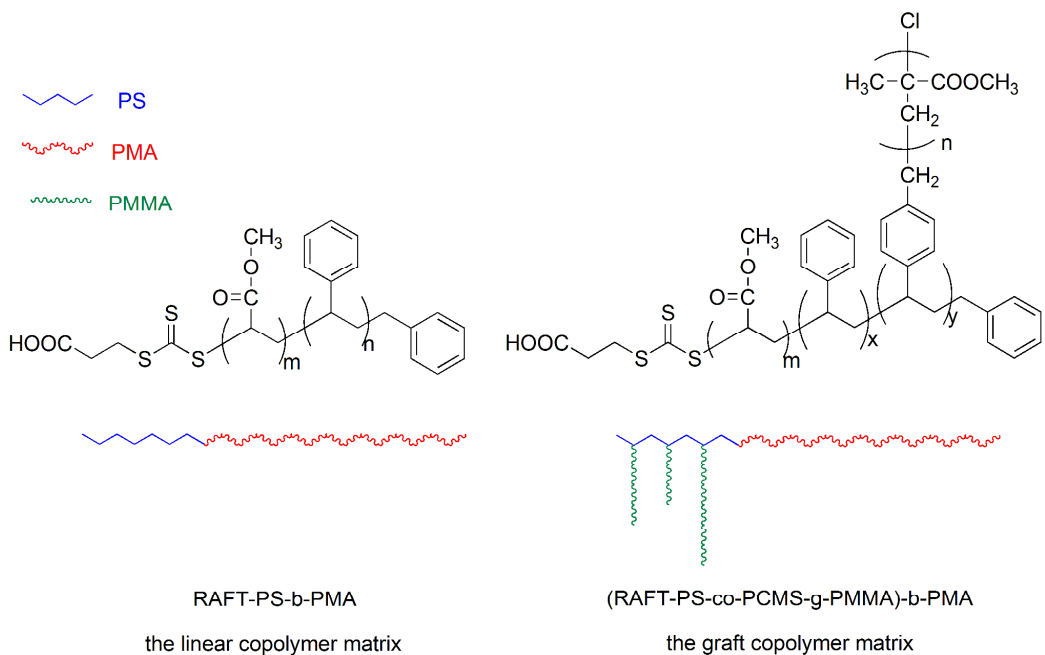
Fig. 3 The structures of RAFT-PS-b-PMA (the linear copolymer matrix) and

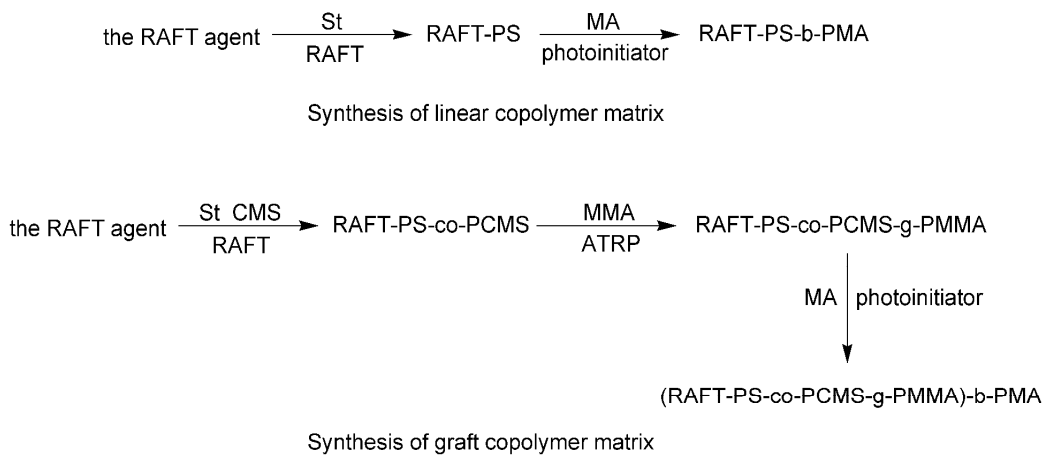(RAFT-PS-co-PCMS-g-PMMA)-b-PMA (the graft copolymer matrix).

Synthesis of linear copolymer matrix

Synthesis of graft copolymer matrix

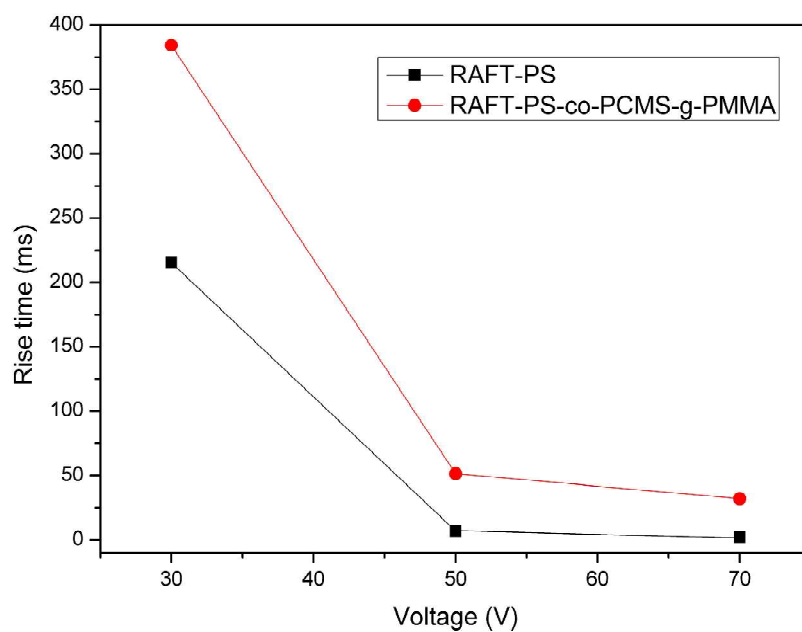**Fig. 4** The basic synthesis reaction scheme.

Fig. 5 Rise times dependence on the applied voltage for two samples with
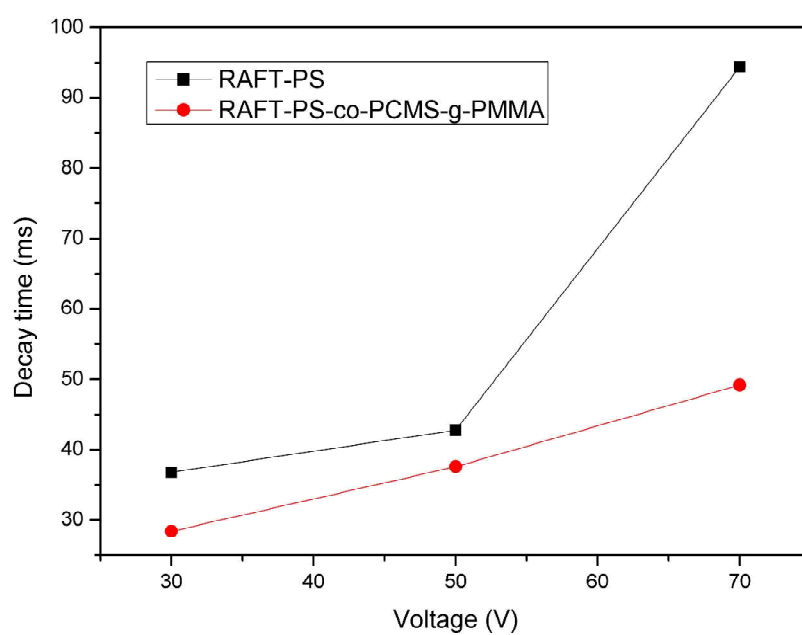
different macroinitiators.

Fig. 6 Decay times dependence on the applied voltage for two samples with
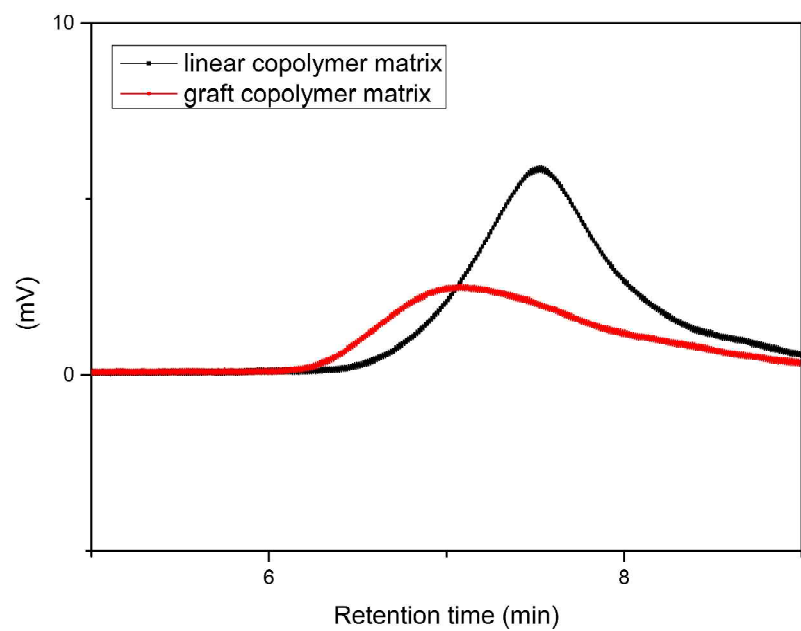
different macroinitiators.
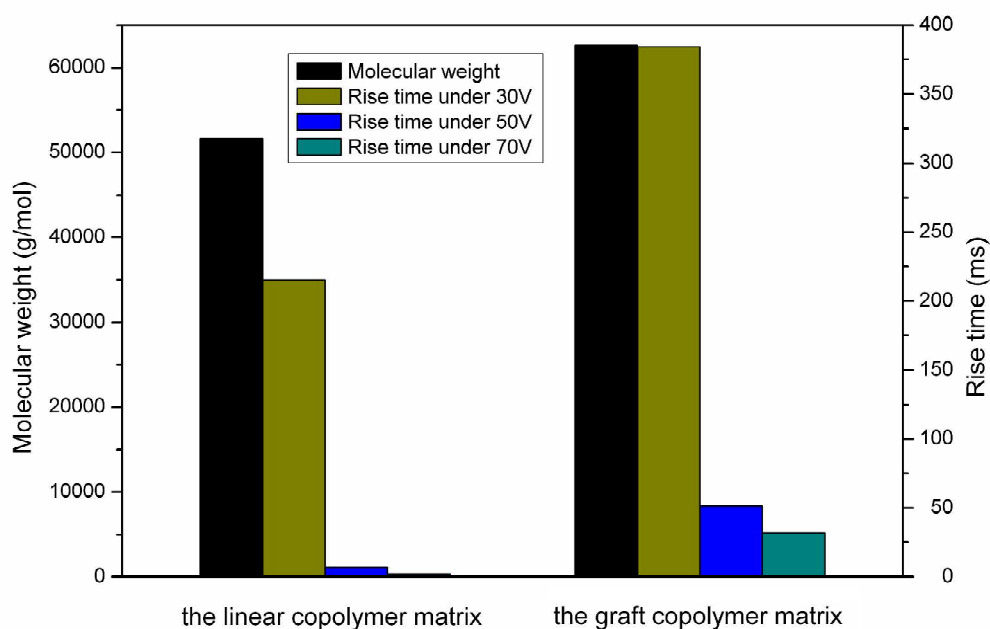

Fig. 7 GPC curves of copolymer matrix.

Fig. 8 Rise times of PDLCs dependence on the molecular weight of copolymer
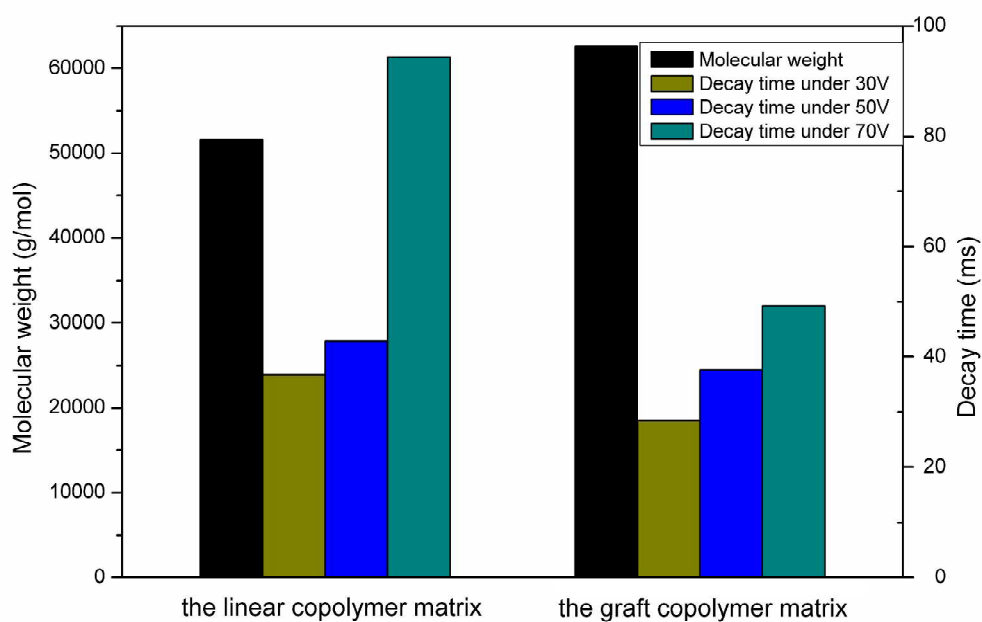
matrix and the applied voltage.

Fig. 9 Decay times of PDLCs dependence on the molecular weight of

copolymer matrix and the applied voltage.

Table 1 The molecular weights of macroinitiators[27] and copolymer matrix

	samples	M_n ($\times 10^{-3}$ g/mol)	M_w ($\times 10^{-3}$)	PDI
The linear macroinitiator	RAFT-PS	3.96	4.78	1.21
	RAFT-PS-co-PCMS	4.77	5.64	1.18
The graft macroinitiator	RAFT-PS-co-PCMS-g-P MMA	13.9	19.7	1.41
The linear copolymer matrix	RAFT-PS-b-PMA	51.6	123.9	2.40
The graft copolymer matrix	(RAFT-PS-co-PCMS-g-P MMA)-b-PMA	62.6	244.4	3.90

Table 2 The composition of samples

Sample[a]	Macroinitiator	Liquid crystal E7 (weight ratio)	Macroinitiator ：MA (number ratio)	Photoinitiator concentration (wt%)[b]
1	RAFT-PS	50%	1：1000	1
2	RAFT-PS-co-PCMS-g-MMA	50%	1：1000	1

[a] All the samples were prepared by exposing to a 100 W UV light from a distance of 20 cm for 1 h at 30 ℃.

[b] The photoinitiator, 1104, was added additionally in wt% of MA.

Table 3 The surface energy of copolymer matrix in PDLC films

Copolymer matrix	Contact angle (°) (Water)			Surface energy (mN/m)
	L	R	M	
linear copolymer matrix	101.8	101.8	101.8	21.92
graft copolymer matrix	123.6	123.6	123.6	9.79