The Effects of a Polymer Network on a Ferroelectric Liquid Crystal

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Abstract   Polymer network stabilised ferroelectric liquid crystals (PNSFLCs) have been produced by in situ polymerisation of a small amount of a cross-linkable monomer in a low molar mass ferroelectric liquid crystal. In the present studies, the amount of prepolymer, which is a UV curable optical adhesive NOA65, is less than 5%. The embedded polymer network strongly affects the properties of the liquid crystal host. A significant change in phase transition behaviour has been observed even when the amount of the polymer network is very small. Both the tilt angle and the spontaneous polarisation of the liquid crystal host are reduced in the presence of the polymer network. The temperature behaviour of these two parameters can be described by an exponential function. However, the values of the parameters of the function are different from those derived using the classical Landau theory based on the mean field approximation. For the pure ferroelectric liquid crystal, the spontaneous polarisation has a linear relation with the tilt angle, and the linearity of between the two parameters is independent of temperature. However, the temperature independence of the linear relation between the two parameters is broken in the presence of the polymer network.

Key words   ferroelectric liquid crystal, polymer network, polymer network stabilised ferroelectric liquid crystal, tilt angle, spontaneous polarisation

（ PNSFLCs）。

NOA65,   5%。

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1   Introduction

Polymer network stabilised liquid crystals (PNSLCs) are two phase composites consist of a low molar mass liquid crystal and at least one polymer component[1~4]. PNSLCs can be produced by in situ polymerisation of a cross-linkable polymer precursor in a low molar mass liquid crystal. These materials have attracted a considerable attention because of their great potential in display applications[3~8] and scientific interests[1,9~11].

Recently, there has been a great interest in producing fast switching PNSLCs using ferroelectric liquid crystals (FLCs)[12~18]. The presence of the polymer network in a ferroelectric liquid crystal will promote many interesting aspects. For example, the phase

transition temperatures of the host liquid crystal are lowered in the presence of a monomer[16, 19]. The rate of the polymerisation will influence the spontaneous polarisation[20, 21]. The electrooptic behaviour can be modified[12, 14, 18].

For a FLC with chiral smectic C (S_C^*) phase, the tilt angle plays an important role. It is considered to be the primary order parameter in the S_A–S_C^* phase transition. For a FLC which exhibits a second order phase transition, the temperature dependence of the tilt angle can be expressed as[22-24]

$$\theta = \theta_0 \left(\frac{T^* - T}{T^*} \right)^U. \qquad (1)$$

Where θ is the tilt angle at temperature T, T^* is the S_C^*–S_A phase transition temperature, θ_0 is a temperature independent parameter with a dimension of the angle, and U a fractional exponent. In the mean-field approximation, U can be derived using Landau´s phase transition theory, and has a value of $U = 0.5$[25].

The spontaneous polarisation P_S is one of the most important physical properties of a ferroelectric liquid crystal. It is a microscopic property which can be used to investigate the microscopic properties of the ferroelectric liquid crystal. For most S_C^* phase FLCs, the P_S is a secondary order parameter and related to the primary order parameter, the tilt angle, θ. In the classical Landau model, there is a linear relation between the two parameters, and the following equation can be derived[26].

$$P_S = T\theta. \qquad (2)$$

Where T is a temperature independent parameter concerned with the flexoelectricity and the chirality of the S_C^* phase. The relation means that for angle $\theta \neq 0$ a local polarisation P_S will appear as a result of the deformation of the S_C^* phase in the absence of an external field.

In the classical Landau model, the temperature dependence of the spontaneous polarisation of the FLC can be described by the following exponential function[27, 28]

$$P_S = C_{Ps} \left(\frac{T_C - T}{T_C} \right)^U. \qquad (3)$$

Where C_{Ps} is a temperature independent parameter with a dimension of $nC cm^{-2}$, and T_C is the critical temperature at which the macroscopic ferroelectric properties of the FLC vanishes.

In the presence of a polymer network, it is expected that all parameters, C_{Ps}, θ_0, T_C, and U in Equations (1) and (3), will vary. In this article, the effects of polymer network on a ferroelectric liquid crystal are presented. The temperature behaviour of the molecular tilt and the ferroelectric properties of the liquid crystal in the network systems is examined.

2 Experiment

In the present studies, a UV curable optical adhesive, NOA65 (Norland, USA), was used as prepolymer. The liquid crystal used was a commercial ferroelectric mixture SCE3 [E. Merck (UK) Ltd.], which has a phase sequence as shown below,

C (< 0) S_C^* 74 S_A 105 N^* 136 I.

A small amount, < 5% by weight, of NOA65 was added into the liquid crystal, and the mixture was mechanically stirred at an elevated temperature (~ 10℃ above the clear point of the host liquid crystal) to get uniformity. Samples for electrical measurement were made by injecting SCE3/NOA65 mixture into cells made using substrates coated with unidirectional rubbed polyimide alignment layer. In the present studies, an empty cell, which had two openings with one on each of the two electrode connections, was heated to an elevated temperature (about 10℃ above the clear temperature of the host liquid crystal). Then a small amount of the mixture was put on one of the openings of the empty cell. At the high temperature, the mixture became less viscous, and was forced into the cell by capillary action. After filling, the sample was carefully cooled down to room temperature at a cooling rate of 1℃/min. The polymerisation of the mixture was carried out by UV curing the optical adhesive when the sample temperature was controlled at 25℃ where the liquid crystal host was in the S_C^* phase. A high-pressure mercury lamp (Philips 93136E) was used as UV light source. The intensity of the UV light, with a wavelength of 365 nm, was 9 mW/cm² on the surface of the substrate. The UV curing lasted for about 60 minutes. A long duration curing is necessary to get well-completed polymerisation for the mixtures with a low concentration of monomer.

The phase transition temperatures for the PNS-FLC systems were measured by means of optical mi-

croscopy. The sample for the phase transition examination was made by sandwiching the FLC/monomer mixture between two untreated glass plates, and then followed by the UV curing of the mixture. The sample was then heated. Phase transition temperatures for the material can be obtained by determining the temperature at that the change in the texture corresponding to the particular phase took place. The texture observation was carried out using a polarising microscope.

Upon application of an electric field, the molecules in a planarly aligned S_C^* phase will be driven and experience the Goldston switch[29], in which each molecule moves in a hypothetical cone, which is determined by the molecular tilt, and is switched to one of the two possible positions. The tilt angle of the S_C^* phase can be measured by means of optical microscopy. In this investigation, a planarly aligned sample cell was placed on the hot-stage which was fitted in a polarising microscope. An AC square wave (~ 50 Hz) voltage was used to switch molecules in the S_C^* phase between their two tilted positions. Using the polarising microscope system, the two tilted positions can be determined by rotating the sample and used an oscilloscope and a photodiode to find out the extinction positions. The difference between the two angles corresponding to the two extinction positions is then the cone angle, which is twice the tilt angle. In the present studies, all microscopic examinations were carried out using a Nikon OPTIPHOT-POL polarising microscope. The microscope was equipped with a rotating stage whose angular position could be set to an accuracy of ± 0.1° with a vernier scale. In order to measure the transmittance of PNSFLC samples, one of the view ers of the microscope was attached with a photodiode. A He-Ne laser was used as light source which produced a light beam with a wavelength of 633 nm. The transmittance of the PNSFLC sample for the laser beam was detected by the photodiode. The output signal of the photodiode detector was monitored by a Hewlett-Packard 54602B oscilloscope. The temperature controller used was a Linkam TMS90 temperature system (Linkam Scientific Instruments Ltd., England).

The spontaneous polarisation of the composites was measured using current reversal method[30, 31]. A triangular waveform voltage, which was produced by a function generator (Thandar TG501) coupled with a high voltage amplifier, was applied to a homogeneously aligned FLC sample. The induced current was converted to voltage signals, which was sent to the oscilloscope. Data acquisition and process were automatically carried out by an IBM PC.

3   Results and discussion

In the present studies, we were interested in the influence of a polymer network on the physical properties of the materials in the temperature range in which the ferroelectricity existed, i. e. in which the materials were in the S_C^* phase. So we focused on the examination of the S_C^* –S_A phase transition temperatures. The S_C^* –S_A phase transition temperature vs. concentration of the polymer is plotted in Fig. 1. It can be seen that the phase transition temperature was lowered in the presence of the polymer network in the liquid crystal. The increase in the amount of the polymer caused further decrease in the transition temperature.
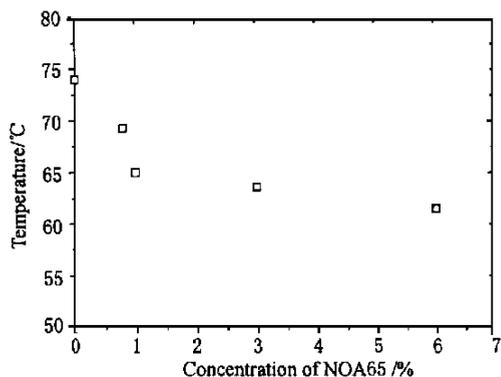

Fig. 1   The S_C^* –S_A phase transition temperature as a function of concentration of NOA65 for SCE3/NOA65 polymer network systems.
□ SmC* /SmA phase transition point

Fig. 2 shows temperature behaviour of the tilt angle of the pure SCE3. It can be seen that the temperature response of the tilt angle follows a power law expressed as Equation (1). The phase transition temperature T^* has been measured. θ_0 and U can be obtained by fitting Equation (1) with the experimental data. A straightforward way to obtain the numerical value of U and θ_0 is to plot log P_s vs. log [(T^* –T) /T^*] to obtain a straight line using experimental data. U is then equal to the slope of the line, and θ_0 is the intercept where log

$[(T^* - T)/T^*]$ is equal to zero. A better result can be obtained by means of the least square method. In Fig. 2, a curve obtained by the theoretical fitting is plotted. It can be seen that the experimental data fits Equation (1) very well. The result indicates that for the pure SCE3, the mean field approximation is held.

Fig. 3 shows the temperature behaviour of the tilt angle for the SCE3/NOA65 network systems contained a small amount of NOA65. As can be seen, the tilt angle was reduced significantly in the presence of the polymer network, and it continued to decrease as the amount of NOA65 was increased. One of the factors which cause the reduction of the tilt angle may be the surface anchoring due to the existence of the polymer network in the liquid crystal host. The formation of the polymer network will create interface between liquid crystal molecules and the polymer stems. The liquid crystal molecules will anchor to the interface and will not be well driven by an external field. This may cause improper movements of the LC molecules, and result in suppression in the molecular cone of the S_C^* phase, and subsequently, the tilt angle becomes smaller. The presence of the polymer network may also induce perturbation which causes changes in the ordering of the liquid crystal host, and causes decrease in the molecular tilt.
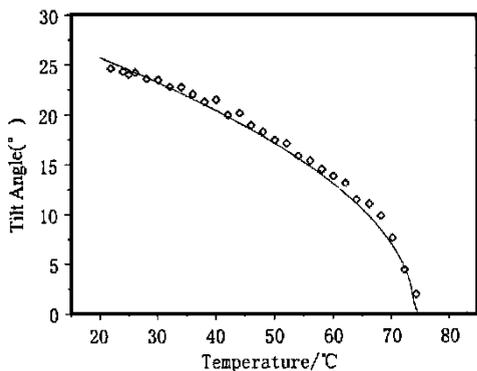

Fig. 2   Temperature response of the tilt angle for SCE3. The solid curve is obtained by fitting the experimental data to Equation (1).
□ Experiment;— Fitting.

In the presence of the polymer network, all three parameters varied. The parameters can be obtained by theoretical fitting. The increase in the amount of polymer network caused the decrease in θ_0 (cf. Fig. 4 and Fig. 7). The exponent U will first increase dramatically

when the amount of the polymer was very small (i. e. 0.8 wt%), and then dropped when the amount of polymer network was further increased (see Fig. 5). The values of U for SCE3/NOA65 systems indicate that the polymer network systems cannot be properly described using the classical Landau theory, and other physical mechanisms must be taken into account. Furthermore, the significant deviation of the values of U for the network systems from that for the pure FLC indicates that the mean field approximation is not held for the PNSFLC systems.

The temperature response of the spontaneous polarisation Ps for the PNSFLCs was measured, and the results were plotted in Fig. 6. The values of Ps for the PNSFLC samples are smaller than that for the pure FLC sample. It can be seen that the Ps decreases as the amount of polymer increases. It is also noticed that the reduction of Ps is not in linear proportion to the amount of the polymer (cf. Fig. 6). The reduction of
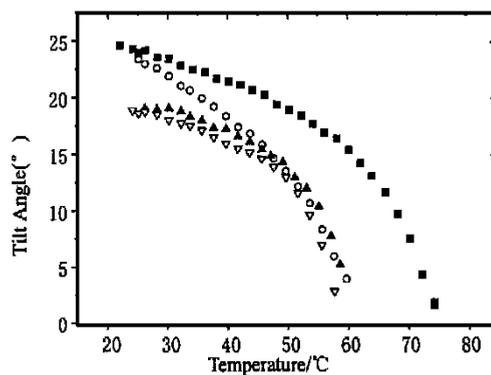

Fig. 3   The temperature behaviour of tilt angle for SCE3/ NOA65 network systems with different concentrations of NOA65.
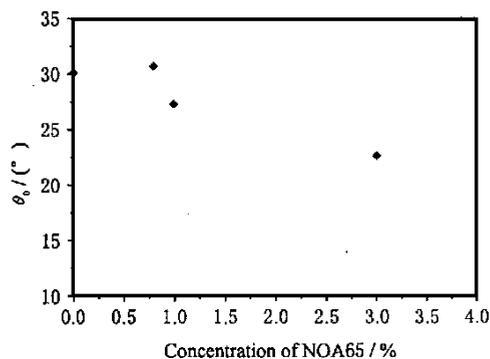■ 0% ;○ 0.8% ;▲ 1% ; ▽ 3%

Fig. 4 θ_0 as the function of the amount of polymer network for SCE3/NOA65 systems.
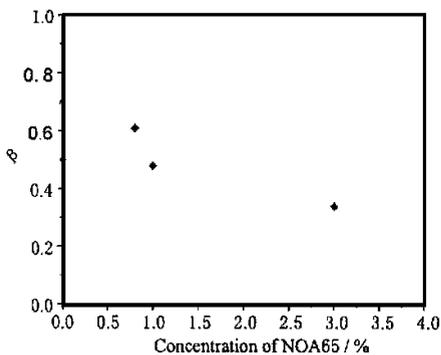
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Fig. 5 U as a function of concentration of the polymer network for SCE3/NOA65 systems. The values obtained by fitting experimental data to Equation (1).
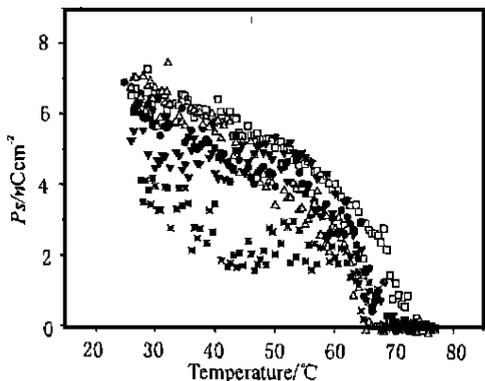

Fig. 6 The temperature response of Ps for SCE3/NOA65 systems with different concentrations of NOA65.
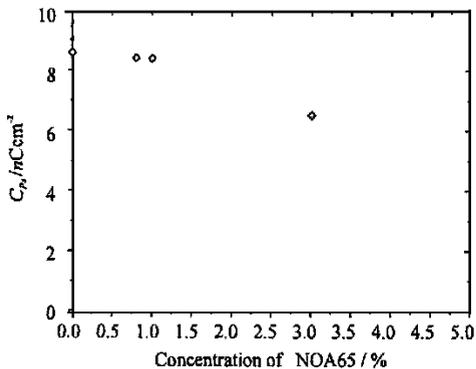□ 0% ; ● 0.8% ; △ 1% ; ▼ 3% ; * 6%

Fig. 7 C_{Ps} values obtained by fitting experimental data to Equation (3) for SCE3/NOA65 polymer network systems.

Ps may be explained by considering the reduction in the number of the FLC molecules, i. e. the number of dipoles, due to the existence of the polymer network. The UV curing of the FLC/NOA65 mixture will result in the cross-linking of the monomer leading to a phase separation and the formation of polymer-rich and FLC-rich domains. Because of the existence of polymer-rich region the volume of the FLC is reduced, and this causes the decrease in the number of active

FLC molecules in the cell. On the other hand, the formation of the polymer network in the FLC creates interface between the FLC and the stems of the polymer network. The molecules in the vicinity of the polymer stems will anchor to the interface and will be strongly held. These anchored molecules would not be driven easily by an external field. So the number of the active molecules was further reduced. As the number of the active molecules is reduced, the density of dipole that made contribution to the reversal current was reduced, and subsequently, Ps decreased. When the amount of the polymer network increases, the size of the FLC-rich domain decreases as the size of the polymer-rich domain increases, and the surface anchoring effect is enhanced as the area of the interface created by the polymer network increases. So as the concentration of the polymer network increases, the net ferroelectric dipoles, and hence the spontaneous polarisation, decreases. It must be pointed out that the mechanism of the reduction in the spontaneous polarisation of the FLC/polymer network systems may be far more complex.

For the pure SCE3, the temperature response of Ps, as expected, behaved in a similar way to that the θ does (cf. Fig. 2 and Fig. 6), and can be described used the power law expressed as Equation (3). The values of the exponent U for the PNSFLCs have been obtained in a previous section. The T_C can be taken to be equal to the S_C^* –S_A phase transition temperature presuming that the S_C^* –S_A transition for the PNSFLC systems is the true second order phase transition. The values of C_{Ps} for the PNSFLC systems can then be obtained by fitting Equation (3) with the experimental data, and are plotted in Fig. 7. C_{Ps} decreases as the concentration of NOA65 is increased. It is noticed that the variation of C_{Ps} with the concentration of NOA65 is less than that of θ_0 (cf. Fig. 4). Fig. 8 shows the theoretical fitting of Equation (3) with the experimental data for the SCE3/NOA65 systems with the theoretical fitting. The results show a very good agreement between the experimental data and the theoretical expectation.
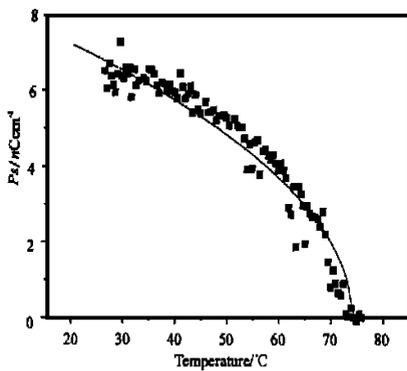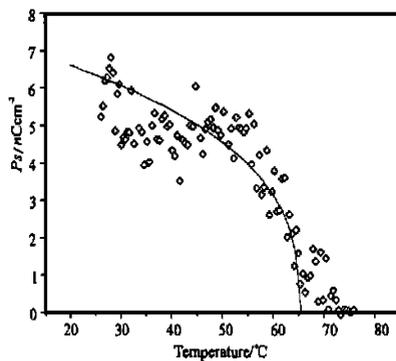
(a)
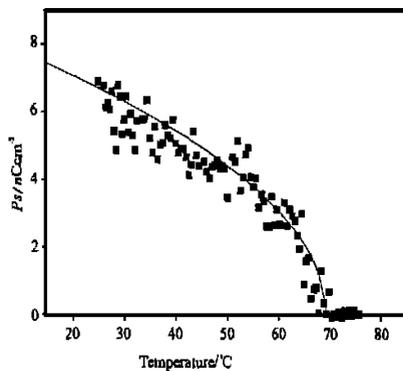
(b)
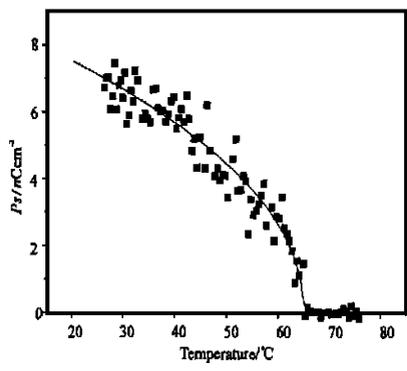
(c)

(d)

Fig. 8   Showing the fitting of Equation (3) with experimental data for SCE3/NOA65 systems with concentrations of (a) 0% of NOA65, (b) 0.8% of NOA65, (c) 1% of NOA65, and (d) 3% of NOA65.
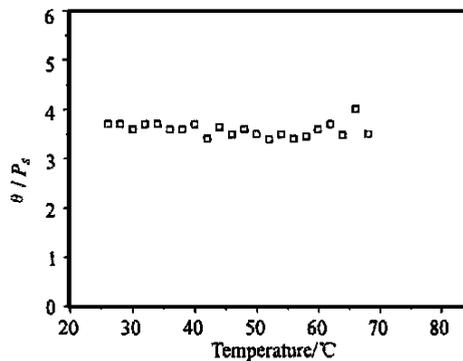□■ Experiment;── Fitting.

Fig. 9   The temperature behaviour of the coupling of tilt angle and spontaneous polarisation for SCE3.

According to Equation (2), if there is a good linear relation between θ and Ps, the coefficient $T = \theta / Ps$ should be a temperature independent constant. For the pure SCE3, a very good linearity in the temperature behaviour of the coupling of θ and Ps can be found (see Fig. 9). This result indicates the FLC is in the mean field regime, and can be described using the classical Landau phase transition theory. Fig. 10 shows the temperature behaviour of the θ / Ps coupling for the SEC3/NOA65 network systems. It can be seen that the linearity of the coupling of the tilt angle and spontaneous polarisation can be held for the SCE3 consisted of as high as 3% NOA65. Further increasing the density of the polymer network will result in the loss of the linearity of the θ / Ps coupling. On the other hand the coupling of θ / Ps is temperature sensitive, and will loses linearity if the temperature of the SCE3/NOA65 composite is higher than $45^\circ C$. The loss of the linearity between θ and Ps may be a result of the changes in the flexoelectricity of the system. The existence of the polymer network in the FLC host may introduce perturbation, and cause changes in the flexoelectricity and the chirality of the FLC. So those effects which are ignored by the classical Landau theory must now be taken into account. In the case of the PNSFLC systems, the parameter T in Equation (2) is no longer a temperature independent constant. The results suggest that the SCE3/NOA65 network systems cannot be simply described by the classical Landau model.
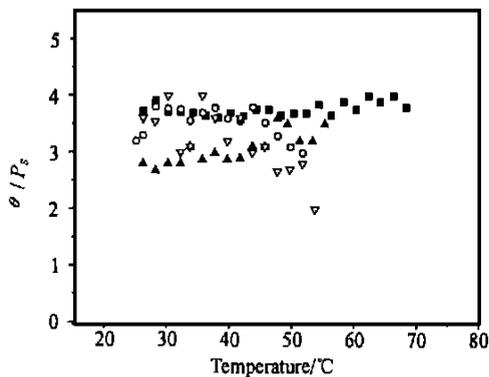
Fig. 10 The temperature behaviour of the coupling of tilt angle and spontaneous polarisation for SCE3/NOA65 systems. Concentration of NOA65: ■ 0% ; ○ 0. 8% ; ▲ 1% ; ▽ 3%

4 Conclusions

It has been shown that the existence of the formation of a polymer network in the ferroelectric liquid crystal will lower the $S_C^* - S_A$ phase transition temperature. The formation of the polymer network may cause changes in the molecular packing structure, and causes the decrease in the molecular tilt. In the SCE3/NOA65 PNSFLC systems, the spontaneous polarisation is reduced. This may result from the reduction in the net ferroelectric dipole due to both the decrease in the size of the FLC volume and the surface anchoring effects of the polymer network. The increase in the amount of the polymer network will cause further decrease in the size of the FLC volume, and further enhance the surface anchoring effect as the area of the interface created by the polymer network increases. These will cause a further decrease in the net ferroelectric dipole, and hence, a further decrease in the spontaneous polarisation. The formation of the polymer network in the FLC host will cause changes in the flexoelectricity and chirality of the FLC system, and the coupling coefficient for the two order parameters θ and Ps is temperature dependent. So, in the PNSFLC systems, the linear relation between molecular tilt and spontaneous polarisation, which is predicted by the classical Landau theory, loses. The temperature behaviour of the ordering and the ferroelectricity of the SCE3/NOA65 PNSFLC systems can still be described using a power law. However, the mean field approximation is no longer held, and the classical Landau phase transition theory cannot describe the systems properly.

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