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EFFECT OF SILVER NANOPARTICLES ON THE PHOTO-INDUCED ORIENTATION OF LIQUID CRYSTALLINE POLYMER BASED ON THE SURFACE PLASMON RESONANCE

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Abstract. Recent theoretical progress in understanding the effect of silver nanoparticles on photo-induced orientation of liquid crystalline polymer was reviewed. The observed enhancement of photo-induced rate results from the surface plasmon resonance (SPR) of silver nanoparticles. And the observed reducing phenomena are attributed to the interaction between materials and silver nanoparticles. And then the both interactions between silver nanoparticles and liquid crystalline polymer strongly depend on polarized light wavelength, concentration and the structure of liquid crystalline polymer. Furthermore, the enhancement mechanism of photo-induced rate, and physical process between silver nanoparticles and liquid crystalline polymer was also discussed in details, which are very important to further improvement of photo-induced orientation rate and application on liquid crystalline polymer for the surface plasmon resonance of silver nanoparticles.

1. INTRODUCTION

Photo-responsive liquid crystalline (LC) polymers have been extensively investigated because of their promising applications in optical data storage, optical switching, and photoelectronics [1,2]. Optical anisotropy achieved by irradiation of linearly polarized light results from reorientation of molecular axis and has attracted increasing interest from both fundamental and practical viewpoints [3]. When linearly polarized light is applied, an excited molecule undergoes reversible trans–cis photoisomerization to give preferentially in-plane reorientation toward the direction perpendicular to the electric vector of the light, leading to photo-induced birefringence of polymer films containing azobenzene moieties [4]. Liquid crystalline group displays reversible trans–cis isomerization, which depends on excitation light and sample temperature, through rotation and inversion mechanisms [5,6]. The rate of isomerization and reorientation plays a key role for potential application such as reversible optical storage and optical switch. Many research activities have been carried out to enhance reorientation rate, such as optimizing chemical structure of the azo molecule [7-9] and irradiation light condition [10], etc. However, the result showed that the effect of chemical structure of LC polymer on rate of reorientation was slight. Although the increase in irradiation light intensity was obvious for the improvement of reorientation rate, it also damages the LC polymer.

Recently, the application of silver nanoparticles on the photo-induced orientation of liquid crystalline

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polymer based on the surface plasmon resonance (SPR) has been investigating. It is well known that the light at the surface plasmon resonance frequency interacts strongly with metal particles and excites a collective electron motion, or plasmon [11]. And, local electromagnetic fields near the particle can be many orders of magnitude higher than the incident fields, resulting in improvement of reorientation rate. The enchantment of reorientation rate of LC polymer was observed by the simple way. And then, the effect of liquid crystalline polymers structure and concentration of silver nanoparticles, polarized light on the photo-induced reorientation of the liquid crystalline group films was also systemic studied [11-14].

Despite a little study done so far in this field, the application of silver nanoparticles on photo-induced reorientation of the liquid crystalline group is a relative new physical process first described about ten years ago. So it is quite usual that most of the work done so far was devoted to the development and optimization of the effect than to a deeper understanding of the mechanism of the physical process. The scope of this paper is to discuss some mechanistic aspects of the physical process between silver nanoparticles on the LC polymer, which are plausible and in line with earlier and new findings of our group, and to compare them with results of the LC polymer based on SPR of noble nanoparticles.

2. THE MECHANISM OF ENHANCEMENT OF THE REORIENTATION RATE

It is well-known that the noble nanoparticles act as both an enhancer and a quencher for reorientation rate of LC polymer according to the previous works [11-14]. The enhancement of reorientation rate from LC polymer is attributed to the large electromagnetic field arising from the excitation of surface plasmon polariton (SPP) of noble metallic nanoparticles, which is similar to surface-enhanced fluorescence of europium complexes based on the surface plasmon resonance (SPR) of noble metal nanoparticles [15-20] as shown in Fig. 1. Here we do not discuses in detail.

However, the mechanism of decrease in the reorientation rate by silver nanoparticles is difference from quenching fluorescence of Europium complexes as reporting in previous works [15-20]. Here the quenching effect results from the following physical process: (1) the excited photon of LC polymer is scattered due to the interaction between the photon and silver nanoparticles, resulting in a decrease of light intensity; (2) the silver as filler on the polymer matrix reduces the free volume of polymer chain, which effective inhibit the movement of LC chain of polymer; (3) The interaction between LC chain in polymer and silver nanoparticles inhibit the movement of LC chain of polymer.

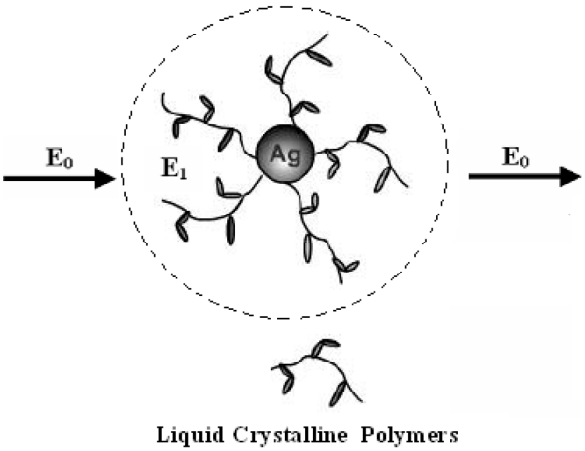

Fig. 1. The representation of the amplified incident field around metallic surface and nonradiative relaxation due to damping of the dipole oscillators by the noble metallic surface.

3. THE EFFECT OF SILVER NANOPARTICLES ON THE PHOTO-INDUCED ORIENTATION OF LIQUID CRYSTALLINE POLYMER

3.1. The effect of structure of LC polymer

When the LC polymer located in close proximity to the noble metallic surface, local electromagnetic fields near the particle can be many orders of magnitude higher than the incident fields, resulting in improvement of reorientation rate. And, LC polymer should contain the functional group that has interaction with noble nanoparticles to be close proximity to the noble metallic surface. In the other way, the reorientation rate is to be reduced due to the interaction between LC unit of polymer and metal nanoparticles, which inhibit the movement of LC unit of polymer. So the structure of LC polymer is very important to obtain enchantment of reorientation rate as reported in previous works [11-14]. The interaction of different molecules (P1 and P2 as shown in Figs. 2 and 3) with noble metallic spheroids leads to a different photophysics and photochemistry. As shown in Fig. 3a, LC chain of P1 has strong

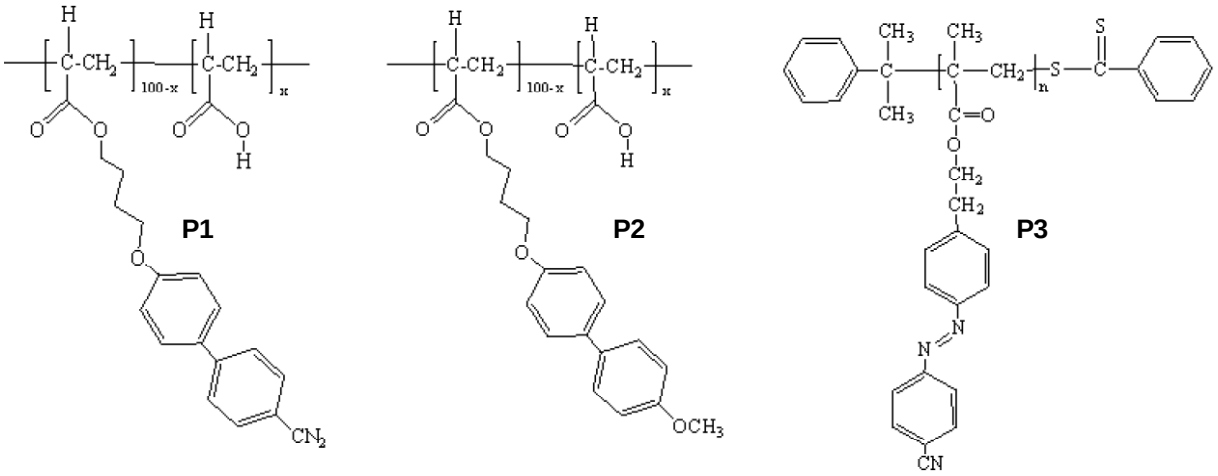

Fig. 2. The scheme of LC polymer with various structures.

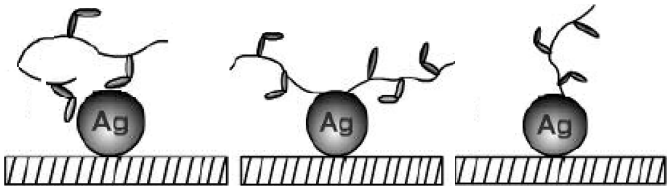

Fig. 3. The representation of the interactions between silver nanoparticles and LC polymer with various structures (a) P1, (b) P2, and (c) P3.

interaction with silver metallic spheroids. So, it leads to a rapid increase in the glass transition and a less-significant decrease in the clearing temperature of P1 as shown in Table 1. As a result, the overall mesophase stability is rapidly decreasing. Contrarily, it shows that P2-Ag nanocomposites are able to form an LC phase, in which the movement of LC chain is not affected by the silver nanoparticles due to no interaction between LC chain of P2 and silver nanoparticles as shown in Fig. 3b. These results indicate that, as in P1-Ag nanocomposites, silver nanoparticles influence negatively the mesophase stability. However, due to the different chemical structure, P2 is less sensitive to this influence.

The data on the phase behavior and structure of the nanocomposites P1-Ag and P2-Ag discussed above let us make the first important conclusion. Nanoparticles are not passive elements of the mesomorphic polymer matrix. On the contrary, they are able to influence significantly the temperature interval of LC phase. It is of evident interest to understand the nature and mechanisms of such influence, as well as its interconnection with the chemical structure of polymer matrix. So, in order to obtain the enhancement of reorientation rate functions, the LC polymer should contain the functional group that has strong interaction with silver nanoparticles, and at the same time, the LC unit should be no interaction with silver nanoparticles.

However, there are lots of LC polymer, in which the LC unit contain the -CN, $-NO_2$, $-NH_2$ groups that have strong interaction with silver nanoparticles. And the enhancement of re-orientation rate is difficult to be observed due to the interaction inhibiting the movement of LC chain as shown in Fig. 3a. Taking this into consideration, here a new synthetic approach of the nanocomposite polymer system has been developed [11]. The key was that -S- groups were introduced to terminus of LC polymer by RAFT

Table 1. The glass transition and clearing temperature of LC polymer containing silver nanoparticles.

	concentration	melt temperature/°C		glass temperature/°C	
		orign	after	orign	after
P1	2%	98	90	35	58
P2	2%	135	130	54	54
P3	50%	168	168	126	126

Table 2. The maximum enhancement ratio from polymer/Silver nanoparticles under polarized light with various wavelengths.

Polarized light wavelength(nm)	365	442	532
Abs of absorbance	0.05	0.4	0.2
Maximum enhancement ratio	1.30	1.45	1.05

polymerization as shown in Fig. 2. It efficiently avoided the interaction between LC units and Ag because the thiol groups tended to form preferentially complexes comparing with other groups (-CN, -NH_2 and so on) of LC units [23] as shown in Fig. 3c. As shown in Table 1, the glass and metal temperature of P3 is almost same with that of the P3 adsorbed on silver nanoparticles. It will provide an opportunity to obtain enhancement of reorientation rate.

3.2. The effect of silver nanoparticles' concentration

It was well known that the surface plasmon polariton (SPP) around LC polymer is strongly enhanced when two or more silver nanoparticles come into close proximity with each other [20]. On the other hand, exciting the plasmon resonance of the particles lead to light absorption and local heating, which clearly makes it easier for the molecules to re-orientate. The above two aspects both promote the photo-induced reorientation of LC units. So, it was clearly seen that the re-orientation rate rapidly increased to 1.68 with the increase of the silver content as shown in previous work [14]. On the other way, however as the sliver content increased further, the enhancement effect began to reduce. The result was attributed that the silver as filler on the polymer matrix reduced the free volume of polymer chain, which inhibited the movement of LC of polymer [24]. Eventually, the reorientation rate of the doped sample was even lower than that of the undoped sample. So, generally the reorientation rate at least for "fast" progress can be largely enhanced when using an appropriate doped content of silver nanoparticles.

3.3. The effect of polarized light wavelength

It was found that the polarized light wavelength also strongly affected on the photo-induced reorientation of the LC polymer/Silver nanoparticles composite films as shown in Table 2. Photo-induced reorientation of the films was performed under polarized light with wavelength at 442 nm, 532 nm, and 365 nm, respectively. It was obviously seen that the largest enhancement ratio (ca.1.45) was obtained when film samples were irradiated with 442 nm light. The enhancement effect began to reduce with increase or decrease in polarized light wavelength (ca.532 nm and ca 365 nm), respectively. The above result was attributed to that the maximum SPR absorption of the composite films was about 450 nm. It was closer to the maximum SPR absorption and the enhancement effect was more obvious. The above results provide a strong evidence for reorientation enhancement of LC groups based on surface resonance plasmon.

4. CONCLUSIONS

Photo-induced orientation of liquid crystalline polymer based on the surface plasmon resonance (SPR) of silver nanoparticles has been studying on improvement of orientation rate of liquid crystalline polymer. And the observed decrease in orientation rate was attributed to the absorption of surface plasmon resonance, scattering of silver nanoparticles and so on. And then the both interactions between silver nanoparticles and liquid crystalline polymer strongly depend on structure of liquid crystalline polymer, metal particle concentration, and polarized light wavelength. However, it has few reports on optical memory polymer materials based on photo-induced re-orientation rate. In addition, the effect of silver particles size and shape on mechanism and physical process of enhancement of photo-induced re-orientation rate have been few reporting.

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