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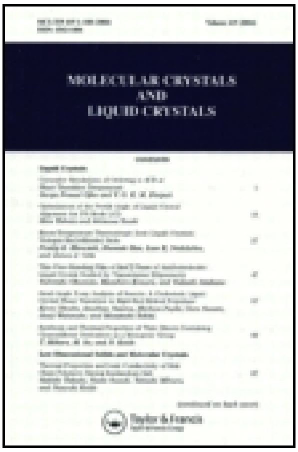

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Gradient-Oriented State of Polymers: Formation and Investigation

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Gradient-Oriented State of Polymers: Formation and Investigation

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The concept of a gradient-oriented state of polymers is formulated for the first time and some regularities of the formation of this state are established. The specific influence of non-homogeneous mechanical fields is demonstrated by means of the example of the creation of gradient birefringence (GB) elements. These are the focus of research into the new non-traditional direction of gradient birefringence (GB) optics. Possible areas of application for GB elements are polarized compensators, polarized holography and photonics, the interference-polarizing GB monochromator, luminescence analysis, etc.

Keywords GB elements; GB monochromator; gradient-oriented state; luminescence analysis; polymers; Regularity

Introduction

The creation and investigation into materials with gradient properties is considered to be one of the main directions of polymer science for the 21st century. Success in developing methods of obtaining materials with inhomogeneous distributions of properties was essentially achieved in the 1970s. The gradient of refraction depends on the heterogeneity of the composition. In such an area the trajectory of the light beam is constantly curvilinear along the free path length, which causes deviation of the light beam and, with proper distribution of the refraction index, the focusing of beams as well. In the 1970s, cylindrical elements were fabricated from polymers with a radial-parabolic distribution of composition, having the ability to transmit and focus light [1]. These elements became known as SELFOC (self-focusing) lenses [2–9].

The introduction of a new parameter in optics – the refraction index gradient – created a new field for theoretical and experimental investigations. In the scientific literature dealing with refraction gradient elements (materials, areas) the term GRIN (Gradient Refractive Index) has been established and for the corresponding field of science, GRIN optics. Some interesting results have been reported in this field [2,10–12].

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Worldwide it appears that the attention of researchers is concentrated on the Refractive Index. At the same time, materials having other optical properties, in particular materials with gradient birefringence, are being investigated too. The first polymer materials (films) having such optical properties were obtained by us [13]. We also contributed the acronym for materials with gradient birefringence (elements, areas), namely GB (gradient birefringence) materials (elements, areas).

By introducing a new parameter in optics, i.e. gradient birefringence, the basis for a new direction of optics was laid, which resulted in widening of the concept of "gradient optics" [12–19]. Nowadays, gradient optics covers two independent directions, namely GRIN optics and GB optics. Both these directions are generally important in the development of polymeric science. GRIN elements and GB elements are formed in different ways. GRIN elements occur as a result of chemical transformations. Many methods have been attempted by means of which the known chemical transformations can be realized in monomer (polymeric) systems in the gradient regime (in selected directions and with the appropriate velocity).

The formation of GB elements is based on the characteristic ability of linear polymers to undergo considerable deformation. During such deformation the polymer passes through a specific, so-called "oriented" state. In this state macromolecular chains (as usual in separate sections) in advantageous positions stretch in a particular direction. The birefringence created at this time is a function of relative lengthening:

$$\Delta n = n_1 - n_2 = \gamma \lambda \tag{1}$$

where: n_1 = an ordinary ray; n_2 = an extraordinary ray; γ = the optical coefficient of deformation; and λ = the relative lengthening. It follows directly that the gradient of relative lengthening determines the gradient of birefringence.

The acceptance of gradient as a polymer property is an important step in the development of polymer science. The state of orientation of a polymer is termed its "gradient-oriented" state. This state is an unused resource in the nature of polymers. The introduction of a new structural characterization of polymers essentially broadens the general problems of research into polymers. Primarily, it increases the possibility of regulating all properties that depend on the degree of orientation (optical, mechanical, thermal, electrical, etc.), encouraging the creation of new scientific directions as has already happened in GB optics [13].

For the creation of a gradient-oriented state, the form of the polymer sample selected was isotropic (i.e. the form of the clamps and their relative location) so that it possessed a preliminarily established gradient of relative lengthening. By varying other parameters (temperature, value, velocity of deformation, etc.) it is possible to regulate the gradient-oriented state of a polymer.

We have reported on several versions of the equipment [18] used for the creation of a preliminarily established inhomogeneous mechanical field. As a result of cohesion in a polymeric body, an established gradient of relative lengthening is formed and, consequently, so is the preliminarily established gradient birefringence.

In this paper, we consider some regularities of formation of the gradient-oriented state, which are connected to some aspects of construction of the equipment used. We also investigate some optical properties of gradient-oriented polymers and discuss possible areas of application.

Experimental

The experiments were carried out on isotropic PVA (polyvinyl alcohol) films (thickness 80–100 μm). Tension of the film was achieved with a specifically constructed apparatus

(T = 358 K, velocity of tension = 20 mm/min). To create a non-homogeneous mechanical field we used clamps with various configurations. To study the optical properties (transparency) of the firms we used an Opton microscope spectrometer.

Derivation of the Basic Relationships

The distribution of the relative lengthening is determined by the profile of clamps $f_1(x)$ and $f_2(x)$, where independent variable x changes in the $[x_1, x_2]$ interval. $f_1(x)$ undergoes parallel displacement across the OY-axis and $f_2(x)$ is a fixed function. If we designate the relative lengthening across the OY-axis as $\Phi(x)$ and the value of parallel transfer as K, then for the distribution of the relative displacement we have:

$$\Phi(x) = \frac{K}{f_1(x) - f_2(x)} \tag{2}$$

We can choose $\Phi(x)$ from the different types of function (linear, parabolic, hyperbolic, sinusoidal, etc.), taking into account the isochromic aspect of the GB element. From equation (2) we have:

$$f_1(x) = K/\Phi(x) + f_2(x) \tag{3}$$

Let us consider different types of $\Phi(x)$ function:
1) If the linear function $\Phi(x) = ax + b$, then:

$$f_1(x) = K/(ax + b) + f_2(x) \tag{4}$$

When $a = 1$, $b = 0$ and the profile of the first clamp is linear, i.e. $f_1(x) = c$, then:

$$f_1(x) = K/x + C \tag{5}$$

Therefore the profile of the second clamp is hyperbolic.
2) If the parabolic function $\Phi(x) = ax^2 + bx + c$, then:

$$f_1(x) = K/(ax^2 + bx + c) + C, \tag{6}$$

When $a = 1$, $b = 0$, $c = 0$:

$$f_1(x) = K/x^2 + C \tag{7}$$

Therefore the profile of the second clamp is also hyperbolic.
3) If the hyperbolic function $\Phi(x) = a/x$, then:

$$f_1(x) = Kx/a + C \tag{8}$$

In this case the form of the second clamp is linear.
4) If the sinusoidal function $\Phi(x) = \sin x$, then:

$$f_1(x) = K/\sin x + C \tag{9}$$

In this case the form of the second clamp is so complicated that it can only be realized under definite, strictly limited conditions.

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Let us assume that the initial length of the sample in the x-axis is greater than the distance between the two clamps, i.e. $\Delta x > [f_1(x) - f_2(x)]$. Then for the relative lengthening, we have:

$$\Phi(x) = K/(f_1(x) - f_2(x) + \Delta x \tag{10}$$

In this case, the profiles of the clamps change considerably.

When $\Phi(x) = ax + b$ (linear function), then

$$f_1(x) = K/(ax + b) + f_2(x) - \Delta x \tag{11}$$

The value of Δx is preliminarily chosen and is always a linear function, i. e. $\Delta\ (x) = \alpha x + \beta$.

When $f_1(x) = C$, then:

$$f_1(x) = K/(ax + b) + C - (\alpha x + \beta) = K/(ax + b) - \alpha x + \gamma, \tag{12}$$

where $\gamma = C - \beta$.

When $a = 1$, $b = 0$, then:

$$f_1(x) = K/(x - \alpha x) + \gamma \tag{13}$$

Therefore the profile of the second clamp is a linear combination of the hyperbola and the line.

When $\Phi(x) = ax^2 + bx + c$ (parabolic function), then:

$$f_1(x) = K/(ax^2 + bx + c) + C - (\alpha x + \beta) \tag{14}$$

In this case, the profile of the second clamp is also a complicated function.

When $\Phi\ (x) = a/x$ (hyperbolic function), then:

$$f_1(x) = K/(a/x + c) - (\alpha x + \beta) = (K/a)x + c - \alpha x - \beta \tag{15}$$

Therefore the profile of the second clamp in this case is linear.

The results obtained allow us to improve the possibilities of existing optical devices. At the same time, it may be possible to plan and create new-generation optical devices.

The profiles of the clamps with all the factors that have an influence on the oriented state of polymers define the optical properties of GB elements. These factors are: molecular and supermolecular structure; average molecular mass and distribution of molecular mass; presence of components and plasticizers; velocity of tensile deformation; values of relative deformation; temperature; environment; and scale factor. We present the experimental results to illustrate some specific cases of the formation of the gradient-oriented state (i.e. the creation of GB elements).

(a) Parallel clamps. In this case, the value of the relative displacement along all the film perpendicular to the direction of tension is constant. Accordingly, there will be no gradient of birefringence. However, in polar scope (crossed Nicols, six times tension, initial length of film 6 cm) sharp isochromes are seen at the free ends of the film at a width of 1 cm. Therefore, at the edge of the film the gradient of birefringence is perpendicular to the tension. There is a homogeneous region in the middle of the sample where the birefringence (Δn) is practically constant. Fig. 1a shows a microphotogram of the film for the wavelength $\lambda = 630$ nm, obtained by means of the microscope spectrometer (crossed Nicols). It can

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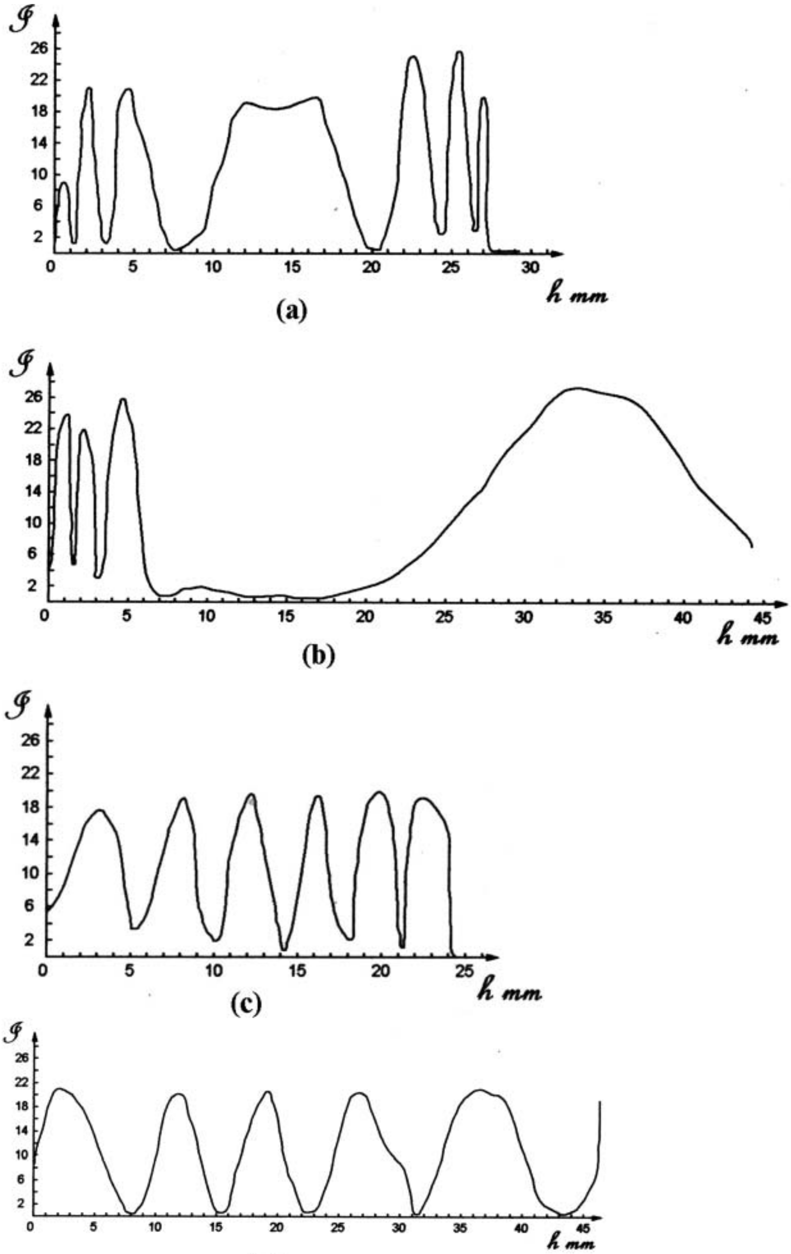

(a)

(b)

(c)

(d)

Figure 1. Dependence of transparency I of gradient-oriented film on the h-coordinate (crossed Nicols). (a) Parallel clamps; film of rectangular form; direction of tension is perpendicular to the clamps. (b) Clamps angled at 45° towards each other; trapezium-form polymer film; direction of tension is parallel to the base of the trapezium. (c and d) Parallel clamps; trapezium-form polymer film; direction of tension is parallel to the alignment of the trapezium; length of one of the free edges of the film (l_2) is greater than the distance between clamps l_1. (e) Parallel clamps; trapezium-form polymer film; direction of tension is parallel to the alignment of the trapezium; relation l_2/distance between two clamps is greater for one film (case c) than that for the other (case d). *(Continued)*

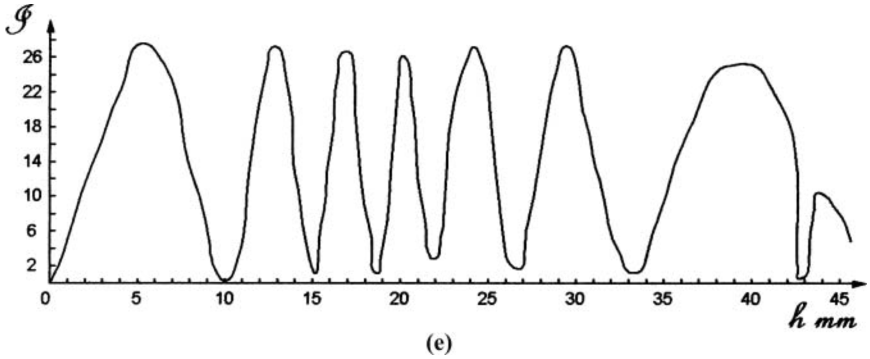

Figure 1. (Continued)

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be seen that in the free region of the given wavelength two isochromic bands are received, the maximum of which corresponds to the half-wave regions $(2n + 1)\lambda/2$. Consequently, theoretically, a gradient will not occur when the tension is parallel, but experimentally, we observe that a gradient does occur. The reason for this lies with the free edges of the film. When it is stretched, the sample becomes narrower and the free edges of the film are bent. As a result, absolute lengthening at the edges is greater than in the middle of the film.

(b) Clamps angled at 45°. In this case $f_1(x) = (\sqrt{2}/2)x$ and $f_2(x) = (\sqrt{2}/2)x$. The equation is then transformed into:

$$\Phi(x) = K/x\sqrt{2} \tag{16}$$

This is an equation of a hyperbola. When such clamps are used to create parallel tension of the film, an oriented polymer film is formed, in which regulation of the distribution of the birefringence gradient perpendicular to the direction of tension is hyperbolic. This was indeed found to be the case. Figure 1b shows microphotograms of these samples. Here the distances between bands corresponding to $(2n + 1)\lambda/2$ have a nearly hyperbolic distribution.

(c, d and e) Parallel clamps. The length of one of free edges of the film is greater than the distance between two clamps (Fig. 2). In this case, according to equation (8), the distribution

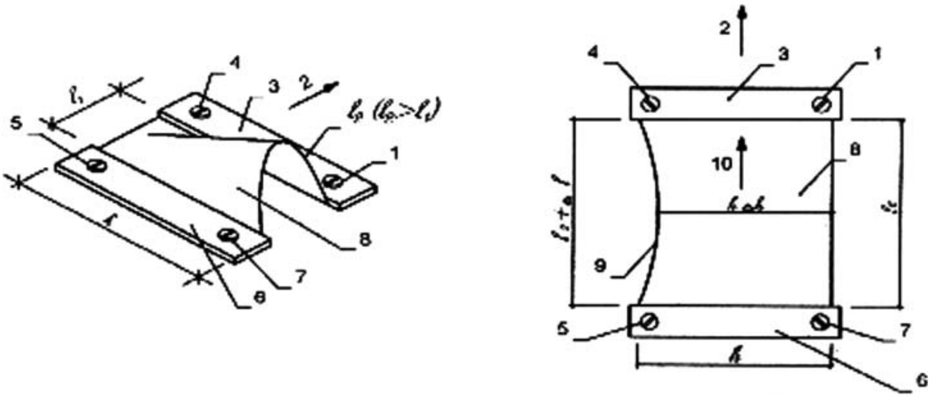

Figure 2. Gradient tension of polymer film. 1, 4, 5, 7 – screws; 2 – direction of tension; 3, 6 – clamps; 8 – polymer film: (a) before tension; (b) after tension. Parallel clamps; isosceles trapezium; direction of tension is across the alignment of the trapezium.

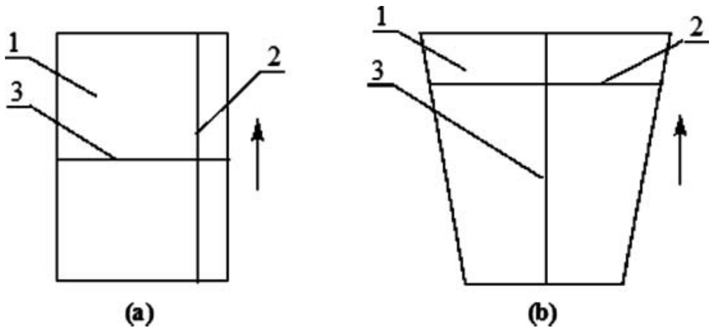

Figure 3. Direction of tension, disposition of isochromes and gradient in gradient-oriented films. 1 – Film; 2 – Disposition of isochromes; 3 – Gradient; arrow shows the direction of tension.

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of the relative lengths may vary. The tension is continued until the distance between the two clamps equals l_2. Figure 1c and 1d show the microphotograms and it can be seen that the distances between the bands corresponding to $(2n + 1)\lambda/2$ are practically equal.

At the same time the relation l_2/distance between the two clamps is greater for the one film (Fig. 1c) than for the other (Fig. 1d).

(f) Parallel clamps: isosceles trapezium, tension across the alignment of the trapezium. The scheme in Fig. 3a shows the directions of tension, the dispositions of the isochromes and the gradients in relation to each other. This case is in contrast to others in that the disposition of these characteristics is different, as described by the scheme in Fig. 3b.

Some Areas of Application of GB Elements

Polarized Compensators

Generally, the fundamental principle behind the operation of compensators is the exclusion of any optical parameter. For example, in the case of ordinary isotropic phase compensators, the thickness and refractive index $(n \cdot d)$ of an optical element have to provide concrete phase shifting $(k.\lambda, \ldots \infty)$. Such compensators are used in interferometer tasks. In the case of anisotropy compensators, the concept of phase shifting does not mean absolute phase shifting for a given wavelength, but rather relative phase shifting $(\Delta n \cdot d)$ between usual and unusual beams (waves). That is why the accuracy of optical measurements has been increased considerably by the use of anisotropy compensators. Nevertheless, the area of practical use of both isotropic and anisotropy compensators is limited, so that in practice they fulfil a reference function. By comparison, the GB compensator is not a reference optical element, but provides both the concrete phase shifts in the whole section of the visible spectrum and any phase shift for the given wavelength.

Polarized Holography and Photonics

For both holography and photonics it has become necessary to envisage the polarized characteristics of light. Generally, only the intensity gradation is important and this is the reason why the dynamic range of the process was sharply limited. In the case of fixation of polarization, it is not the intensity gradation (which is limited) that is decisive, but the fixation of practically boundless (infinite) versions of polarization. Consequently, it may be necessary to provide complex space polarized light modulation. One of the ways of doing

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this is to use GB elements with a complex structure, which allows the formation of light waves with specific polarized characteristics to be realized.

The application of GB elements in photonics (in photochemistry) is of special importance, so at present intensive investigations are being carried out into both the linear and nonlinear Veigert effects [19]. It is hoped that the GB elements will provide an accurate and simple relation between the linear and nonlinear Veigert effects. In particular, the calibrated (divided) GB elements give the possibility of realizing the radiation simultaneously by means of all types of polarization. It is very important that in corresponding sections of polarization the power exposition should be extremely similar, which is automatically realized. This is particularly important since it will exclude the necessity for labour-intensive and less accurate photometric measurements. In photonics, the GB elements will fulfil the function definite standard polarized modulators.

Interference-Polarizing GB Monochromator

The issue of miniaturization of spectral devices is very current. Clearly, miniature monochromators in the form of gradient multi-layer filters have already been created. The filters are distinguished by the fact that the thickness of separate dielectric layers of multi-layer systems changes constantly along the filter, which ensures maximum transparency in the red section of spectrum on the one side and in the violet section on the other side [20]. The drawback of such monochromators is their low capability of spectral distinction ($>10A^0$). It is possible to improve the capability of spectral distinction if the interference-polarizing filter is created under similar principles. At the same time, in such a monochromator not only a multi-layer structure of alternative thicknesses will be used, but also an additional gradient anisotropic structure (GB structure), the multiple of the wavelengths of which will coincide ($\Delta n \cdot d = n \cdot \lambda$) with the maxima of the transparency spectrum of the monochromator. Such a monochromator will have a capability of spectral distinction of the order of 0.1 Å. The sizes of a monochromator may be from 5.1 mm^2 to 50–100 mm^2.

Luminescence Analysis

It is very interesting to consider the application of anisotropic films in luminescence analysis, especially as it occurs in oriented organic films as a matrix. The radiation of installed luminescent paints is partially polarized and in this case the degree of luminescence (fluorescence) polarization depends mainly on the structure of the luminescent material (molecules) itself and on the quality of matrix orientation. If the matrix orientation changes along the film, i.e. if we have a gradient anisotropic matrix, the quality of the luminescence polarization is also characterized by a definite distribution, i.e. by the gradient in the same direction. If the degree of luminescence polarization, let's say along the X-axis, is expressed by $P_1(x)$, and the degree of matrix polarization or distribution of anisotropy by $P_m(x)$ or $\Delta n(x)$, then the relative value is:

$$K = P_1(x)/P_m(x) \quad \text{or } K = P_1(x)/\Delta n(x) \tag{17}$$

In total, luminescence intensity and spectral characteristics should determine the definite features of given luminescent materials unambiguously. This approach has decided advantages, also for the possible broadening of the investigation into laser effects.

For the development of GB optics (similarly to classical optics), processing is a universal method, which will allow us to realize GB structures for concrete functional purposes by creating various pieces of technological equipment and controlling their technical parameters. In the case of simple one-dimensional compensators, the main determining technological parameters could be the relative lengthening, profile and scale of the clamps. In the case of relatively complex two-dimensional compensators, three main parameters are added to the coordinated parameters, which means that simultaneous orientation to the orthogonal, or generally to any other direction, is possible too. If we add to these materials a space modulation of the temperature field as well, e.g. gradient heating, the configuration of the GB elements obtained can be changed within a wide range, according to their ultimate purpose.

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Conclusion

The concept of a gradient-oriented state of polymers has been formulated for the first time and some regularities of the formation of this state have been established. We discussed some concrete cases of the creation of GB elements and possible areas of application for these elements.

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