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A novel soft matter composite material for energy-saving smart windows: from preparation to device application

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Nowadays, with the ascending energy consumption of buildings and the continuous improvement of human living standards, architectural glass with multi-functional features of large-scale manufacturing, safety and energy saving has become the mainstream trend. In this paper, a series of cholesteric side-chain liquid crystal polymers (ChSCLCPs) are designed and synthesized to composite with the widely used laminating material for safety glasses, ethylenevinyl acetate (EVA), to endow the windows with IR light shielding property, simultaneously. The synthesized ChSCLCPs have desired reflection wavelengths and thermal stability. Preparation methods of EVA/ChSCLCP composite materials are investigated and different ratios of the contents and various film treatment conditions are attempted. Interestingly, when the contents of EVA and ChSCLCP are equal, "sky-blue" areas are found under polarized optical microscopy (POM) and the film exhibits stronger light scattering and selective reflection properties. Taking advantages of this phenomenon, a new kind of IR shielding film is manufactured by powder blending method and it not only performs broadband reflection, but also exhibits strong light scattering. Then model buildings equipped with and without the film are set up and an energy conservation efficiency up to 40.4% is obtained, which proves the film of practical applications in energy-saving smart windows.

Introduction

Born with a variety of forms such as liquid crystals (LCs), gels, membranes and other polymeric materials, soft matter or soft materials are also called structured fluids.^{1,2} Their distinguished properties, especially being able to respond to external stimuli, endow them wide applications in sensors, controllers and electric devices.³⁻⁵ Materials scientists never stop learning from nature, it has been found that the cuticle of the crab *Carcinus mænas* performs the cholesteric structure with a pitch gradient,^{6,7} which equips the creature who spend plenty of time on beach a reflector to prevent itself from over-heating by the sunshine. Why cannot the buildings be equipped with that kind of "skin" to reduce the power supply for air-cooling system?

Attributing to the unique helical supra-molecular structure, cholesteric liquid crystals (ChLC) perform selective light reflection property and reflect the circularly polarized incident light whose handedness is identical with the helical axis.⁸ The reflection wavelength is given by **Equation 1**,

 $\lambda = n \mathbf{P} \quad (1)$

where *n* is the average of the ordinary (n_o) and extraordinary (n_e) refractive indices of the ChLC, P is the cholesteric pitch corresponding to the length of a 2π molecular rotation. The reflected bandwidth $(\Delta\lambda)$ is given by **Equation 2**,

$$\Delta \lambda = (n_e - n_o) \cdot \mathbf{P} = \Delta n \mathbf{P} \quad (2)$$

where Δn is the birefringence of the LC. Since Δn is typically limited to 0.5, the bandwidth of a single-pitch ChLC is usually less than a hundred nanometers, which is insufficient for the applications such as brightness enhancement films, wide-band reflective polarizers, smart reflective windows and so on. To broaden the bandwidth, different methods have been employed such as forming a pitch gradient^{9,10} or creating a non-uniform pitch distribution.^{11,12} In recent years, many theoretical studies¹³⁻¹⁵ and experimental methods¹⁶⁻¹⁸ have been developed to achieve broadband reflection. The first example was introduced by D. J. Broer in 1995, and he obtained broadband reflection of the entire visible spectrum by introducing a pitch gradient in the cholesteric polymer networks via UV-induced polymerization of chiral LC diacrylate/nematic monoacrylate/photoinitiator blends.^{19,20} M. Mitov and his colleagues employed two layers of polymer-stabilized ChLCs (PSChLCs)^{21,22} or glassy cholesteric polysiloxane LC oligomers^{23,24} to prepare wide-band reflection film with pitch gradient by a simple thermal diffusion method. Results showed that the optical properties of the bilayer system were not the sum of the individual properties, and the wavelength bandwidth greater than 300 nm covering visible and near-IR areas were successfully obtained, which provided potential applications for the manufacture of white-or-black polarizer-free screens with high brightness and smart windows for buildings. L. Li et al. created a non-linear pitch gradient by polymerization induced molecular re-distribution exploiting ChLC materials which contained one polymeric LC component and other non-reactive LCs.^{25,26} The obtained polarizing films exhibited excellent thermal stability and adjustable spectral bandwidth of about 2000 nm covering from UV to the entire visible spectrum and up to near-IR. Numerous immediate applications such as brightness enhanced liquid crystal display (LCDs), switchable energy-saving/privacy windows, and energy saving IR reflective paints and coatings were also discussed. Based on the properties of polymer dispersed liquid crystal (PDLC) and PSChLC, Prof. H. Yang also conducted a lot of researches. A composite of polymer network, nematic liquid crystal, and chiral dopant exhibiting chiral nematic (N^*) phase at room temperature has been developed and the bandwidth of the selective reflection spectrum could become wider and narrower reversibly with increasing and decreasing temperature.²⁷ Moreover, much effort was focused on the broadband reflection of ChLC by the formation of pitch gradient or non-uniform pitch distribution and several methods were invented: (1) In a PSChLC system containing non-reactive LC, a nematic diacrylate and cholesteryl compounds of different functionality, the concentration of chiral centers near or away from the backbone were non-uniform and this resulted in different pitch lengths;^{28,29} (2) Due to the increasing of the pitch of CLC composite caused by rising temperature, a single layer CLC film with non-uniform pitch distribution was achieved by regulating the temperature; ³⁰⁻³² (3) Employing the UV curable LC monomers/chiral dopants/bulk LC system, a PSChLC film with pitch gradient can be fabricated by UV induced polymerization of the photopolymerizable acrylate monomers.33-35

Side-chain liquid crystalline polymers (SCLCPs), which combine the ordered structures of liquid crystals and the excellent properties such as good thermal stability and processability, have been focused on in recent years due to their extensive applications in actuator, sensor, engineering plastics and other functional materials.^{36,37} When the side groups (at least partially) are chiral, a helically twisted structure (also called cholesteric structure) can be obtained. Owing to the thermal,^{40,41} electrical,^{42,43} special optical,^{38,39} and mechanical^{44,45} properties, ChLC are of potential applications in photonic crystal materials,46 self-organization functional materials,⁴⁷ and wide-band reflective devices.^{48,49} With the rational design and efficient synthesis of novel cholesteric SCLCPs (ChSCLCPs), numerous advanced functional materials have been obtained.50-52

high flexibility and cohesiveness, and other good mechanical properties, ethylene-vinyl acetate (EVA) copolymer is widely used in laminated safety-glasses of building and vehicle windows. The combination of EVA and ChSCLCPs could not only endow the materials with good adhesion properties, which ensure the safety, but also make the composite films reflect or shield the light of IR region to lower the transmittance of IR light, so as to achieve the purpose of energy conservation. However, which ratio between EVA and ChSCLCPs could endow the composite film with the best comprehensive performance is a very interesting and meaningful issue to study. Furthermore, smart windows have various applications in controllable reflectance mirrors and in energy saving windows, attributing to their transmittance modulation range in the visible and whole solar spectrum.53 Several methods have been investigated to functionalize the traditional ones such as employing the electrochromic⁵⁴⁻⁵⁶ and thermochromic^{57,58} compositions. However, for smart windows to serve on the windows of skyscrapers, large scale manufacturing and safety of the windows are essential. And one of the best ways is to composite EVA and ChSCLCP, with the aid of the performances of the original laminating glass and the new materials, to achieve the purpose of energy saving without weakening the mechanical properties. In this paper, we report the synthesis and characterization of a series of ChSCLCPs with different reflection wavelengths covering IR region. Composite films with different EVA/ChSCLCPs ratios were first prepared under heating and pressure in vacuum conditions, and the optimum conditions of proportion and preparation method were determined. Different from the work reported previously, the IR shielding film for smart windows was successfully prepared by "stacking" of the EVA/ChSCLCP film powders with different center reflection wavelengths in IR region. The resultant composite film is therefore a model system to investigate the effect of the phase transition of the ChSCLCPs and the ratio of EVA and ChSCLCPs on the optical properties of the film that is designed to be used in smart windows.

Due to the excellent properties such as optically transparency,

Results and Discussion

Mesomorphic and Optical Properties of the Polymers

From our previous studies, we have found that the center reflection wavelength of chiral compounds was mainly dependent on temperature and the content of the chiral component.⁵⁹⁻⁶¹ With increasing content of the chiral groups, the center reflection wavelength blue shifted. According to this rule, we designed these polymers with selective reflective wavelength centers covering different IR regions. As shown in Support Information Scheme S1 and S2, the polymers were obtained via conventional free radical polymerization of nematic and cholesteric liquid crystalline monomers (M1 and M2) of different ratios.

The chemical structures of the monomers and polymers were verified by combination of ¹H-NMR and FTIR (see Supporting Information Figure S1 and S2). The molecular characteristics of the polymers are summarized in **Table 1**. By adjusting the proportion between M1 and M2, three polymers with high yield

were successfully prepared. Thermogravimetric analysis (TGA) results showed that all the polymers performed good thermal stabilities under nitrogen atmosphere and their 5% weight loss temperatures (T_d 's) were all above 300 °C.

Table 1. Synthetic and Characterization Data of the ChSCLCPs										
Sample	M2 [mol%] ^{a)}	Yield [%]	$M_{n, GPC}$ [×10 ³] ^{b)}	PDI ^{b)}	T_{d}	T_{g}	T_{i} $[^{\circ}C]^{d}$	λ [nm]		
P1	20	86	2.69	1.24	309.5	59.0	252.7	990		
P2	15	83	2.70	1.18	317.3	58.4	253.7	1420		
P3	10	84	2.68	1.11	315.8	57.6	254.4	1870		

^{a)} The molar fractions of M2 were based on (M1+M2); ^{b)} The number-average molecular weight ($M_{n,GPC}$) and polydispersity indices (PDI) were measured by GPC with THF as the eluent and PS as standards; ^{e)} The temperatures at 5% weight loss of the samples under nitrogen were measured by TGA heating experiments at a rate of 10 °C min⁻¹; ^{d)} The glass transition temperatures (T_g) and clearing temperatures (T_i) were determined by DSC under nitrogen at a scanning rate of 20 °C min⁻¹.

The phase transition behaviours of all the polymers were examined by a combination of differential scanning calorimetry (DSC) and POM measurement. In order to avoid thermal degradation, all the characterizations were conducted at temperatures well below $T_{\rm d}$. As shown in **Figure 1(A)**, two endothermic peaks at about 60 °C and about 250 °C, which may be related to the glass transition and the isotropization of the polymers from a possible LC phase, were detected in each of the DSC curves for all the synthesized polymers during the heating process.

To further confirm the phase behaviours and structures of all the polymers, POM technique was utilized. The polymers were filled into the cells whose inner surfaces had been planar orientated by capillary action. Figure 1(B) shows the typical LC textures of all the polymers at different temperatures obtained from isotropic state. At ambient temperature, the whole field of view was black and almost no birefringence was observed. Upon heating, the polymers developed LC phase immediately after the glass transition temperatures and it disappeared slowly after the isotropic temperatures. While cooling from the isotropic state, the oily streak texture, a characteristic of a Ch phase, developed again. Interestingly, further cooling to the temperatures below T_g , the oily streak textures could be maintained to a very low temperature. Combined the results of DSC and POM, we concluded that all the polymers developed a wide Ch phase structure during the heating and cooling process, which was useful for the applications of smart windows with wideband reflective films.

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Figure 1. A) Differential scanning calorimetry curves of the polymers P1, P2, and P3 during the first cooling and second heating scans at a rate of 20 °C min⁻¹. B) Typical Polarized optical microscope images of P1, P2, and P3 at different temperatures cooled from isotropic states: a) P1 at 263.6 °C; b) P1 at 53.8 °C; c) P2 at 257.2 °C; d) P2 at 54.9 °C; e) P3 at 255.1 °C f) P3 at 55.3 °C.

Figure 2 shows the typical profile of the transmission spectra of all the polymers under normal incidence. As expected, the center reflection wavelengths of the polymers were red shifted with the decreasing ratio of the cholesteric liquid crystalline monomer M2 and they covered almost the entire IR region. This was because lower amount of M2 provided fewer chiral centers, which weakened the helical twisting power and resulted in the film with longer reflection wavelength. When the molar ratios of M2 were 20%, 10% and 5%, the center reflection wavelengths of the polymer films were located in about 1000, 1400 and 1800 nm, respectively (as shown in Table 1).



Figure 2. The chemical structures and the transmission spectra of P1, P2, and P3 (the molar ratios between x and y were 80:20, 85:15, and 90:10, respectively).

Optical Properties of the EVA/ChSCLCP Composite Films

Then EVA/ChSCLCP composite films with different weight ratios were prepared and characterized in order to find out the optimal proportion. **Figure 3** represents the typical POM photographs of the EVA/P1 composite films with EVA ratios ranging from 5% to 95%. When EVA ratios were below 20%, it aggregated and formed "droplet" shape domains (As shown in Figure 3a-3c). As EVA ratios ascended to 40%, EVA and ChSCLCP aggregated respectively, and formed separately amorphous domains. Moreover, when EVA content was relatively low, severe shrinkage occurred after the annealing process. The boundaries of the shrinkage areas are noted with milky-blue curves in Figure 3a-e. However, with the further increasing content of EVA, the severity of shrinkage was relieved gradually, and no obvious shrinkage could be observed when EVA content reached over 50%. Interestingly, when the ratios of EVA and P1 were almost the same (as can be seen in Figure 3f), no black area detected under POM and "sky-blue" colour filled the entire region instead. This was unbelievable since the amount of EVA was still considerable. In order to elucidate whether the phenomenon occurred occasionally, we also tried long annealing time and different heating and cooling rates for several times, "sky-blue" areas could be still observed.

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Figure 3. Typical polarized optical microscope images of the EVA/P1 composite films with different EVA ratios cooled to room temperature: a) 5%; b) 10%; c) 20%, d) 30%; e) 40%; f) 50%; g) 60%; h) 70%; i) 80%; j) 90%; k) 95%. The boundaries of the shrinkage areas are marked out with milky-blue curves in a)-e).

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To further investigate the optical properties of the composite films with different EVA contents and what interesting characteristics could the "sky-blue" appearance represent, UV/VIS/IR spectra and diffuse reflectance study were conducted, as shown in Figure 4 and Supporting Information Figure S3. It can be seen clearly that when EVA ratio was similar to that of P1, which was correspondence to the "skyblue" phenomenon under POM, the composite film exhibited the optimal selective reflection properties and the light scattering was also very strong, which are desirable to the preparation of IR shielding films for the application of smart windows. When EVA content was in minority in composite films, the light scattering gradually decreased with the decreasing of EVA content, probably due to the reduce of specific surface areas in the films originated from the phase separation of EVA and P1, while the selective light reflectance were not weakened obviously. However, when EVA proportion was higher than 50%, the light scattering of the composite films deceased gradually since the surface areas became fewer and the selective reflection also became less obvious due to lower amount of P1. Moreover, the phenomenon of other composite films EVA/P2 and EVA/P3 were similar to that of EVA/P1.



Figure 4. The transmission spectra of the EVA/P1 composite films with different ratios.

Device Application of the Composite Films as IR Shielding Films in Smart Windows

According to the results described above, when EVA and ChSCLCP contents were similar, the composite film exhibited the optimal properties which were favorable to the application in smart windows. Thus, an IR shielding film was prepared by stacking of the EVA/ChSCLCP composite film powders with different center reflection wavelengths as shown in Figure 5a. POM results showed that planar texture of cholesteric phase with visibly different morphology formed and "sky-blue" appearance developed after heating-compression action (as can be seen in Figure 5c). Then UV/VIS/IR experiment was conducted and results illustrated that the obtained wide-band reflective film not only maintained the reflection properties of the original single composite films (P-I, P-II and P-III), but new center reflection wavelengths, which were probably corresponding to the new pitch lengths arising from two adjacent different powders (B-I and B-II), were detected and the reflection bandwidth was also significantly broadened. We consumed that there may be thermal-diffusion between neighboring composite film powders. Scanning electron microscopy (SEM) demonstrated our consumption, Figure 5d shows SEM image of the fractured surface of the film. The dimension of the three bands in the fine structure on the fractured plane is P, corresponding to a 2π cholesteric molecular rotation. It can be seen clearly that non-uniform pitch lengths, changing from about 510 nm to about 930 nm, distributed in different domains in the fracture plane. Additionally, new pitch lengths at about 590 nm and about 810 nm were observed in the neighboring areas between different powders and P1 < P4 < P2 < P5 < P3. By adjusting the composition of M1 and M2, the IR light broadband reflective films can be obtained.

(b)

Transmittance / %

60

55

50

45

40

(d)

35∟ 800

1100

1400

/P4

Wavelength / nm

Journal Name

P2

EVA

Heating

Compression

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(a)



B-II

IP2

1 P5

3 <u>µm</u>

2000

1700



Figure 5. a) Schematic drawing of the preparation of the IR shielding film. b) The transmission spectra of the IR shielding film in different areas. c) Polarized optical microscope photograph of the IR shielding film. d) Scanning electron microscope image of the cross-section of the IR shielding film. Then the film was attached on the window of a model house to

<u>500 µm</u>

investigate its energy conservation effect. Energy conservation efficiency (η) , which defined as the ratio of the IR energy obstructed by the film was calculated according to Equation 3, $Q_{CTRL} - Q_{ISF} _ C_{air} m \Delta T_{CTRL} - C_{air} m \Delta T_{ISF} _ \Delta T_{CTRL} - \Delta T_{ISF}$ ΔQ

$$\eta = \frac{1}{Q_{CTRL}} = \frac{1}{Q_{CTRL}} = \frac{1}{C_{air}m\Delta T_{CTRL}} = \frac{1}{\Delta T_{CTRL}}$$
(3)

where Q_{CTRL} and Q_{ISF} represent the absorbed energy of the model buildings with and without the EVA/ChSCLCP composite film, ΔT_{CTRL} and ΔT_{ISF} represent the indoor

temperature changes of the corresponding model buildings over a period of time, c_{air} and *m* represent the specific heat capacity of air and the mass of air, respectively. As shown in Figure 6a, ΔT_{CTRL} and ΔT_{ISF} are calculated as being 4.95 °C and 2.95 °C, Q_{CTRL} and Q_{ISF} are calculated as being 20.68 J and 12.32 J, respectively. The indoor temperature of the model building equipped with the EVA/ChSCLCP composite film was significantly restrained and an energy conservation efficiency of 40.4% was obtained.

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Figure 6. a) The temperature changes of the module house during exposure under sunlight. ISF: the house with the IR shielding film attached to its window, CTRL: the house with two layers of PET film laminated with EVA attached to its window. b) Peeling strength results of the corresponding samples.

Furthermore, to make sure that the EVA/ChSCLCP composite film could serve on the windows for huge buildings, the safety characteristics was tested and the peeling strength was obtained. As can be seen in Figure 6b, compared with the control group of pure EVA laminated film, the EVA/ChSCLCP composite film presented almost the same peeling strength. Combined with the result of energy conservation efficiency, the composite film exhibited relatively excellent comprehensive performance, and proved to have practical application in energy conservation smart windows.

Experimental Section

Materials

The ChSCLCP were obtained via conventional free radical polymerization of nematic and cholesteric liquid crystalline monomers and detailed synthetic routes were elaborated in the Supporting Information. EVA (TPC, Singapore, MA-10) were commercially available and used without further purification.

Measurements

The molecular weights and molecular weight distributions of the polymers were determined by a GPC equipped with Waters 2410 instrument equipped with a Waters 2410 RI detector and three Waters μ -Styragel columns (103, 104, and 105 Å), using THF as the eluent at a flow rate of 1.0 mL min⁻¹ at 35 °C. The calibration curve was obtained by using polystyrene (PS) as standards. TGA was performed on a TA Q50 instrument under nitrogen at a heating rate of 10 °C min⁻¹. DSC was utilized to study the phase transitions of the polymers using a Perkin-Elmer DSC 8000 calorimeter under nitrogen flow (30.0 mL min⁻¹) and the heating/cooling rate were 10 °C min⁻¹ under a dry nitrogen purge. POM (Carl Zeiss AxioVision SE64) was used to observe the LC textures of the samples with a Linkam LTS420 hot stage calibrated to an accuracy of ± 0.1 °C and a digital camera (AxioCam MRc 5). Spectral characterization conducted unpolarized UV/VIS/IR was by an spectrophotometer (JASCO V-570) in transmission mode at normal incidence. Diffuse reflectance (DR) study was conducted using an UV/VIS/IR spectrophotometer (Perkin-Elmer Lambda 950) with a DR attachment with an integrating sphere coated by BaSO₄. SEM was used to observe the morphology of the cross-sections of the samples on a HITACHI S-4800 instrument. The peeling strength experiment was practiced on a universal tensile test machine (Instron 5969).

Preparation of the Cells Filled with ChSCLCPs

To induce planar orientation of ChSCLCP molecules, the inner surfaces of the glass cells were coated with a 3.0 wt% polyvinyl alcohol (PVA) aqueous solution. The deposited film was dried at 90.0 °C for 1 h and then rubbed with a textile cloth under a pressure of 2.0 g cm⁻² along the same direction. Polyethylene terephthalate (PET) films of 20 μ m thickness were used as cell spacers. The polymers were filled into the cells by capillary action at 180 °C, and these samples filled with P1, P2 and P3 only were named as Sample P1-0, P2-0, and P3-0, respectively.

To investigate the influence of EVA and ChSCLCPs compositions on the optical and mechanical properties of the composite films and to search the optimal proportion between them, different ratios of EVA and ChSCLCP were attempted as shown in Table 2. A series of composite films Pn-x (where n represents the polymer, x represents the weight percentage of the EVA component) were prepared by solution evaporation method. Take the preparation of sample P1-5 as an example, a mixture of EVA (1.8 mg) and P1 (33.2 mg) was dissolved in CH₂Cl₂ under magnetic stirring at room temperature for 4 h, the micropearls of 12 µm were added to control the thickness of the composite film. About 0.2 mL of the homogeneous solution was dropped on a clean glass substrate of 1 cm² and kept for 6 h at room temperature to evaporate the solvent slowly, then coated the film with another glass substrate. Afterwards, the composite device was treated in a vacuum oven at 120 °C for 5 h under a pressure of 200.0 g cm⁻².

Table 2. Compositions and Weight Ratios of the EVA/P1 Composite Films										
Commla	EVA	ChSCLCP	EVA	CH_2Cl_2						
Sample	[mg]	[mg]	[wt%] ^{a)}	[mL]						
P1-5	1.8	33.2	5	0.5						
P1-10	3.5	31.5	10	0.5						
P1-20	7.0	28.0	20	0.5						
P1-30	10.5	24.5	30	0.5						
P1-40	14.0	21.0	40	0.5						
P1-50	17.5	17.5	50	0.5						
P1-60	21.0	14.0	60	0.5						
P1-70	24.5	10.5	70	0.5						
P1-80	28.0	7.0	80	0.5						
P1-90	31.5	3.5	90	0.5						
P1-95	33.2	1.8	95	0.5						

^{a)} The weight fractions of EVA were based on the total weights of EVA and ChSCLCP.

Preparation of the IR Shielding Films for Model House

After determination of the optimal proportion between EVA and ChSCLCPs, the IR shielding film for smart windows was prepared by "stacking" of the EVA/ChSCLCP composite film powders with different center reflection wavelengths in IR region. The three composite films with appropriate composition were selected, cut into small pieces, and blended homogeneously. Then the mixed powders were sandwiched between two glass substrates and treated in a vacuum oven at 120 °C for 5 h under a pressure of 200.0 g cm⁻². Finally, the film was attached on the window of a model house, whose walls had been equipped with thermal insulation materials. After the indoor temperature was regulated to 26 °C, it was exposed under sunshine (environment temperature: 32 °C) for 20 minutes and the temperature change was recorded. Meanwhile, a control group was set up with two layers of PET film laminated with EVA attached on the window.

Conclusion

In summary, employing the selective light reflection characteristic of ChSCLCP, by "stacking" of the EVA/ChSCLCP composite film powders with different reflection wavelengths, a novel soft matter composite material for laminated glass has been successfully developed with an energy conservation efficiency of 40.4% and relatively strong bonding performance for the first time. The energy conservation mechanism was attributed to the broadband reflection of the ChSCLCP in the IR region as well as the light scattering because of the formation of "sky-blue" areas, which was confirmed by the results of POM, transmission and reflectance spectra, and SEM experiments. It is believed that the composite soft material with relatively high energy conservation efficiency and strong bonding features has great potential application in large-scale laminating glass windows with the dynamic control of solar light. Future work will be focused on the formation mechanism of the "sky-blue" area and further enhancement of the energy saving efficiency of the film.

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A novel soft matter composite material for energy-saving smart windows: from preparation to device application

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A novel soft-matter composite film of ethylene-vinyl acetate and liquid crystal with an energy conservation efficiency of 40.4% is developed.