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Rubber elasticity of polyacrylamide gels in high network concentration

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Shear modulus of polyacrylamide (PAAM) gels has been measured with the network concentration ranging from 0.02 to 1.0 g/cm^3. In the low concentration region, the shear modulus is a scaling function of network concentration with the exponent equal to 1/3, which is expected by classical rubber elasticity theory. As the concentration increases, the behaviour of shear modulus deviates the scaling law significantly. This deviation has been observed from all six series of gels with cross-linking concentrations varying from 0.61 to 4.91 mol%. The modified Mooney theory which incorporated a second higher order term is used to explain the results. This second term is believed to be a result of gel inhommogeneity. The measured shear modulus data can be fitted well with the new theory, with two exponents equal to 0.33 and around 2.0–2.5, respectively. The crossover concentration from the classical behaviour to the non-classical behaviour was found to be cross-linking concentration dependent. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Gels are three-dimensional networks of cross-linked polymers immersed in solvent. The mechanical properties of polymer gels are determined by the bulk modulus and shear modulus and have subjected extensive investigation[1-5]. The application of scaling methods to these elastic moduli has led to some dramatic successes in both theoretical understanding and experimental applications [6]. A variety of polymer gel systems have been tested and it was found that the concentration dependent shear modulus of gels follows the classic theoretical scaling law with the scaling exponent equal to 1/3[7-9]. To our knowledge, all of these tests were performed on gels which have the network concentration below 0.25 g/cm^3. The higher concentration is hard to obtain using the conventional deswelling methods which rely on osmotic pressure to squeeze water out[7-9]. It is of interest to explore the scaling behaviour at high concentrations

In this paper, we present network concentration dependence of shear modulus of polyacrylamide (PAAM) gel over a broad concentration ranging from 0.02 to 1.0 g/cm^3. The experiment clearly shows that the relationship between the shear modulus and polymer network concentration deviates from the single scaling law with the scaling exponent of 1/3 in a high network concentration regime. The modified Mooney rubber elastic theory based on the heterogeneity of the gel network seems to describe our data well.

The free energy of a gel can be written as a summation of two terms:

$$F = F_1(\phi) + F_2(\alpha_x, \alpha_y, \alpha_z). \tag{1}$$

where ϕ is the polymer concentration, α_i's are the principal elongation ratios relative to the gel dimensions when it was made. The first term is network concentration dependent, corresponding to the free energy of an uncross-linked polymer solution. The second term, F_2, is sensitive to the network swelling anisotropy, and is usually called the elasticity term. In the classical rubber elasticity theory[10]†, this term is expressed as:

$$F_2 = B[\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3]. \tag{2}$$

where B is the temperature and gel cross-linking concentration dependent. For a gel with concentration equal to ϕ, F_2 can be written as:

$$F_2 = B\left(\frac{\phi}{\phi_0}\right)^{-2/3} [\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2 - 3], \tag{3}$$

with Λ the elongation ratio relative to the isotropic state at concentration equal to ϕ,

$$\Lambda_i = \alpha_i \left(\frac{\phi}{\phi_0}\right)^{1/3}. \tag{4}$$

If a cylindrical gel is uniaxially elongated along its z-direction with $\Lambda_z = \Lambda$, then the deformations perpendicular to the elongation axis are $\Lambda_x = \Lambda_y = \Lambda^{-1/2}$. The elongation pressure, defined as the force divided by the cross-section area of the undeformed gel, can be obtained from equation (3) as:

$$P = \frac{2B}{V_0}\left(\frac{\phi}{\phi_0}\right)^{1/3} [\Lambda - \Lambda^{-2}] = G\,[\Lambda - \Lambda^{-2}] \tag{5}$$

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† We choose to use the simpler elasticity expression over other refined theories since these refined ones do not change the major conclusions of our study.

where G, by definition, is the shear modulus of the gel,

$$G=G_e\left(\frac{\phi}{\phi_e}\right)^m \tag{6}$$

with $G_e=(2B/V_0)(\phi_e/\phi_0)^m$. The exponent m is equal to 1/3 here.

The exponent m has been measured for several systems[7-9]. For all these systems studied, the gel network concentrations were less than 0.25 g/cm^3, and were controlled by osmotic deswelling, i.e. by placing the gel samples in semi-permeable bags immersed in a polymer solution. Due to the practical limit of the polymer concentration, the osmotic pressure is limited to a certain range. Therefore, the highest network concentration due to the osmotic deswelling is limited. Here, we varied the network concentration by evaporating a controlled amount of solvent. This method allowed us to explore gel properties in the whole concentration range.

EXPERIMENTAL

The samples measured (all cylindrical) were six series of polyacrylamide gels cross-linked with methylene-bis-acrylamide (BIS)[11]. The monomer (acrylamide) concentration of all samples at polymerisation was 5 wt%. The cross-linker concentrations were varied as 0.61, 0.92, 1.23, 1.84, 2.46 and 4.91 mol% relative to acrylamide number concentration. In the following, we will use a BIS concentration of 1.23 mol% as a standard unit for convenience. Thus the six BIS concentrations will be represented by BIS equal to 0.5, 0.75, 1.0, 1.5, 2.0 and 4.0, respectively. Fully swollen and pre-cut samples were placed in a 45°C oven for a varying amount of time to evaporate a desired amount of the gel water. Then the samples were sealed in vials for several days to ensure uniformity of the network concentration.

The shear modulus, defined by equation (5), was measured using a simple compressional method, similar to the one described in Ref. 7. The maximum deformation ranged from 10 to 30%, depending on samples. For each sample, the compressional force and sample height were recorded during both force increasing and force decreasing processes. The two processes yielded almost identical stress–strain relations and the average value of G obtained from them was used. Based on the resolution of the force gauge and the sample height measurement, the uncertainty in shear modulus value was estimated to be about 3%. The sample weight loss (water evaporation) during the measurements was found to be insignificant (less than 2%), which satisfied the constant volume requirement of the technique. The sample network concentrations were calculated by knowing the weights of the samples and their dry weights, obtained after the shear modulus measurements. To further reduce the evaporation, and to overcome the gravitational effect on weakly cross-linked gels, we immersed some of our samples in vacuum pump oil (TKO-19 + , Kurt J. Lesker Co.) during the shear modulus measurement. No difference was observed between the results obtained from samples in air and in oil. This indicates again that the loss of solvent is negligible in our experiment.

RESULTS AND DISCUSSION

Figure 1 is the network concentration dependence of shear modulus G of samples of different cross-linking concentrations. The data have been shifted to the indicated amount in the figure for clarity. The first data point of each sample (the ones with the lowest network concentration) is the shear modulus of the fully swollen sample. For the network concentration below 0.2 g/cm^3, the classical exponent of m = 1/3 was obtained. As the network concentration increases, the concentration dependence deviates from m = 1/3, drastically. These data indicate that the concentration dependence of shear modulus cannot be described by a single scaling exponent.

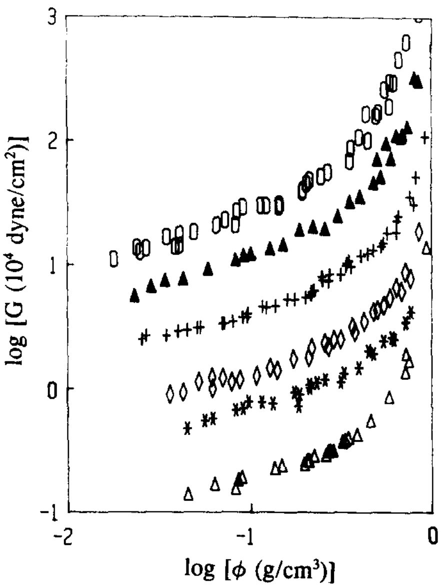

Figure 1 Network concentration dependence of shear modulus for PAAM gels with different degrees of cross-linking. All data were collected at room temperature. The BIS concentration is represented by the number immediately following the symbols. For clarity, the data have been shifted by constant multiplication factors which are indicated by the numbers in parentheses: ○, 0.5 (16); ▲, 0.75 (4); +, 1 (x1); ◇, 1.5 (1/3); ★, 2 (1/6); and △, 4 (1/16)

The deviation is expected from modified Mooney theory[12], which shows that the higher order term of shear modulus has to be considered at high polymer network concentration:

$$G=\phi^{\frac{1}{3}}[C_1+C_2(\phi)] \tag{7}$$

where C_1 is independent of ϕ and C_2 is a function of ϕ. For a small ϕ, $C_2(\phi)$ approaches zero, corresponding to low polymer network concentration.

The deviation of concentration dependence of gel shear modulus suggests that at high concentration, a different mechanism dominates the contribution to shear modulus. One likely mechanism is the compressional energy associated with the structural heterogeneity of the network. It is well known that the network structures of gels, in general, are highly heterogeneous[13-16]. These heterogeneities are mostly related to the gelation processes, especially when the process is free radical polymerisation[14]. For instance, when BIS is used as a hydrogel cross-linker, its hydrophobicity causes clustering of BIS in the network to form dense domains[13]. In general, the network structure will be heterogeneous when the reaction rates involved are drastically different. When the chemical reaction involves ionic species (e.g. sodium acrylate), the electrostatic interaction generates lattice-like domain structure in the network, which has been observed by small angle neutron scattering [15]. Therefore, structure domains are

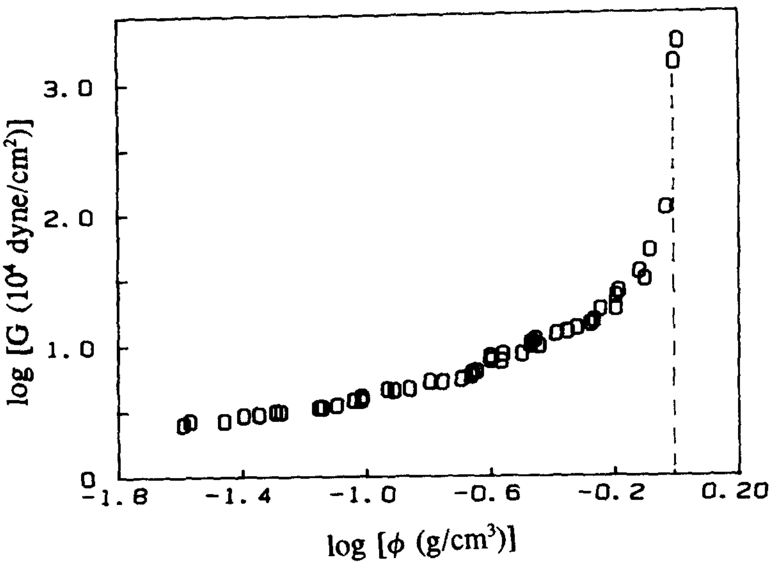

Figure 2 Network concentration dependence of shear modulus for PAAM gel with BIS = 1. The data were collected at room temperature. The glass transition point is located at around 1 g/cm^3 as indicated by a dashed line

characteristics of gel networks and are intrinsic properties. In our case, the domains are mostly due to the hydrophobicity of cross-linkers (BIS). These heterogeneities of gels, even the highly transparent ones, can be detected easily by light scattering techniques[17–20]. As a laser beam scans through a polyacrylamide gel sample, the scattered intensity changes dramatically with spatial correlation length around 25 microns[14,15]. The network heterogeneity has a direct impact on gel properties, including solvent permeability[13,21]. It was also speculated that the gel heterogeneity has an impact on the measured critical exponents of its volume phase transition[22]. *Figure 3* shows the two-phase heterogeneity model originally proposed by Weiss *et al.* to explain their gel permeability data [13]. To determine the form of $C_2(\phi)$ in our case, we assume that the network has two phases: the dense phase and the dilute phase. The dense phase is highly cross-linked and has higher mechanical strength. As the gel is deswelled, the polymer concentration of the dilute (highly swollen) regions will be affected more than that of the dense regions at first. However, further deswelling will result in the dense domains getting closer and closer to each other. The compressional energy arising from the dense domain–domain repulsive interaction mutual exclusion effect is related to the distance between them. This energy can therefore be written as:

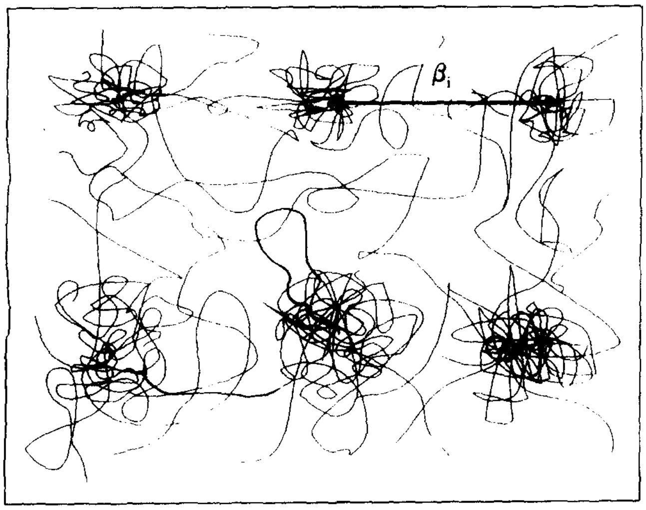

Figure 3 A sketch of gel structure inhomogeneity with dense and dilute domains

$$F_3 \sim (\beta_x^{-t} + \beta_y^{-t} + \beta_z^{-t}) \tag{8}$$

where β_i is the average distance between adjacent dense domains in the i-th direction (*Figure 3*). The power t is a measure of the interaction. The β_i's are related to both the network concentration ϕ and the compression ratio Λ_i,

$$\beta_i \sim \Lambda_i \phi^{-1/3} \tag{9}$$

The total elastic free energy of a highly deswelled gel is therefore,

$$F_{\mathrm{ela}} = B\left(\frac{\phi}{\phi_0}\right)^{-2/3} [\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2] + A'\left(\frac{\phi}{\phi_0}\right)^{t/3} \times [\Lambda_x^{-t} + \Lambda_y^{-t} + \Lambda_z^{-t}]. \tag{10}$$

A' is expected to be positive since F_3 is repulsive. The elongational pressure is then,

$$P = G_e\left(\frac{\phi}{\phi_e}\right)^{1/3} [\Lambda - \Lambda^{-2}] + G_e\frac{tA'}{2}\left(\frac{\phi}{\phi_e}\right)^{1+t/3} \times [\Lambda^{(t-2)/2} - \Lambda^{-(t+1)}]. \tag{11}$$

To the first order of $\Delta = (1 + \Lambda)$,

$$P = G_e\left[\left(\frac{\phi}{\phi_e}\right)^{1/3} + A\left(\frac{\phi}{\phi_e}\right)^{1+t/3}\right] 3\Delta \tag{12}$$

where A measures the relative contribution between the two terms ($A = t^2A'/4$). The shear modulus of a highly concentrated gel is therefore,

$$G = G_e\left[\left(\frac{\phi}{\phi_e}\right)^{m_1} + A\left(\frac{\phi}{\phi_e}\right)^{m_2}\right] \tag{13}$$

where $m_1 = 1/3$ and $m_2 = 1 + t/3$. The two terms in the bracket contribute to G equally at the crossover concentration $\phi = \phi_c = \phi_e/A^{1/(m2-m1)}$. It was found that all of our data can be well fitted by equation (13). *Table 1* lists the fitting parameters obtained from the data. No significant difference was found when the data were fitted with the

Table 1 Fitting parameters obtained by fitting the data to equation (13). The cross-linking concentration (BIS) is in the unit of 1.23 mol%. The unit of ϕ_c is g/cm^3. The parameters from the fitting with m_1 fixed at 1/3 are included as well

BIS	Φ_e	All parameters floating			With m_1 fixed		
		m_1	m_2	100A	m_1	m_2	100A
0.50	0.018	0.32	2.49	0.25	(1/3)	2.50	0.24
0.75	0.023	0.37	2.46	0.28	(1/3)	2.39	0.35
1.00	0.026	0.33	1.99	0.96	(1/3)	1.99	0.97
1.50	0.036	0.27	2.15	1.00	(1/3)	2.28	0.67
2.00	0.045	0.36	2.48	0.44	(1/3)	2.39	0.56
4.00	0.045	0.37	3.38	0.062	(1/3)	3.27	0.083

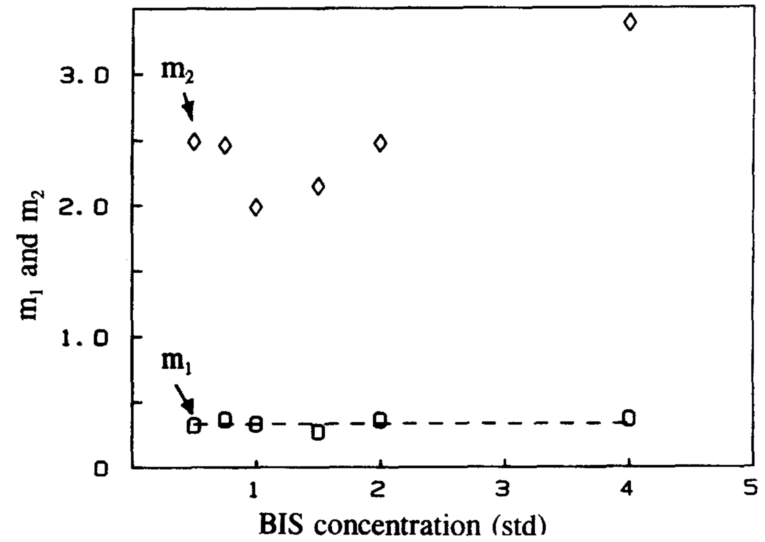

Figure 4 The exponents m_1 and m_2 *versus* cross-linking concentration. The dashed line represents the classical exponent value of 1/3

value of m_1 fixed at 1/3. The two exponents m_1 and m_2 are plotted in *Figure 4*. As shown in this figure, the value of m_1 is approximately equal to 0.33 ± 0.06, in agreement with the observations made by other groups[7–9]. The value of m_2 is 2.3 ± 0.3. The values of exponents of BIS = 4 series deviate significantly from values of other series and have not been used for statistical analysis. *Figure 5* shows the fitting of equation (13) to BIS = 1 samples. The contributions from the first term (dashed line) and the second term (solid line) are shown. From this figure, it is clear that at low concentration, the first term dominates. At higher concentration, the heterogeneity term becomes significant. The crossover concentration ϕ_c, is plotted in *Figure 6*. The higher the cross-linking concentration, the higher the crossover concentration. This indicates that the higher the BIS concentration, the smaller, but denser, are the dense domains. The relative change of the crossover concentration, $\Delta\phi_c/\phi_c$, affected by $\Delta(m_2 - m_1)$ is estimated to be about 40%.

We have also considered that the deviation from classical rubber elasticity may be caused by the glass transition. Since in general, the higher the polymer concentration, the higher the glass transition temperature. When the glass transition temperature is higher than room temperature, the polymer stiffening effect can increase the network elasticity. For poly(hydroxyethyl methacrylate) (PHEMA) network, the glass transition temperature drops from 125°C for a dry gel to about 0°C with 40% water content[23]. It had been reported that for poly(vinylpyrrolidone) the amount of 'bound' water at a given temperature is about one-third of the amount of

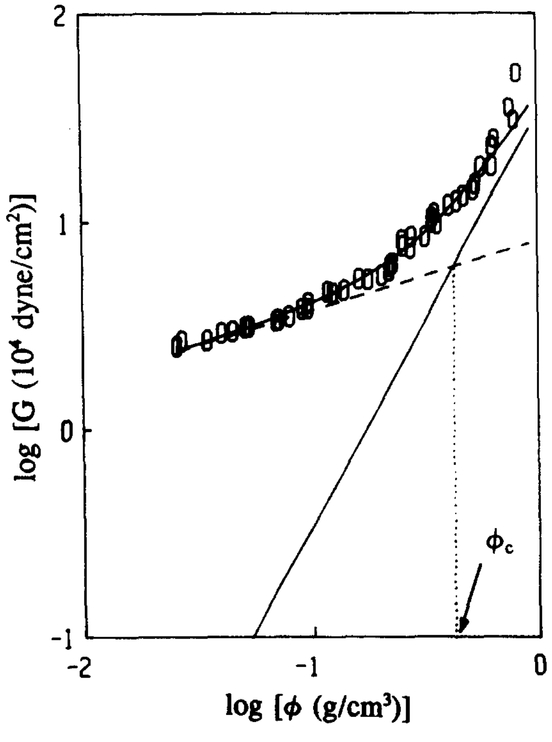

Figure 5 Detailed log–log plot of shear modulus *versus* polymer concentration for BIS = 1 series. The solid curve is the least square fit to equation (13). The dashed and solid lines represent the first and second terms in equation (13), respectively

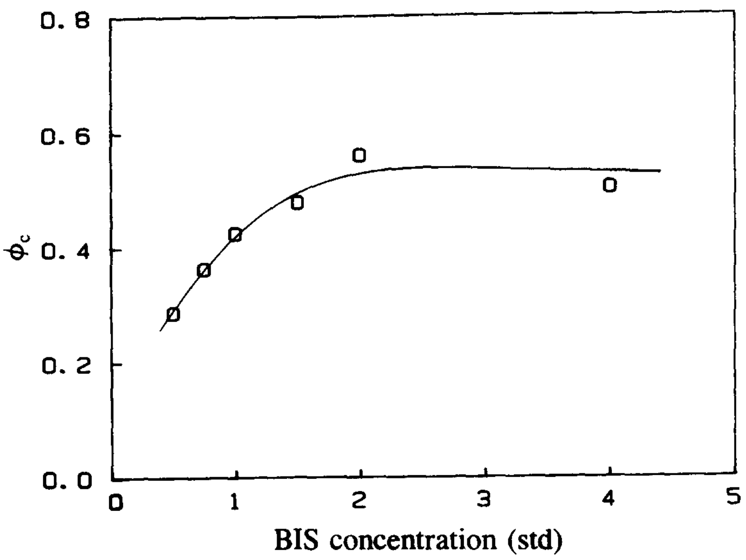

Figure 6 The crossover network concentration of gels with different cross-linking concentrations. As shown, the crossover concentration increases as the cross-linking concentration increases

water needed to reduce the polymer glass transition to the same temperature[24]. In the case of PHEMA gel, the factor is about half since the bound water of PHEMA is about 20%[25]. The bound water of swollen N-isopropylacrylamide (NIPA) gel is around 15% [26]. Therefore it is reasonable to assume that with about 30% water, the glass transition temperature of a NIPA gel network is around 0°C. Since an acrylamide network is more hydrophilic than the NIPA network, the reduction of glass transition at a given water content should be even higher. That is, the glass transition temperature of the acrylamide gel network is expected to be below 0°C for the network concentration below 0.7 g/cm^3, which corresponds to 40% water content. At room temperature, the glass transition appears around 1 g/cm^3 at which the shear modulus increases sharply as shown in *Figure 2* for gel samples with BIS = 1. Therefore, the observed room temperature elasticity for the acrylamide gel network concentration below 0.7 g/cm^3 cannot be explained by the glass transition effect.

As a final note, the free energy term F_3 has an effect on isotropic swelling as well. The osmotic swelling pressure contribution from it is

$$\omega \sim \phi^2 \frac{\partial F_3}{\partial \phi} \sim \phi^{m_2} \qquad (14)$$

The concentration dependent exponent of the osmotic pressure from the polymer solution term F_1 is 2.25, which is about the same as m_2. Therefore, the effect of F_3 cannot be easily detected by analysing the exponent of swelling osmotic pressure.

CONCLUSION

Measurement of shear modulus of PAAM gel has been performed over a broad network concentration range. It has revealed that the single scaling law with an exponent of 1/3 can be applied only to the low concentration region, i.e. below 0.25 g/cm^3, in agreement with available experimental and theoretical results. As the network concentration increases beyond this region, the modified Mooney's theory has to be considered to explain the experimental results. In our case, the modified Mooney's formula can be expressed as the summation of two terms. The origin of the higher order term is due to the two-phase inhomogeneity. This inhomogeneity term can be characterised by an exponent m_2 with its value between 2.0 and 2.5. The comparison between the theory and experiments has been made for six series of samples which have different cross-link concentrations ranging from 0.61 to 4.91 mol% and the agreement is excellent.

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