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The Effect of Polymer Stabilization on Phase Transitions in a Series of Antiferroelectric Heterocyclic Esters

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We used optical Bragg reflections to study the effects of photo-polymer networks on the phase transitions of four heterocyclic esters that exhibit various frustrated chiral smectic phases. When polymerization is carried out in the SmC^* phase, this phase is stabilized at the expense of the intermediate phases. However, in non-radiated samples, which contained traces of the polymer, the intermediate phases are stabilized at the expense of the SmC^* phase. The wavelengths selectively reflected by the SmC_A^* phase are longer than those reflected by the SmC^* phase and the stability of the SmC_A^* is unaffected by polymerization.

Keywords: antiferroelectric; Bragg reflection; phase transitions; polymer stabilization

INTRODUCTION

The constant search for new materials with enhanced properties has led to the study of polymer/liquid crystal blends. Materials that combine the unique optical and electro-optical properties of a liquid crystal with the mechanical strength of a conventional polymer would be quite attractive industrially. However, in order to fully exploit the synergies that such blends would offer, the effect of the polymer on the phase behaviour of the liquid crystal (and vice versa) must first be fully investigated.

Photo-polymerization plays a central role in the fabrication of polymer-liquid crystal blends. It entails the use of radiation to

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polymerize and cross-link photo-reactive-monomers. This technique has many advantages over thermal curing. These include fast curing times, uniformity and ease of controlling the reaction. Also, low polymerization temperatures reduce the possibility of chemical degradation.

Antiferroelectric liquid crystals show complex and intriguing phase behaviour. The phases appear in the order SmC^*_A-FI_L-SmC^*_γ (SmC^*_{FI1})-FI_H-AF (SmC^*_{FI2})-SmC^*-SmC^*_α-SmA, with increasing temperature, if all phases exist [1]. The ferroelectric SmC^* phase and the antiferroelectric SmC^*_A phase are the fundamental phases. The additional phases are usually referred to as the intermediate or subphases. The SmC^*_α phase is a tilted phase with nearly zero optical rotation [2]. The AF(SmC^*_{FI2}) phase is antiferroelectric while the SmC^*_γ (SmC^*_{FI1}), FI_H and FI_L phases are ferrielectric [3,4]. Bragg scattering is a very sensitive probe for identifying phase transitions in chiral smectic liquid crystals whose pitches are comparable to visible wavelengths.

In this study we investigated the effect of polymer networks on the temperature dependence of Bragg reflections in some antiferroelectric liquid crystals. Polymer networks formed by photo-polymerization of reactive monomers in a liquid crystal matrix have been shown to follow the local director orientation of the liquid crystal [5,6]. As the temperature of a polymer-liquid crystal blend changes, the polymer network attempts to preserve its original configuration by exerting torques on the liquid crystal matrix. Dierking, Osipov and Lagerwall [7] found that when polymerization is performed well into the SmC^* phase, an increase of the spontaneous polarization of the liquid crystal mixture is observed in the vicinity of the SmC^*-SmA transition for increasing polymer concentration. On the other hand, the spontaneous polarization at the corresponding reduced temperature is decreased when polymerization is carried out in the SmA phase.

TABLE 1 Range (in °C) of the SmC^* and SmC^*_A Phases in the Pure, Doped and Cross-linked Samples of the Materials used. The Doped Materials Contain Traces of Polymer But they were not Irradiated with UV Light

AFLC	SmC^* (pure)	SmC^* (doped)	SmC^* (crosslinked)	SmC^*_A (pure)	SmC^*_A (doped)	SmC^*_A (crosslinked)
AS612	10.3	8.1	11.2			
AS618	13.2	11.8				
AS620	10.4	9.3	10.9			
AS661	7.3	4.1	9.8	25.6	24.8	26.4

THEORY

The Landau model describing phase transitions of an antiferroelectric liquid crystal may be expressed in terms of the antiferroelectric and ferroelectric order parameters respectively: $\xi_a = (\xi_1 + \xi_2)/2$ and $\xi_f = (\xi_1 - \xi_2)/2$, where $\xi_i = (n_{ix}n_{iz},\ n_{iy}n_{iz})$ is a two-dimensional tilt order parameter [8,9]. The Landau free energy density is given by:

$$\begin{aligned} g(z) = &\frac{1}{2}\alpha_a\xi_a^2 + \frac{1}{2}\alpha_f\xi_f^2 + \frac{1}{4}\beta_a\xi_a^4 + \frac{1}{4}\beta_f\xi_f^4 + \frac{1}{2}\gamma_1\xi_a^2\xi_f^2 \\ &+ \frac{1}{2}\gamma_2(\vec{\xi}_a \cdot \vec{\xi}_f)^2 + \delta_a\left(\xi_{ax}\frac{\partial\xi_{ay}}{\partial z} - \xi_{ay}\frac{\partial\xi_{ax}}{\partial z}\right) \\ &+ \delta_f\left(\xi_{fx}\frac{\partial\xi_{fy}}{\partial z} - \xi_{fy}\frac{\partial\xi_{fx}}{\partial z}\right) + \frac{1}{2}\kappa_a\left(\frac{\partial\xi_a}{\partial z}\right)^2 + \frac{1}{2}\kappa_f\left(\frac{\partial\xi_f}{\partial z}\right)^2 \end{aligned} \tag{1}$$

It is assumed that only the coefficients of the quadratic terms are temperature dependent. Hence:

$$\alpha_a = a(T - T_{a,o}) \text{ and } \alpha_f = a(T - T_{f,o}) \tag{2}$$

where $T_{a,o}$ and $T_{f,o}$ are temperatures where the coefficients change their signs. The δ terms are Lifshitz terms, which appear due to the chirality of the molecules and the κ terms represent elastic constants. The γ terms represent coupling between the two order parameters. If there is no coupling between the two order parameters ($\gamma_2 = 0$), each one would form it own helicoidal structure.

In order to investigate the directional relationship between ξ_a and ξ_f we express the order parameters as:

$$\xi_a = (\theta_a \cos qz, \theta_a \sin qz) \text{ and } \xi_f = (\theta_f \cos qz, \theta_f \sin qz) \tag{3}$$

where $q = 2\pi/\text{pitch}$ is the wave vector of the helix. If the free energy is minimized with respect to θ_a, θ_f and q, four stable solutions exist. Namely,

$$\begin{array}{llll} \theta_a = 0, & \theta_f = 0 & \text{SmA} & \\ \theta_a = 0, & \theta_f \neq 0 & \text{SmC}^* & \\ \theta_a \neq 0, & \theta_f = 0 & \text{SmC}_A^* & \\ \theta_a \neq 0, & \theta_f \neq 0 & \text{SmC}_\gamma^* & (\text{SmC}_{\text{FI1}}^*) \end{array}$$

In order to account for the existence more than one intermediate phase, sixth-order terms [10,11] have been added to the Landau expression. This term also ensures that transitions from the intermediate phase(s) to the SmC^* and SmC_A^* phases are both first order (as observed).

EXPERIMENT

Blends of the antiferroelectric liquid crystals AS661, AS612, AS618 and AS620 (see Fig. 1 for the chemical structures) with the monomer 4,4′-bis(6-(acryloyloxy)-hexyloxy) biphenyl (BAB6) and photo-iniator Irgacure 651(in the ratio 98.8:1:0.2) were prepared by photo-polymerization with UV-Visible light of intensity 2 $mWcm^{-2}$ for about ten minutes. It assumed that the monomer and the phot-iniator do not react unless they have been exposed to UV radiation.

Polymerization was performed *in-situ* on the microscope stage. Under these conditions, complete polymerization is expected to Occur [12]. In order to conserve materials and still retain the desired ratio, BAB6 and Irgacure 651 were dissolved in dry dichloromethane and the relevant amount was added to the liquid crystals. The blends were then dried at 60°C. The AFLC was purchased from Kingston Chemicals and the photo-polymer from Ciba-Geigy.

MATERIALS

The apparatus for detecting optical Bragg peaks has been described in detail elsewhere [13]. The samples were placed on the hot stage of a reflecting polarizing microscope, heated into the isotropic phase and then allowed to equilibrate. The samples were then cooled slowly to the desired temperature and kept fixed for 5 minutes before any

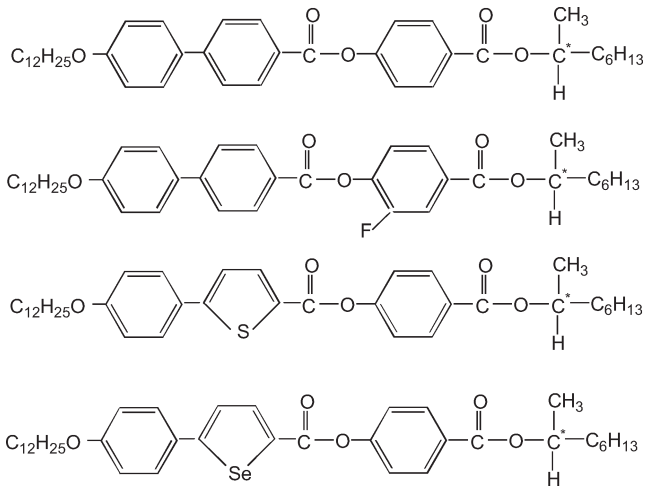

FIGURE 1 Chemical structures of the materials used. From top to bottom: AS618, AS661, AS612 and AS620.

measurements were taken (all in the cooling mode). This time far exceeds the time required for data acquisition ($\sim$1 m). A Linkam hot stage (TMS600) and temperature controller (TMS93) combination provided temperature control to $\pm 0.1^{\circ}$C. The liquid crystals were contained between cover slips, which were coated with aqueous Cetyltrimethylammoniumbromide, thus ensuring that the helical axis was normal to the glass substrates (homeotropic alignment).

RESULTS AND DISCUSSION

It is helpful to report a few general trends for the materials before discussing each in detail. The greatest change of pitch (pure materials) was found to occur over a narrow temperature interval just below the SmA-SmC* transition. Bragg peaks were observed in the SmC* phase for each sample but similar reflections in the SmC_A^* phase were detected only for AS661. The pitch of the SmC* phase in AS661 changes with temperature far more than the pitch of the SmC_A^* In all cases, the SmA-SmC* transition temperatures are reduced by the addition of the reactive monomer. Photo-polymerization produced a further reduction in this transition temperature. The ferrielectric phase(s) which form(s) between the SmC* and SmC_A^* does not Bragg reflect visible light.

The wavelengths selectively reflected from pure and doped sample of AS618 are shown in Figure 2. Of the materials studied, only AS618 forms the SmC_α^* phase which exist between the SmA and SmC* phases. The SmC_α^* phase has a pitch of $\sim$200 nm and hence does not reflect in the visible region [14]. Also, the Bragg wavelengths observed in AS618 are longer than those of the other samples. Hence, this raises the question whether the SmC_α^* phase becomes stable as the pitch increases. We did not detect any Bragg peaks in the cross-linked sample. Hence, cross-linking shifts the Bragg peaks to the infra-red region in this material since we have detected Bragg peaks in cross-linked samples of AS661, AS612 and AS620.

Bragg reflections for pure AS612 and well as the doped and irradiated samples are shown in Figure 3. There are well-defined maxima in the data for the pure sample and the doped sample. Though most stable, the irradiated sample shows a weak temperature dependence. As with AS618, Bragg peaks are detected only in the SmC* phase. The light reflected by the SmC_A^* phase in both AS612 and AS618 is beyond the scope of our apparatus which effectively covers only visible wavelengths. The topology of the temperature dependence of the wavelengths selectively reflected in pure samples of AS612 and AS618 are quite similar.

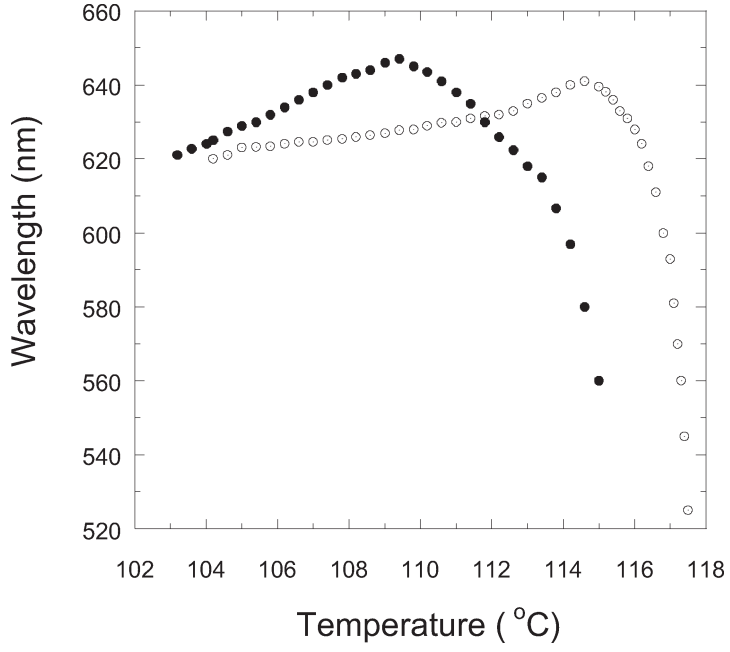

FIGURE 2 Wavelengths selectively reflected from the SmC* phase of AS618: Pure material (open circles); material doped with polymer (solid circles).

The phase transitions of AS620 are somewhat more complicated that either AS612 or AS618 in that it forms the SmI^*_A and the SmI* phases (but only in the cooling mode [14]). However, we did not detect either of these phases. Also, the greatest change in pitch in the SmC* phase is seen in AS620 (see Fig. 3). There is a well-defined maximum in the data even for the cross-linked sample, which is an indication that good alignment is preserved in the presence of the polymer matrix. The molecular length of AS620 (deduced from the layer spacing in the SmA phase) is the shortest of all the materials studied and this may be the reason for the strong reflection observed in the cross-linked sample. Also, the reflections in the SmC^*_A phase are outside the visible region.

Bragg peaks are detected in both the SmC* and SmC^*_A phases for AS661. Figure 4 shows the temperature dependence of optical Bragg reflections from pure AS661. Three distinct regions are clearly visible and these are marked in Figure 4. The corresponding temperature intervals are 7°C, 4.3°C and 25.6°C. These results are consistent with what has appeared in the literature [14].

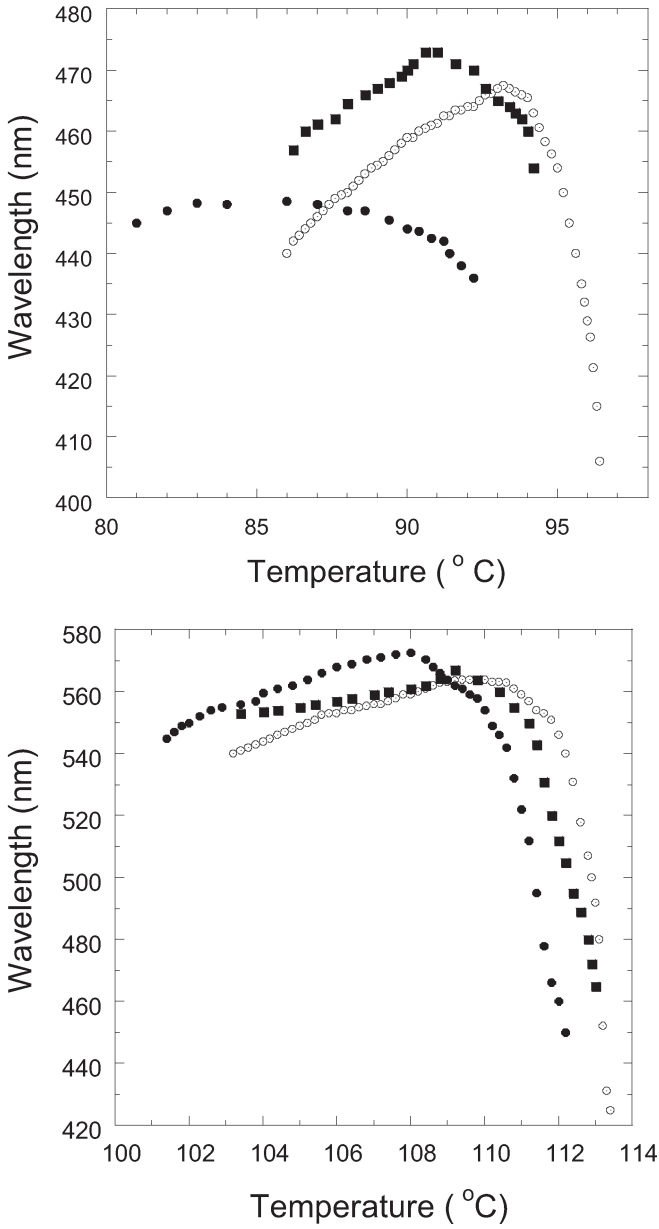

FIGURE 3 Bragg wavelengths selectively reflected from the SmC* phase of AS612 (Top) and AS620 (Bottom); pure state (open circles): doped but uncrossed-linked (solid squares): crossed-linked (solid circles).

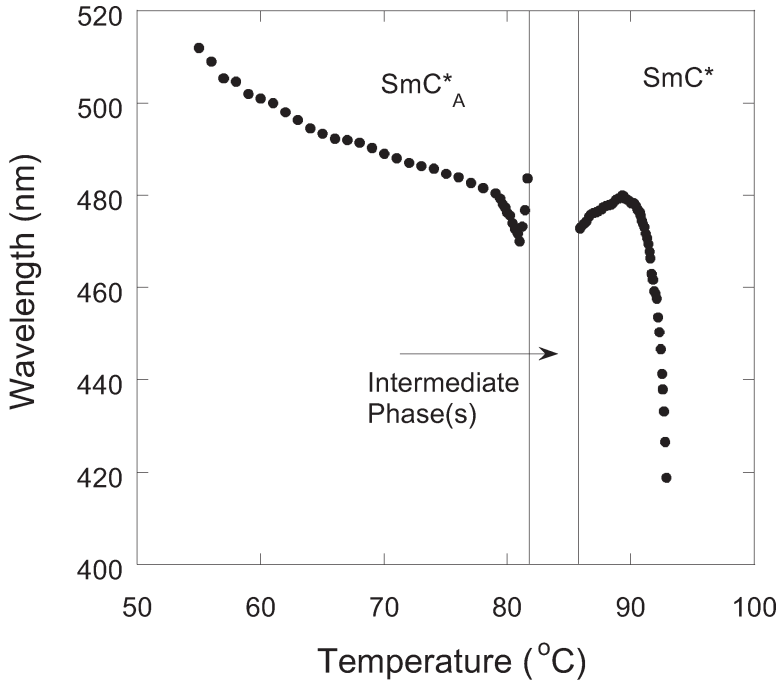

FIGURE 4 Bragg wavelengths selectively reflected by pure AS661.

The reflection data contains a minimum for SmC^*_A phase intermediate phases and a maximum for the SmC^* phase. The detection of Bragg peaks in the visible region for both phase has been attributed to full pitch reflections in the SmC^* phase and half-pitch reflections in the SmC^*_A phase [15–17]. This means that AS661 has the shortest pitch of the materials studied ($\sim$ one half of the other materials).

The corresponding data for a doped sample of AS661 is shown in Figure 5. There is now a marked change in the Bragg reflection spectrum. The maximum in the SmC^* data and the minimum in the SmC^*_A; data are now absent. Also, the intermediate phase(s) is stabilized at the expense of the SmC^* phase; while the range of the Sm^*_A phase is unchanged. The temperature interval of the SmC^* is reduced from 7°C to 4.1°C and there is a simultaneous increase in the range of the intermediate phase(s) from 4.3°C to 7.1°C. The range of the SmC^*_A; phase is essentially unchanged but the wavelengths are shifted to longer wavelengths (increased pitch).

Figure 6 shows the temperature dependence of Bragg reflections from a cross-linked sample of AS661. As with the pure and doped samples,

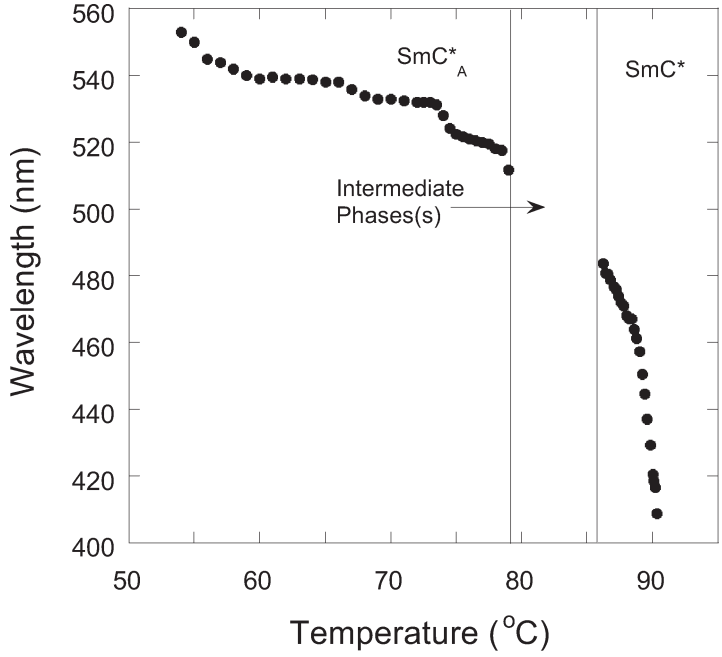

FIGURE 5 Bragg wavelenghts selectively reflected from a doped sample of AS661.

three distinct regions can be identified. The helical pitch in the SmC* phase shows a strong temperature dependence for $\sim 2.5^{\circ}$C and then becomes saturated (for $\sim 7.5^{\circ}$C). In the absence of external forces, the helical pitch of the chiral smectic phases will increase if the temperature is decreased. However, this natural evolution is altered by the presence of the network, which tries to preserve its original configuration [18]. The competition between these two opposing factors may be responsible for the step-like Bragg spectrum in the SmC* phase.

The wavelengths selectively reflected from the SmC^*_A phase, are also affected by the chiral network. The temperature dependence of the Bragg peaks shows a linear increase in wavelength with decreasing temperatures. However, the difference between the maximum and minimum wavelengths is ~ 20 nm which is at least a factor of two smaller than the pure or doped material.

CONCLUSION

The phase behaviour of materials that exhibit antiferroelectric phases is both complex and intriguing. Bragg scattering is a sensitive tool for

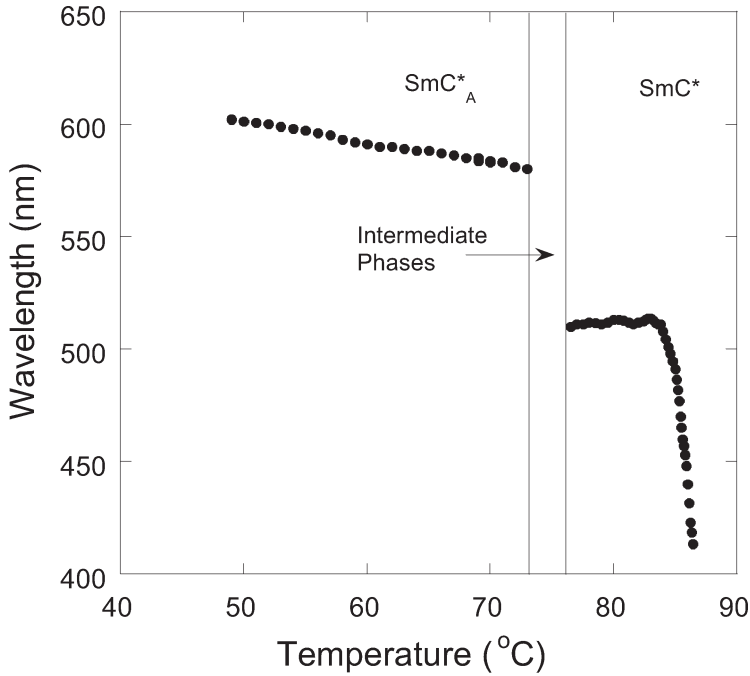

FIGURE 6 Bragg wavelengths selectively reflected from a cross-linked sample of AS661.

identifying transitions of such liquid crystals. Polymer networks affect the optical and thermodynamic properties of an antiferroelectric liquid crystal differently by exerting different elastic forces on the liquid crystal. Hence, it may be possible to tailor such materials for different applications by varying the polymerization conditions. The stability of the SmC* and possibly the intermediate phase(s) are sensitive to impurities. When polymerization is carried out in the SmC* phase, this phase is stabilized at the expense of the intermediate phase(s).

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