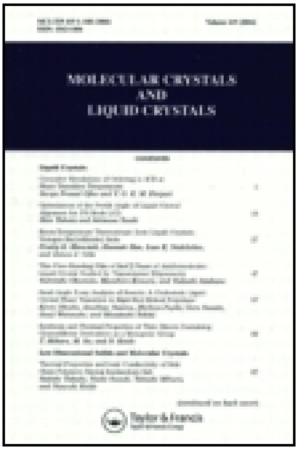

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Laser-Induced Temperature Distribution in Photo-Alignment of Azobenzene Liquid Crystalline Side Chain Polymers

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A theoretical model has been worked out to describe a temperature field, which is established within a film of isotropic *trans* azobenzene liquid crystalline side chain (LCSC) polymers when a linearly polarized laser beam illuminates it, and contributes to the photo-induced alignment behavior of LCSC polymers at an ambient temperature below the glassy transition temperature (Tg). The distribution of the temperature field is analyzed and the mechanism that the mesogens align perpendicular to the electric vector of the light is discussed with this model. The minimum light intensity I_{off} required to achieve the photo-induced phase transition of LCSC polymers at a certain temperature below T_g is calculated. A prediction of existence of an offset photo-alignment temperature T_{off} is made based on this theory model, while below this temperature no photo-induced phase transition can be observed when a light of certain intensity illuminates the sample.

Keywords: Photo-alignment; Temperature distribution; Azobenzene liquid crystalline side chain polymers

INTRODUCTION

Since the first introduction of azobenzene groups to polymer system, azobenzene-containing polymers have received more and more attentions due to their prospective application in optical storage[1,2,3], optical switching[1,4,5] and nonlinear optics[6]. Azobenzene side chain polymers and polymers doped with azobenzene groups have been extensively studied[7–13]. While many recent researches

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focus on the photo-alignment properties and theories of azobenzene LCSC polymers[7–19], the details of the reorientation process in these polymers has not been clarified[14]. Several theories have been proposed, which may explain the temporal behavior, intensity dependence and the long-term stability of photo-induced anisotropy[20], but none can fully account for the details of photo-alignment behavior of LCSC polymers under Tg. The fact is that the orientation of mesogens in isotropic polydomain azobenzene LCSC polymers can be modified by linearly polarized light in a temperature below Tg through photochemical *trans-cis-trans* isomerization, even though the free movement of azobenzene mesogen groups are commonly thought to be frozen under that temperature. After absorbing of light, the mesogens may undergo a photochemical *trans-cis-trans* isomerization, but no alignment should be observed since the mesogens are fixed in their own positions under Tg. On the other hand, there is only a casual relation between the light absorption of mesogens and the alignment behavior since there are still some difficulty in the proposed theory that the light absorbing process can provide with the torque of the reorientation. In this work, a laser-induced steady state temperature field is proposed to account for the phenomena.

Generally, heating effects are neglected as a possible mechanism of photo-alignment behavior[21] because experiments are preformed in a system that are usually thought to be temperature steady and the heat produced can be eliminated at once. At the same time, the heat produced in the system is considered to be not enough to bring a macroscopic temperature rise that could influence the process of reorientation. However, in our model, a temperature field is established with the use of a polarized laser beam. It is found that the heat produced in the illuminated region of the sample can lead to a temperature rise as high as over 30°C, quite enough to overcome of the temperature barrier between operating temperature and Tg. With this model, a temperature field explanation of photo-alignment mechanism is given.

The mechanism of the reorientation process can be described as that when treated with linearly polarized light, the *trans* form of azobenzene groups in the initial isotropic film may absorb light and are excited to a high state of energy. Then they will transmute to *cis* form and undergo a back-isomerization process to recover the *trans* form. In this cycle, if we neglect the energy difference between initial isotropic state and the final nematic state of azobenzene mesogens, the energy absorbed by mesogens is given off totally in the form of heat, which contributes to the temperature rise of the sample in a small region around the absorbing mesogen. The heat diffuses into local region and when the system finally reached a thermal equilibrium, the illuminated area of the sample reaches a higher temperature that may exceeds Tg. Once the temperature of the small region exceeds Tg, the free movement of the mesogens is possible and the mesogens can align to any possible directions. But the mesogens that are parallel to the electric vector of light will continue to be excited to high energy state, while those mesogens perpendicular to the electric vector of light will not absorb the light and remain in low energy state. Since mesogens tend to stay in a more stable position, the final equilibrium will favor an orientation perpendicular to the electric vector. In this point of view, the trend of azobenzene groups to undergo reorientation even in a temperature below Tg is logical and consequential.

THEORY MODEL

Consider a homogeneous isotropic azobenzene LCSC polymer film sandwiched between two glass plates. A Gaussian laser beam with wavelength 366nm penetrates the film along the z-axis, which is the thick direction of the film. A polarizer is placed between the laser and the sample. However, an absorption angle θ is defined as the angle between the transition dipole moment of the mesogen and the electric vector of linearly polarized laser beam. And in the initial isotropic sample, the angle of mesogens may range from 0 to 360° with equal opportunity. For the special kind of mesogens with an absorption angle θ, the light absorption of these mesogens is[14]

$$\mathrm{I}(r,z) = \frac{P}{\pi\omega^2}\mathrm{e}^{-r^2/\omega^2}\mathrm{e}^{-\alpha z}\cos^2\theta \tag{1}$$

Here P is the input power of the polarized light, ω is the radius of the laser beam i.e., the waist of the laser beam, a is the absorption coefficient.

Suppose that the thermal equilibrium constructed in the sample in a very short time, before the reorientation takes place in the film, the system reaches a thermal steady state while the sample remains in initial isotropic form. The heat diffusion equation of this steady state is

$$k\left(\frac{\partial^2 \mathrm{T}}{\partial r^2} + \frac{1}{r}\frac{\partial \mathrm{T}}{\partial r}\right) + k\frac{\partial^2 \mathrm{T}}{\partial z^2} = -\alpha I \tag{2}$$

$$k_s\left(\frac{\partial^2 \mathrm{T}_s}{\partial r^2} + \frac{1}{r}\frac{\partial \mathrm{T}_s}{\partial r}\right) + k_s\frac{\partial^2 \mathrm{T}_s}{\partial z^2} = 0 \tag{3}$$

Here k is the heat conductivity of the sample and $k_s$is the heat conductivity of the glass plates. T(r,z) and $\mathrm{T_S}$(r,z) is the temperature rise in sample and glass plates respectively. The temperature dependence of the heat conductivity and the absorption coefficient is neglected in this model and assuming the usual boundary conditions given by (4) and (5),

$$T_s|_{z=0} = T|_{z=0}, \quad T_s|_{z=L} = T|_{z=L} \tag{4}$$

$$k_s\frac{\partial T_s}{\partial z}|_{z=0} = k\frac{\partial T}{\partial z}|_{z=0}, \quad k_s\frac{\partial T_s}{\partial z}|_{z=L} = k\frac{\partial T}{\partial z}|_{z=L} \tag{5}$$

the temperature rise of these special kind of mesogens with an angle θ at thermal equilibrium is[15]:

$$T(r,z) = \int_0^\infty \lambda\widetilde{T}(\lambda,z)J_0(\lambda r)d\lambda \tag{6}$$

$$\widetilde{T}(\lambda,z) = -\frac{P\alpha Cos^2\theta}{2\pi k}\frac{e^{-\lambda^2\omega^2/4}}{\lambda^2-\alpha^2}(e^{-\alpha z} + F1(\lambda)e^{\lambda z} + F2(\lambda)e^{-\lambda z}) \tag{7}$$

$$F1(\lambda) = \frac{\alpha-\lambda}{2\lambda}e^{-(\alpha+\lambda)L} \tag{8}$$

$$F2(\lambda) = -\frac{\alpha+\lambda}{2\lambda} \tag{9}$$

in which $J_0(\lambda, z)$ is the zeroth-order Bessel function, and L is the thickness of the film. By numerically resolve the temperature rise[23], we can obtain the distribution of the temperature field.

RESULTS AND DISCUSSION

The contour of the temperature field is shown in Figure 1, for the system described above, using data in Ref. 15[24]. The color in the figure demonstrates the extent of temperature rise, with the dark red color the highest temperature rise and the blue the least temperature rise. A maximum temperature rise occurs in the middle of the laser beam r=0 and near the halfway of thick direction. As the distance away from the center of the laser beam increases, i.e., the increase of r, the temperature rise decreases. At the same time, as both sides of the sample are in contact with a colder glass substrate, the temperature rise is smaller in the outer layers of the sample compared with that of the inner layers because the glass plates have higher heat conductivity. Heat diffuses from the polymer sample to the glass plates and a maximum temperature rise occurs in the thick direction. It is notable that the maximum temperature rise does not occur at z=1/2L, because the intensity of light decreases as z increases due to the light absorption of the film and that the temperature rise obtained in figure 1 is obtained for the kind of mesogens whose absorption angle θ is 0.

The temperature rise at thermal equilibrium is influenced by several factors θ, *k, P, a* and ω. Each factor has its own contribution on the temperature rise, which

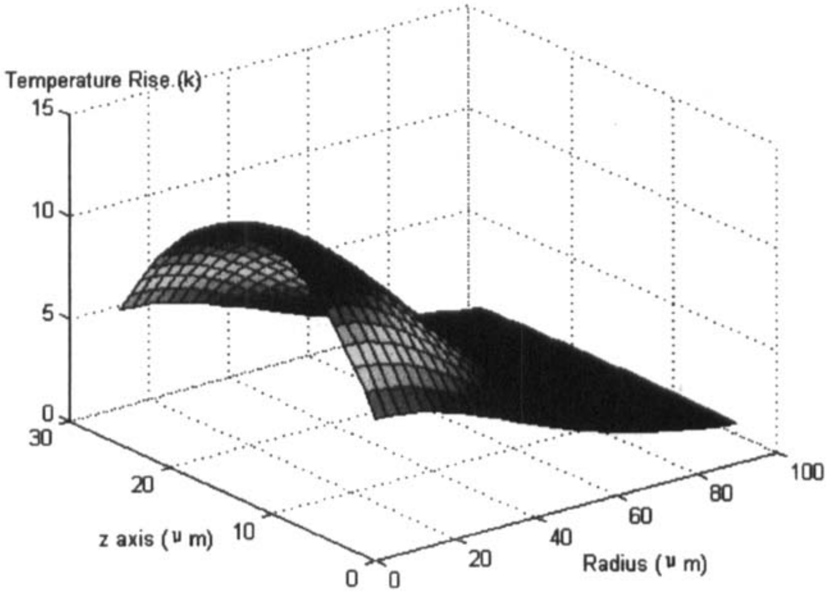

FIGURE 1 The contour of the temperature field, in which $\theta=0°$, P=13mW, k=0.24W°C^{-1}m^{-1}, $a=1.0^{*}10^{4}$m^{-1}, k_s=1.411 W°C^{-1}m^{-1}, ω=38 μ m and L=25 μ m^{24} (See Color Plate IX at the back of this issue)

is studied in Figure 2–4. From data shown in Figure 2, it is found that the higher the value of heat conductivity, the faster the heat diffuses into the local region and the flatter the temperature rise curve. The maximum temperature rise is proportional to 1/k within limited region of k as we may see in equation (7) and the insert figure of Figure 2. When k<0.1 W°C^{-1}m^{-1}, the max temperature rise decreases very fast and when k>0.2 W°C^{-1}m^{-1}, the max temperature rise decreases much slower. The influence of the laser power on the temperature rise is shown in Figure 3. With the increases of the output power of laser, the temperature rise is greater. A linear relation is also found between the laser power and the maximum temperature rise, Figure 6. The radius of the laser beam is another influence factor of the temperature field, Figure 4. The smaller the ω, the sharper the curve of temperature rise at certain laser power P and the heat distribution is confined in a smaller area. The maximum temperature rise is higher since the light intensity in per unit area is much higher.

To demonstrate the influence of temperature field on the photo-induced alignment behavior, the angular dependence of the temperature field is studied and the

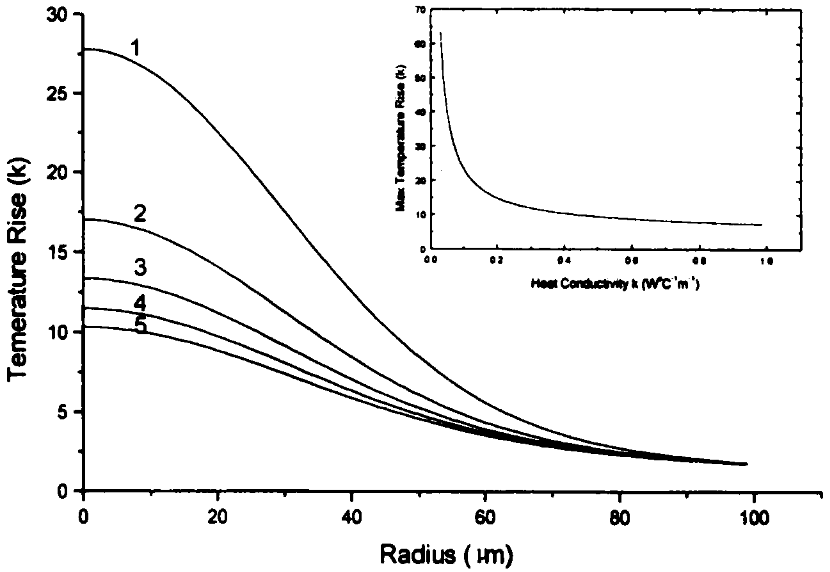

FIGURE 2 Influence of heat conductivity k on the temperature rise of the sample. From 1 to 5, k=0.08W°C^{-1}m^{-1}, k=0.16W°Cm^{-1}, k=0.24W°C^{-1}m^{-1}, k=0.32W°C^{-1}m^{-1}, k=0.40W°C^{-1}m^{-1} respectively, in which z=12.5 μ m, θ=0°, P=13mW, a=1.0*10^{4}m^{-1}, k_s=1.411 W°C^{-1}m^{-1}, ω=38 μ m and L=25 μ m. Insert Figure: The influence of heat conductivity on the maximum temperature rise, in which r=0, z=12.5 μ m, θ =0°, P=13mW, a=1.0*10^{4}m^{-1}, ω=38 μ m, k_s=1.411 W°C^{-1}m^{-1} and L=25 μ m

result is shown in Figure 5. It is found that the highest temperature rise occurs for the kind of mesogens with θ =0, 180° which are parallel to the electric vector of the incident light, and the temperature rise is zero while the mesogens with θ =90°, 270° with are perpendicular to the electric vector of the incident light. This finding is identical with the explanation of alignment behavior of azobenzene groups as described in the introduction of this paper.

Most experiments of photo-alignment behavior under Tg are comported at a temperature somehow 30°C[9,22] to 40°C[19] below Tg. No observation of photo-alignment behavior under a lower temperature below Tg is reported. In this model, a highest temperature rise of 30°C to 40°C is quite possible. In figure 6 point A, the temperature rise is 30°C at an incident polarized laser power of 32mW.

The existence of an offset light intensity has been observed in the photo-induced N-I phase transition of azobenzene LCSC polymers[9]. Since photochemical reaction is very fast and does not have activation energy, the observed

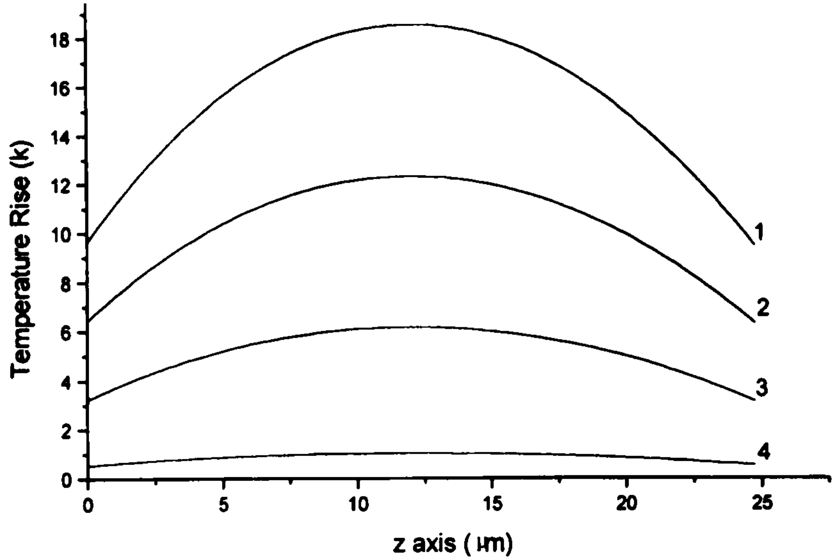

FIGURE 3 Influence of laser output P on the temperature rise of the sample. From 1 to 4, P=18mW, P=12mW. P=6mW, P=1mW respectively, in which r=0, $\theta=0°$, $a=1.0^{*}10^{4}\mathrm{m}^{-1}$, $k=0.24$ W°C^{-1}m^{-1}, $k_s=1.411$ W°C^{-1}m^{-1}, $\omega=38$ μ m and $L=25$ μ m

experimental phenomenon is hard to explain. Mean field theory gives a tentative explanation without numerical solution. In this model, assuming to overcome the temperature barrier is the solo requirement in order to achieve photo-alignment, at a certain temperature below Tg, the difference between Tg and this temperature is Δ T, the lowest intensity of the incident light to achieve photo-alignment I_{off} can be numerically solved. For example, the lowest intensity of the incident light I_{off}, to achieve photo-alignment at a temperature barrier of 30°C, can be represent by the input laser power of 32mW as point A in Figure 6.

On the other hand, as we have mentioned above, most of the observed photo-alignment behavior is reported at a temperature somehow 30°C to 40°C below Tg. No observation of photo-alignment behavior under a lower temperature below Tg is reported. Weather this is due to the fact that at a lower temperature below Tg no photo-alignment can be achieved is not clarified. However, the phenomenon of no photo-alignment of one LCSC polymers occurs at a low temperature is observed in recent works[22]. As in this model, an offset photo-alignment temperature is predicted on the assumption that only when the maximum temperature rise could overcome the temperature barrier, can the photo-induced alignment be observed. For example that the maximum temperature rise is Δ

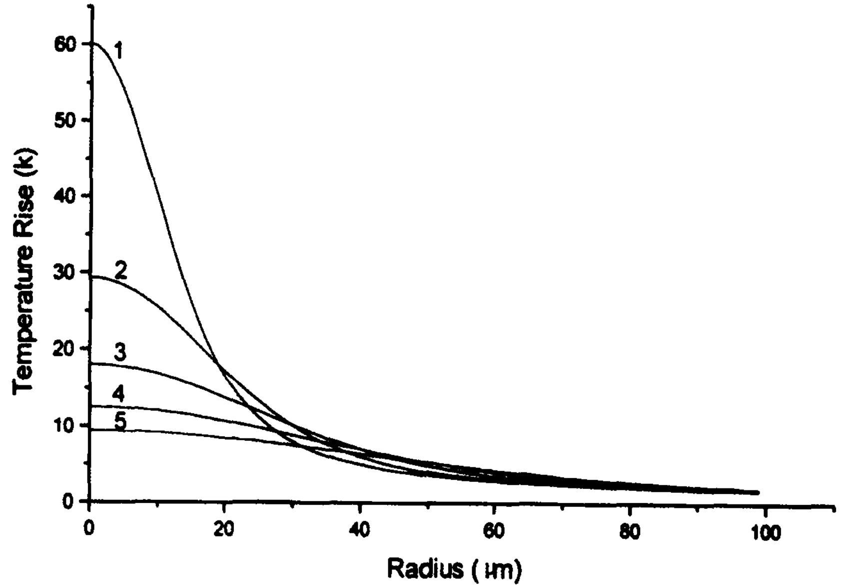

FIGURE 4 Influence of laser radius ω on the temperature rise of the sample. From 1 to 5, ω = 10 μ m, ω=20 μ m, ω =30 μ m, ω =40 μ m, ω =50 μ m respectively, in which z=12.5 μ m, θ=0°, *P*=13mW, $a=1.0^{*}10^{4}\text{m}^{-1}$, $k=0.24\ \text{W°C}^{-1}\text{m}^{-1}$, $k_s=1.411\ \text{W°C-1m}^{-1}$ and *L*=25 μ m

T_{max}, let $T_{off}=T_g-\ \Delta\ T_{max}$. At an ambient temperature below T_{off}, no photo-induced alignment behavior should be observed; while above this temperature, photo-induced alignment is possible. Numerically, at an incident light intensity of 32mW and the glassy transition temperature Tg of the sample is 45°C, T_{off}=45°C-30°C=15°C. So no photo-alignment behavior should be observed below 15°C.

The steady state temperature field theory has brought light to the understanding of the phenomena of photo-induced alignment of azobenzene containing liquid crystalline polymers. Actually the alignment process is accomplished in a limited period in various experiments. A time-resolved temperature field theory developed on this model will be discussed in our next paper.

CONCLUSION

A theoretical model of laser-induced temperature distribution of azobenzene liquid crystalline side chain (LCSC) polymers is constructed by assuming of the

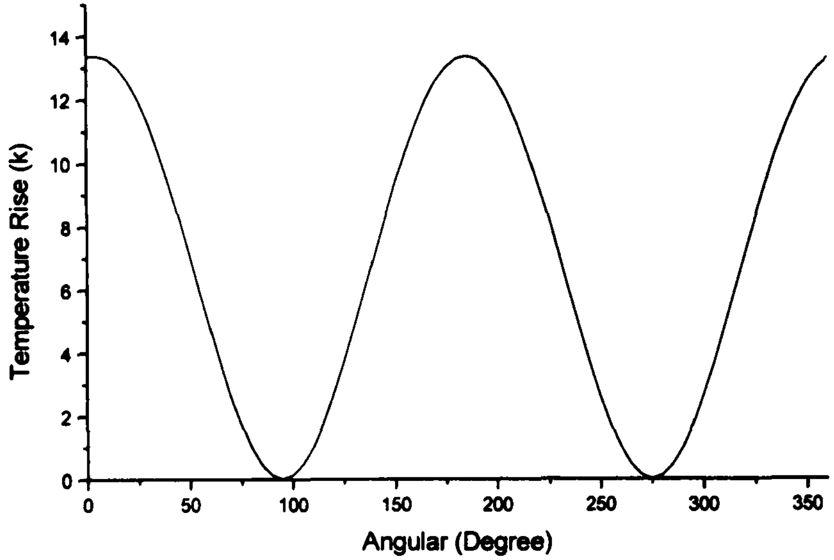

FIGURE 5 The angular dependence of temperature. r=0, z=12.5 μ m, P=13mW, a =1.0*10^4m^{-1}, k=0.24 W°C^{-1}m^{-1}, k_s =1.411 W°C^{-1}m^{-1}, ω=38 μ m and L=25 μ m

steady state. With the numerical solution of the model, we analyze the influence of intensity of incident light, ambient temperature and absorption angle etc. on the photo-induced reorientation behavior of these azobenzene LCSC polymers. A tentative explanation is founded to be account for the photo-induced reorientation below Tg. It was found that at ambient temperature below T_g, the laser-induced temperature rise is high enough to reach beyond T_g, which is the main reason why photo-induced alignment can take place under room temperature below the glass transition temperature. The temperature field induced in this situation contributes to the mechanism of the alignment of mesogens perpendicular to the electric vector of the incident light.

Acknowledgements

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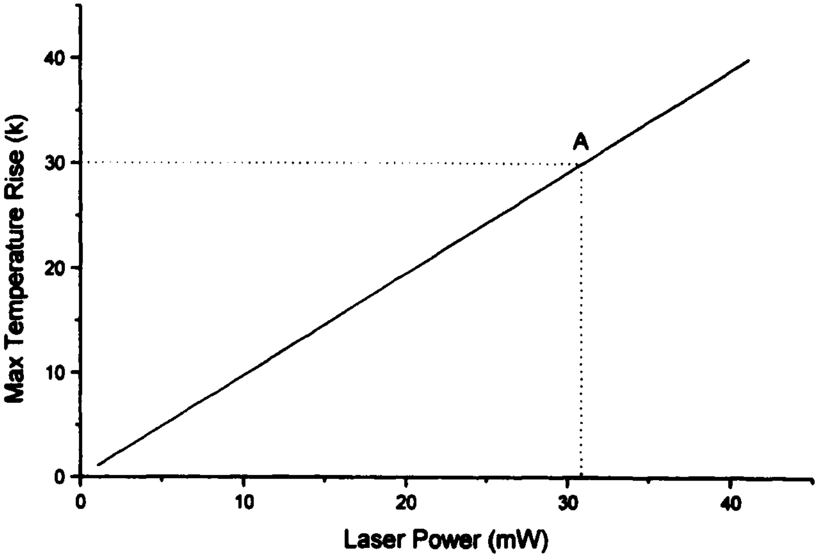

FIGURE 6 The linearly relationship of the maximum temperature rise in the sample with the laser power P. r=0, z=12.5 μ m, θ=0°, a=1.0*$10^4 m^{-1}$, k=0.24W°$C^{-1}m^{-1}$, k_s =1.411 W°$C^{-1}m^{-1}$, ω=38 μ m and L=25 μ m

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