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Photoinduced polymerization and relaxation in liquid sulphur

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Abstract. In order to study the dynamics of the polymerization in liquid sulphur we have measured the transient absorption spectra after illuminating with a pulsed laser below and above the polymerization temperature, T_p . We have found that photoinduced polymerization occurs below T_p and there exist two kinds of relaxation process, that is, the fast and slow ones. The slow one can be observed after illumination with a very weak pulsed laser and the relaxation time is of the order of ten minutes. The fast one is observed just after stopping the illumination of a rather stronger pulsed laser and the relaxation time is about 30 seconds. The fast one is always followed by the slow one. On the basis of these findings we conclude that the fast relaxation process corresponds to the relaxation from a polymeric chain to a charge transfer complex and the slow one the relaxation from the charge transfer complex to the most stable ring molecule. With further increase of the intensity of the pulsed laser we have found that giant molecules with colloidal form are generated and they lie on parallel lines. The relaxation time is about one minute.

1. Introduction

The polymerization in liquid sulphur has attracted considerable experimental as well as theoretical attention for many decades [1]. Between the melting point (113 °C for orthorhombic sulphur) and the polymerization temperature of 159 °C sulphur forms a light-yellow liquid with low viscosity consisting of S_8 molecules which have the shape of puckered ring. Above 159 °C it forms a highly viscous liquid in which a significant fraction of S_8 rings polymerize to long polymeric chains. The chains contain as many as 10^6 atoms and increase their concentration with increasing temperature accompanying the rapid colour change. It is known that the structure [2] and thermodynamic properties such as viscosity [3], heat capacity [4, 5] and density [6, 7, 8, 9] substantially changes at the polymerization temperature. Recent measurements of the optical reflectivity [10] and the optical absorption coefficient [11] have also revealed that the polymerization includes considerable changes in the electronic energy levels of liquid sulphur. For the understanding of the mechanism of the polymerization it is obvious that studies on the dynamical behaviour of the conversion between S_8 rings and polymeric chains are important. Tobolsky and Eisenberg [12] discussed in detail the polymerization process based on the idea of the chemical reaction to explain the abrupt increase of viscosity at the polymerization temperature. However, we have had no effective experimental approaches for the investigation on the dynamics of the polymerization until now. In the present paper we report the results of the measurements of transient absorption spectra induced by the illumination of pulsed laser for liquid sulphur. Our study has the following main aims. The first is related to the question of whether

the polymerization can be induced or not when the pulsed laser with the band gap energy illuminates S_8 rings in liquid sulphur. Sulphur has an s^2p^4 valence configuration. Two of the p electrons form σ bonds leaving s and two lone-pair electrons. The lone-pair states lie at the top of the valence band and the antibonding σ^* orbitals form the conduction band. As is well known the lone-pair electrons play a crucial role in stabilizing the S_8 ring structure. The excitation of lone-pair electrons by the illumination of a laser with the band gap energy may cause an instability of S_8 rings eventually producing polymeric chains. The second aim is to determine the relaxation time in which photoinduced polymeric chains are relaxed to rings in the thermal equilibrium. Studies of the temperature variation of the relaxation time are specifically useful.

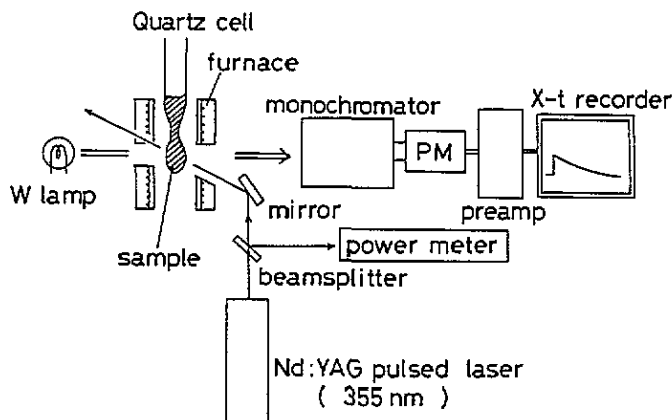


Figure 1. Schematic diagram of the apparatus used for the present experiment.

2. Experimental details

Figure 1 shows the schematic diagram of the apparatus used in the present experiment. The third harmonics (355 nm) of the Nd:YAG pulsed laser (Spectra-Physics Lasers, Inc. Quanta-Ray GCR-16) was used for the photoexcitation of lone-pair electrons in liquid sulphur. The width of a pulse was 5–6 ns. The intensity of a pulsed laser was measured by using a power meter (Ophir Optronics, Inc. Nova and PE-25) combined with a beam splitter. The pulsed laser was reflected by a mirror and then illuminated the liquid specimen contained in the quartz cell. There are two windows on the side wall of the furnace which are used for the illumination of the pulsed laser and also for the transmission of a probe light. A tungsten lamp with a power of 30 W was used as the probe light. We have measured the intensity of the transmitting probe light with different photon energies by using a monochromator (Jasco CT25GD) and a photomultiplier (HTV R374). The time variation of the intensity of the transmitting light before and after the illumination of the pulsed laser could be measured by using an X-t chart recorder because the relaxation time was quite long as seen in the next section.

In order to study the spectral change of liquid sulphur accompanying the polymerization it is necessary to use an optical cell with a very thin sample space. Our recent measurement of the optical absorption spectra in a wide absorption range [11] has revealed that a substantial change in the spectra accompanying the polymerization occurs in the high-absorption region with an absorption coefficient exceeding 10^4 cm^{-1} . Therefore, the

thickness of liquid sulphur should be less than $1\ \mu\text{m}$. We have developed a specially designed optical cell made of quartz as shown in figure 2. As seen in the lowest part of the figure two quartz plates with round shape face each other. The diameter of the round surface is about 1 cm. The edges of these two plates were connected together by glass fusing work. A very thin and uniform sample space was realized between them. This part was connected with another two pieces shown in the figure. The thickness of the sample space was determined by the optical interference method. The pulsed laser illuminated the round surface from the normal direction. A more detailed description of the cell construction will be given elsewhere [13]. In the present experiment we have used three cells with different thickness of the sample space; 7, 1 and $0.3\ \mu\text{m}$.

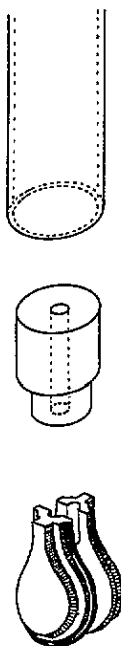


Figure 2. Optical cell made of quartz. Three separate parts are connected together. At the lowest part two quartz plates with round shape face each other. There is a very thin and uniform gap between them.

The sample space was filled with liquid sulphur in the following way. The inside of the cell was evacuated and the sample space was heated to $130\ ^\circ\text{C}$. The solid sulphur sample with a purity of 99.9999% loaded in the sample reservoir located at the top of the sample space was melted and then Ar gas with atmospheric pressure was introduced into the cell to force the liquid specimen into the sample space. The temperature of the liquid specimen was measured by the chromel–alumel thermocouple attached to the surface of the cell using alumina cement. The temperature of the sample was controlled within $\pm 0.5\ ^\circ\text{C}$.

3. Results and discussion

3.1. Photoinduced changes below T_p

Figure 3 shows the logarithmic plots of the fractional change in the transmission, $\Delta T/T$, versus time of liquid sulphur at 130, 140 and $150\ ^\circ\text{C}$, where T is the transmittance in the thermal equilibrium state and ΔT the photoinduced change of the transmittance. The wavelength of the transmitting probe light is 390 nm. A single pulse of a laser illuminates the area with 7 mm diameter of liquid sulphur. The values of the intensity of the pulsed

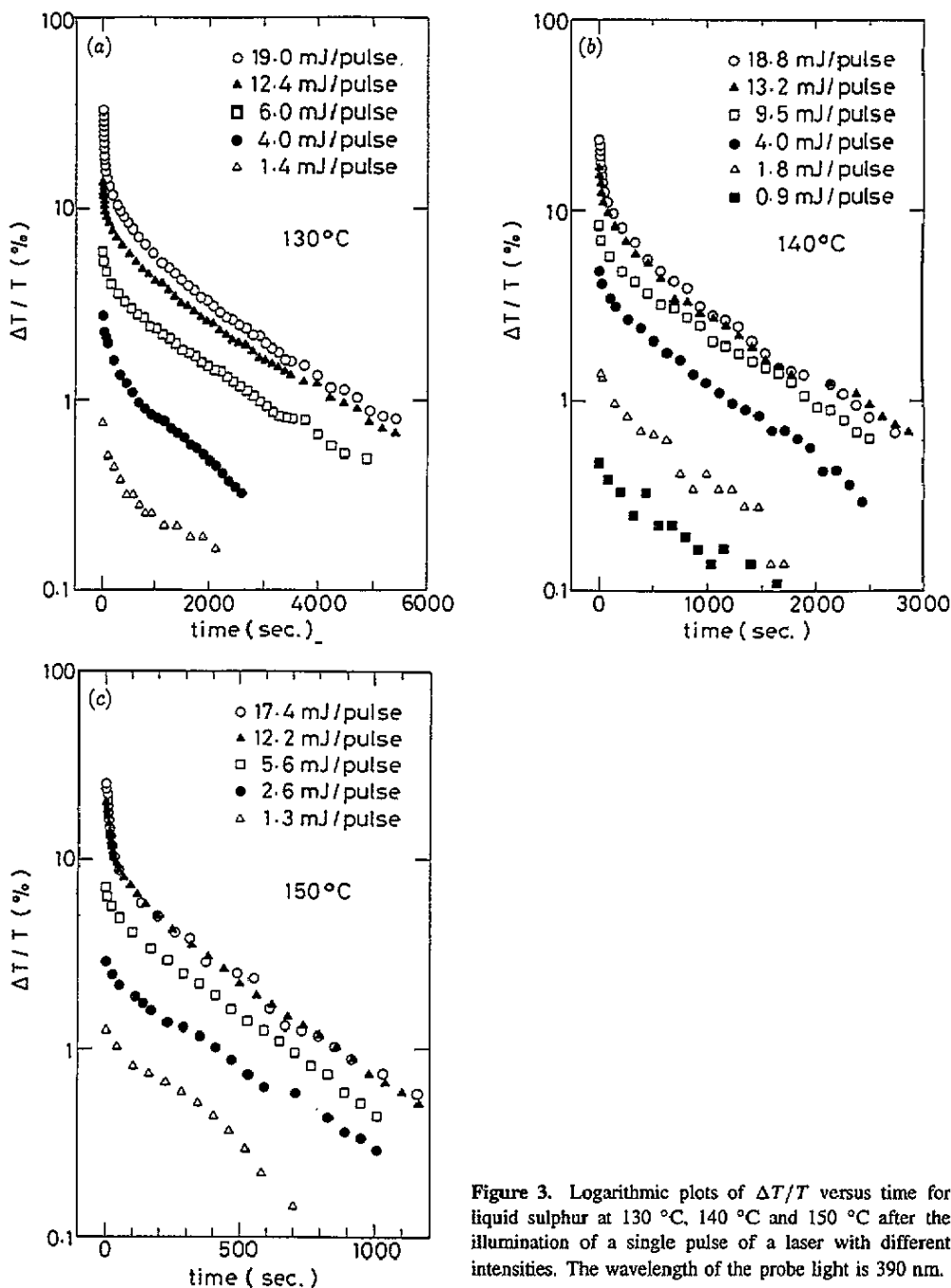


Figure 3. Logarithmic plots of $\Delta T/T$ versus time for liquid sulphur at 130 °C, 140 °C and 150 °C after the illumination of a single pulse of a laser with different intensities. The wavelength of the probe light is 390 nm.

laser are denoted on the right-hand side of each curves in the figure. The photoinduced change is clearly observed by the illumination of a weak pulsed laser with the intensity of about 1.0 mJ/pulse. With increasing laser power the value of $\Delta T/T$ increases, while the relaxation time is unchanged. Note that a new transient absorption with a short relaxation

time appears on illumination with a pulsed laser stronger than about 10 mJ/pulse. It should be noticed that there exist two kinds of relaxation process with short and long relaxation time in each data when the intensity of the laser becomes large. The values of the short and long relaxation time at 130 °C are found to be 60 seconds and 40 minutes, respectively. With increasing temperature the relaxation time becomes short.

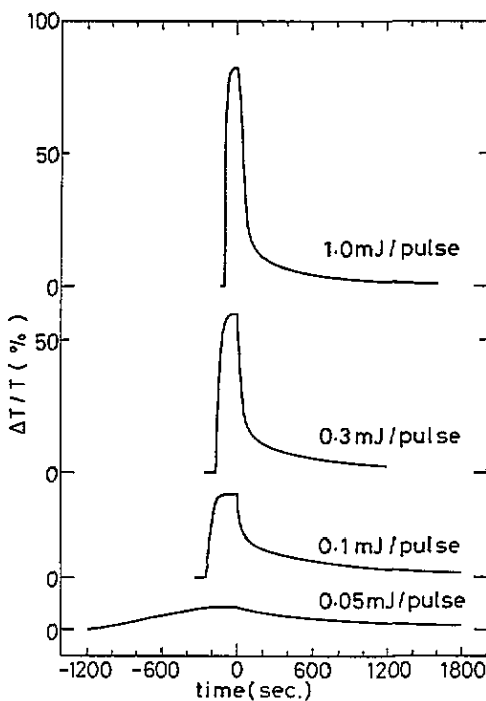


Figure 4. Plots of $\Delta T/T$ versus time for liquid sulphur at 130 °C during the repeated illumination of a pulsed laser at 10 Hz and after stopping the illumination.

For the understanding of the origin of these photoinduced changes observed for liquid sulphur below T_p we have examined whether or not the phenomena are caused by the laser heating which may raise the temperature of the liquid sample above T_p . We have performed the experiment to study the effect of the repeated illumination of a very weak pulsed laser. Figure 4 shows the plots of $\Delta T/T$ versus time at 130 °C during the repeated illumination of a pulsed laser at 10 Hz and after stopping the illumination. Four curves are obtained for different intensities with 0.05, 0.1, 0.2 and 1.0 mJ/pulse. The intensity of the pulsed laser is quite small compared with that used for the experiment in figure 3. When the pulsed laser with 0.05 mJ/pulse is illuminated, $\Delta T/T$ gradually increases with time eventually being saturated after 15 minutes. After stopping the illumination $\Delta T/T$ exponentially decreases. When the stronger pulsed laser with 0.1 mJ/pulse is illuminated the saturated value of $\Delta T/T$ becomes large and the time necessary for reaching the saturation value becomes short. Note that there appears a new absorption with a short relaxation time. Such a fast relaxation process becomes clear when the intensity of the pulsed laser increases. The logarithmic plots of $\Delta T/T$ after stopping the illumination are shown in figure 5 in which we can see a clear crossover between the fast and slow relaxation processes. The values of the relaxation time are 60 seconds and 10–20 minutes, respectively, which are almost the same as those obtained from the data at 130 °C in figure 3.

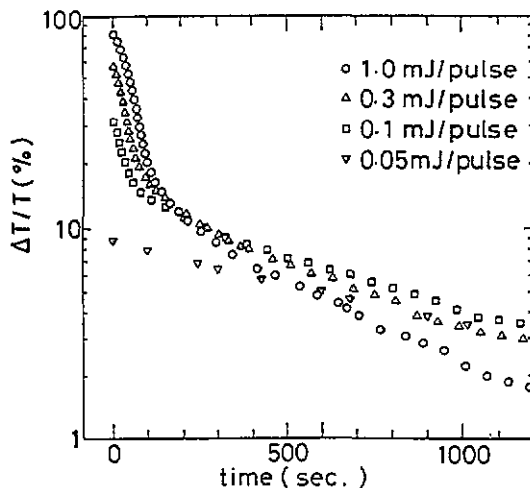


Figure 5. Logarithmic plots of $\Delta T/T$ versus time for liquid sulphur at 130 °C after stopping the repeated illumination of the pulsed laser.

Assuming that the photon energy is totally used for the heating of the sample, the temperature rise of a liquid sulphur sample is estimated to be 1 °C when one laser pulse with the intensity of 0.1 mJ/pulse illuminates the sample. Since the thickness of the liquid sulphur sample is very small and the thermal contact between the sample and the quartz cell is quite good, the heat of the sample easily escapes to the quartz cell within the time interval of 0.1 s. Furthermore, the heat capacity of the quartz cell is large compared with that of the sulphur sample. Therefore, it is expected that the heat of the sample is not accumulated and the temperature increase of the liquid sample is negligibly small. We have measured the temperature of the quartz cell during the repeated illumination of the pulsed laser. The temperature rise was found to be less than 0.5 °C.

The characteristic features of the photoinduced phenomena observed for liquid sulphur below T_p are as follows. Firstly, the phenomena are not caused by a laser heating of the sample up to or above T_p . They must be strongly related to the structural instability of the S_8 ring induced by the photoexcitation of the lone-pair electrons located at the highest occupied states of the molecular orbitals of the S_8 ring. Secondly, we have two kinds of product with different relaxation time, that is, short- and long-lived products. When the value of $\Delta T/T$ becomes large enough to exceed about 10% the fast relaxation process appears to be observed. The concentration of the long-lived products seems to be accumulated by the repeated illumination of a weak pulsed laser. When the concentration of the long-lived products exceeds a critical value the short-lived products are created. It is interesting to note that when the short-lived products are on the way back to the thermal equilibrium state after stopping the illumination, the long-lived products start to appear with the same critical concentration corresponding to the value of $\Delta T/T$ equivalent to about 10%.

3.2. Fast relaxation process

In order to identify the short- and long-lived products we have measured the transient absorption spectra. We have used a quartz cell with the sample thickness of 1.0 and 0.3 μm , so we could measure the optical absorption coefficient, α , in the high-absorption range from 4×10^3 to $2 \times 10^5 \text{ cm}^{-1}$. The transient absorption spectrum after the illumination of a single

pulse of a laser or during the repeated illumination of a pulsed laser was found to be quite different from that before illumination: the spectrum substantially shifts to the low-energy side and a shoulder appears around 3.5 eV, and then changes back to that of the initial state after stopping the illumination.

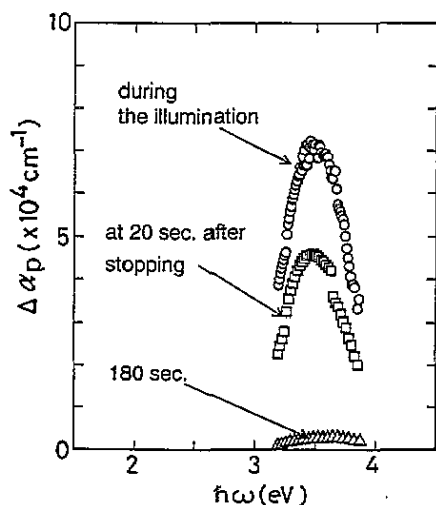


Figure 6. Plots of the photoinduced deviation from the absorption coefficient in the thermal equilibrium, $\Delta\alpha_p$, during the repeated illumination (O) of a weak pulsed laser with the intensity of 1.0 mJ/pulse, at 20 seconds after stopping the illumination (\square) and at 180 seconds (Δ) for liquid sulphur at 130 °C.

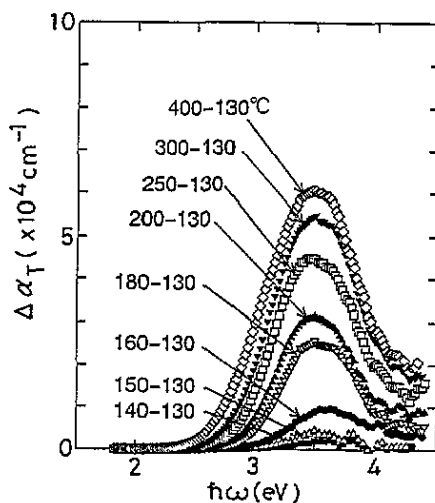


Figure 7. Plots of $\Delta\alpha_T$ versus photon energy. $\Delta\alpha_T$ is defined by $\Delta\alpha_T = \alpha_T - \alpha_{130\text{ }^\circ\text{C}}$ at different temperatures, where α_T is the optical absorption coefficient in the thermal equilibrium state at a temperature of T . These difference spectra are obtained from the data in our previous paper [11].

Figure 6 shows the plots of the photoinduced deviation from the absorption coefficient in the thermal equilibrium, $\Delta\alpha_p$, during the repeated illumination (O) of a weak pulsed laser with the intensity of 1.0 mJ/pulse, at 20 seconds after stopping the illumination (\square) and at 180 seconds (Δ) for liquid sulphur at 130 °C. As seen in the figure a clear maximum in the spectrum has been observed around 3.5 eV. From the experiment shown in figures 4 and 5 we have learned that the short-lived products are created by the repeated illumination of a pulsed laser at 1.0 mJ/pulse. Therefore, the spectra denoted by the symbol O and the symbol \square are those of the short-lived products and the spectrum Δ the long-lived products.

Figure 7 shows difference spectra, $\Delta\alpha_T$, defined by $\Delta\alpha_T = \alpha_T - \alpha_{130\text{ }^\circ\text{C}}$ at different temperatures, where α_T means the optical absorption coefficient in the thermal equilibrium state at a certain temperature. These difference spectra are obtained by analysing the data in our previous paper [11]. As seen in figure 7 a distinct peak appears around 3.5 eV in the spectra above the polymerization temperature. It is well known that these spectral changes above T_p are strongly connected to the creation of long polymeric chains containing 10^6 sulphur atoms [11].

We can easily find the similarity between the spectra O, \square shown in figure 6 and the spectra above T_p in figure 7. Therefore, we conclude that the short-lived products consist of long polymeric chains of sulphur atoms. The comparison between two spectra denoted by O in figure 6 and \diamond in figure 7 tells us that the concentration of the photoinduced polymeric chains in liquid sulphur is estimated to be about 60% [14]. The spectrum after stopping the

illumination (Δ) in figure 6 is quite similar to that below T_p in figure 7.

3.3. Slow relaxation process

It is not easy to identify the long-lived products from the shape of the transient spectrum. The conclusion deduced from our experiment is that long-lived products are generated when a weak light illuminates S_8 rings and the concentration of the long-lived products increases with illuminating time. When the concentration exceeds the critical value polymeric chains are produced. These polymeric chains come back again to the most stable S_8 rings after stopping the illumination. It should be noticed that long-lived products appear *intermediately* on the relaxation process from the polymeric chains to the S_8 rings. Therefore, the long-lived products may consist of *short-chain* molecules which are disturbed to come back soon to the most stable S_8 rings.

The most probable candidate for the long-lived products is the charge transfer complex which Wiewiorowski and Touro [15] have proposed to explain the presence of stable S_8 chains below T_p . The charge transfer complex is considered to consist of an S_8 chain and S_8 rings surrounding the S_8 chain which are combined with the Coulomb attractive interaction between the positively charged S_8 chain and the negatively charged S_8 rings. Such a charged state comes from the transfer of the unpaired electrons at the ends of an S_8 chain to the surrounding S_8 rings. The unpaired electrons are considered to be delocalized and to make spin pairing states, which explains the experimental fact that ESR signals [16] are not observed in spite of the existence of S_8 chain molecules below T_p [17]. Wiewiorowski *et al* [18] consider that the well known phenomenon of the freezing point depression observed in liquid sulphur is caused by the existence of a small number of charge transfer complexes in liquid sulphur. From the experiment on the freezing point depression they have found that the concentration of the charge transfer complex below T_p is estimated to be a few per cent in the thermal equilibrium state and the concentration slightly increases with increasing temperature. They have studied the creation process of the charge transfer complex and found that 200 minutes are necessary to realize the thermal equilibrium when the sample is heated up very fast to 130 °C from low temperatures.

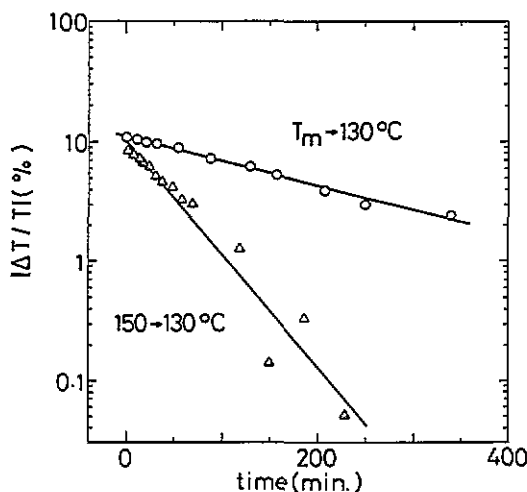


Figure 8. Variations of $\Delta T/T$ with time when the sample is heated up very fast to 130 °C from the melting temperature and cooled down to 130 °C from of 150 °C which are denoted by open circles and triangles, respectively. The wavelength of the probe light is 382 nm.

We have studied the time variation of $\Delta T/T$ when the sample is heated up and also cooled down to the thermal equilibrium state. Figure 8 shows the variation of $\Delta T/T$ with

time when the sample is heated up very fast to 130 °C from the melting temperature and cooled down to 130 °C from the higher temperature of 150 °C which are denoted by open circles and triangles, respectively. We have found that the relaxation time is about 200 minutes for the heating procedure which is consistent with the result by Wiewirowski *et al* [18] and about 45 minutes for the cooling procedure which is almost the same as the relaxation time of the long-lived products. There is a large difference between two relaxation times. These results suggest that it is more difficult to produce the charge transfer complex through the thermal break of the covalent bond of the S₈ ring than to change the excess complexes back to the S₈ ring.

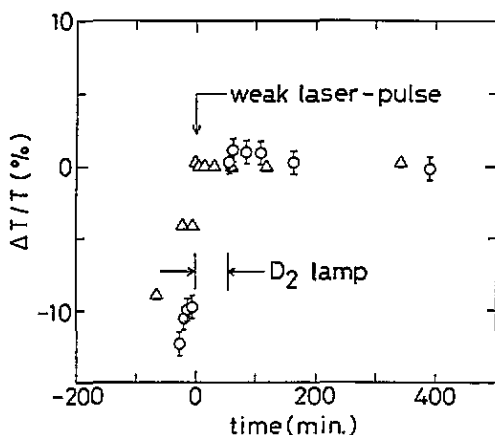


Figure 9. Plots of $\Delta T/T$ versus time when the very weak light of a deuterium lamp or a weak pulsed laser illuminate liquid sulphur which is on the way back to the thermal equilibrium state after the fast heating up to 130 °C from the melting point. Open circles indicate the data obtained by the illumination using the deuterium lamp continuously for one hour, where the illumination time is indicated by the interval between two arrows. Open triangles show the data obtained by the illumination of a weak pulsed laser. The arrow indicates the moment of the laser illumination. The wavelength of the probe light is 382 nm.

Figure 9 shows the plots of $\Delta T/T$ versus time when the very weak light of a deuterium lamp or a weak pulsed laser illuminates the sample which is on the way back to the thermal equilibrium state after the fast heating up to 130 °C from the melting point. Open circles show the data obtained by continuous illumination for one hour using the deuterium lamp, where the illumination time is indicated by the interval between two arrows. Note that the value of $\Delta T/T$ after one hour illumination becomes that of the thermal equilibrium. Open triangles show the data obtained by the illumination of a weak pulsed laser. The arrow indicates the moment of the laser illumination. It is obvious that the thermal equilibrium is realized immediately after the illumination. From these results we conclude that such an illumination of very weak light seems to help liquid sulphur to approach the thermal equilibrium state producing a number of charge transfer complexes. If the intensity of the illumination becomes strong a large number of excess complexes exceeding those in the thermal equilibrium state are generated. After stopping the illumination the number of excess complexes decreases again to those in the thermal equilibrium state with the relaxation time of 40 minutes. As a conclusion, the long-lived products must be the same ones appearing in the heating and cooling processes and existing in the thermal equilibrium.

The effect of the illumination of light on the physical and chemical properties of liquid sulphur near the melting point was investigated at the end of the last century and at the beginning of this century. Lallemand has discovered that a kind of sulphur insoluble in the carbon disulphide (CS₂) [19] appears in a liquid mixture of sulphur and CS₂ illuminated by solar light. Berthelot [20] has found that such an insoluble sulphur can be created in liquid sulphur by the illumination of solar light which depresses the freezing point. From the result of the freezing point depression measurement Wigand [21] has estimated the molecular weight of the insoluble sulphur molecule and predicted that the insoluble sulphur must consist of eight sulphur atoms. We consider that the insoluble sulphur found by these

previous investigators might be the same as our long-lived product generated by the weak illumination of a pulsed laser and identified as the charge transfer complex.

An alternative idea has been proposed by Steudel and Mausel [22] to explain the origin of insoluble species existing below T_p . Their basic idea is that insoluble species consist of a variety of S_n rings ($n \neq 8$) such as S_6 , S_7 , S_9 , S_{12} and S_{20} . Based on this idea they have succeeded in explaining several experimental facts. At present it is difficult to give a definite answer to the question of which one is the best candidate for the long-lived products, the charge transfer complexes or S_n rings. The results shown in figures 4 and 5, however, may be helpful for understanding. The most important result we obtained is that the repeated illumination of a very weak pulsed laser accumulates long-lived products and the polymerization starts to occur when the critical value of $\Delta T/T$ is exceeded. In the relaxation process, furthermore, the slow relaxation happens to appear when $\Delta T/T$ during the fast relaxation process decreases down to the critical value, about 10%, which does not depend on the laser power. It seems that the explanation using the charge transfer complex is much more acceptable for the understanding of our results in figures 4 and 5.

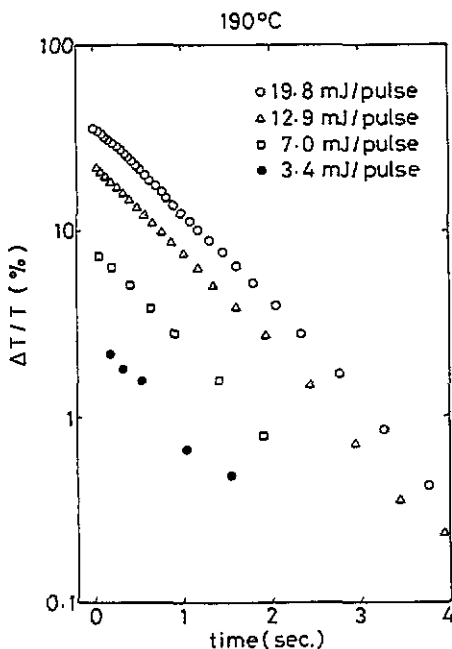


Figure 10. Logarithmic plots of $\Delta T/T$ versus time for liquid sulphur above T_p , at 190 °C, after illumination with a pulsed laser.

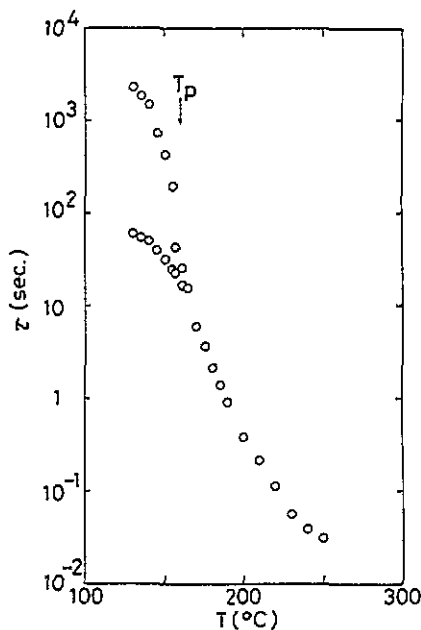


Figure 11. Temperature variation of relaxation time, τ , in a wide temperature range below and above T_p .

3.4. Temperature variation of the relaxation time

Figure 10 shows the logarithmic plots of $\Delta T/T$ versus time for liquid sulphur above T_p , at 190 °C, after illumination with a pulsed laser. It is obvious that there exists only one relaxation process in the range of the present laser power. The relaxation time is 0.9 seconds which is very short compared with those below T_p . As is well known there exist a large number of S_8 rings together with polymeric chains above T_p . The illumination of a

pulsed laser is also expected to cause the opening of S_8 rings. The transient spectra above T_p , obtained by the measurement of $\Delta T/T$ at different photon energies, revealed that the products must be polymeric chains because transient spectra also show maximum around the photon energy of about 3.5 eV.

Figure 11 shows the temperature variation of relaxation time in a wide temperature range below and above T_p . It is obvious that there exist two relaxation processes below T_p and only one above T_p . The relaxation time in the slow relaxation process substantially decreases with increasing temperature and drops by a factor of 10^2 around T_p . In the contrast the relaxation time in the fast relaxation process gradually decreases. Note that plots of relaxation time for slow and fast relaxation processes cross at T_p .

A possible explanation for these photoinduced phenomena is as follows. Below T_p we may have three states with minimum energies which correspond to states for the ring, the charge transfer complex and the polymeric chain; the ring is the most stable, the complex metastable and the polymeric chain unstable. A single shot of a weak pulsed laser easily produces the charge transfer complexes through the excitation over the potential barrier between two minimum states corresponding to the ring and the complex. With increasing intensity of the single shot of the laser a direct excitation from the most stable state (ring) to the unstable state (polymer) may occur in which an instantaneous polymerization is expected because a large number of S_8 chains are instantaneously produced. The fast relaxation from the polymer to the complex, being followed by the slow relaxation from the complex to the ring, takes place below T_p as seen in the figure.

The most interesting is the phenomenon induced by repeated illumination with a very weak pulsed laser as shown in figure 4 and 5. The results reveal that the number of complexes becomes large with repeated illumination and polymeric chains can be generated when the concentration of complexes exceeds a critical value. This fact suggests that a kind of structural instability takes place in complexes at the critical concentration. The instability may be caused by an electro-static interaction between complexes, such as dipole-dipole interaction, when the concentration becomes large. The nature of the polymerization induced by repeated illumination with a weak laser seems to be cooperative.

These results are helpful for the understanding of the polymerization induced by the temperature rise. Charge transfer complexes exist below T_p and the concentration is balanced with that of rings in the thermal equilibrium. The concentration of complexes increases with increasing temperature. When the critical concentration is realized at T_p the polymerization starts to occur and charge transfer complexes are no longer stable. Above T_p it is considered that there are only two states with minimum energies corresponding to the ring and the polymer. Illumination with a laser generates excess polymeric chains which come back to rings through one relaxation process.

3.5. Chain rearrangement and the memory effect

We have observed interesting phenomena in the slow relaxation process by the detailed investigation varying the conditions of laser illumination. The data in figure 5 being carefully examined we can find a difference in the slow relaxation process after repeated illumination with different laser powers. The relaxation time becomes shorter with increasing laser power. We can also find distinct differences in the slow relaxation process when the illumination time is changed. Figure 12 shows plots of $\Delta T/T$ with time after repeated illumination with a pulsed laser with the intensity of 0.2 mJ/pulse for liquid sulphur at 155 °C. The data points in the fast relaxation process after stopping the illumination with three different illumination times lie on a straight line. In contrast, the behaviours in the

slow relaxation process are completely different to each other. The relaxation time becomes short with increasing illumination time. Note that the deviation from the linear plots in the fast relaxation process starts to occur at the value of $\Delta T/T$ of about 10%. Thus, the relaxation time in the slow relaxation process is clearly changed by changing the intensity of the laser or changing the illumination time when the repeating pulsed laser is illuminated. It seems that the illumination time affects the relaxation time much more efficiently. We have not observed such phenomena when a single pulse of a laser is illuminated.

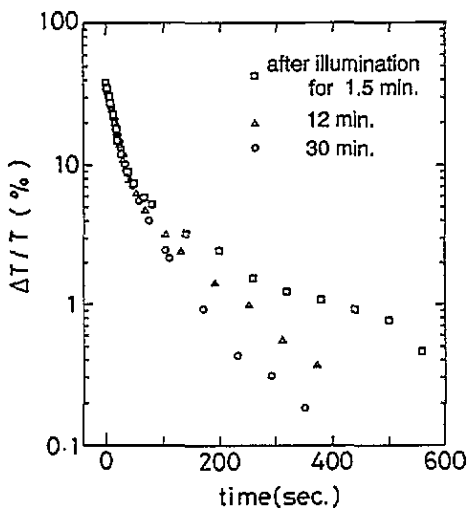


Figure 12. Plots of $\Delta T/T$ with time after repeated illumination with a pulsed laser with different illumination times for liquid sulphur at 155 °C. The intensity of the laser is 0.2 mJ/pulse.

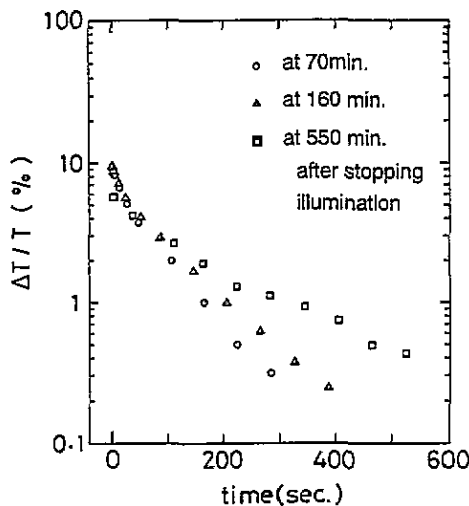


Figure 13. Three different relaxation processes after long pauses of 70, 160 and 550 minutes.

As seen in the previous section the repeated illumination of a laser causes the opening of S_8 rings and charge transfer complexes are created. When the concentration of the complexes increases up to the critical value there appear long polymeric chains. The repeated illumination may give rise to the excitation of lone-pair electrons in the polymeric chain resulting in the bond breaking or bond switching of polymeric chains. A kind of rearrangement of the polymeric species may occur during the repeated illumination because the long chains are strongly restricted within a space narrower than the chain length as discussed in the next section. It is reasonable to consider that the rearrangement of chains may result in some kind of ordering of polymeric chains, for example, a parallel arrangement of chains. The relaxation from such ordered polymeric chains to the most stable S_8 rings may occur much more easily.

Figure 13 shows three different relaxation processes after long pauses of 70, 160 and 550 minutes in liquid sulphur which might have experienced a chain rearrangement as mentioned above. With increasing pausing time the relaxation time is elongated and recovers to the same value as a single pulse is illuminated. This means that the memory of the rearrangement of polymeric chains is lost with time.

3.6. Generation of giant molecules

We have also investigated the effect of much stronger illumination.

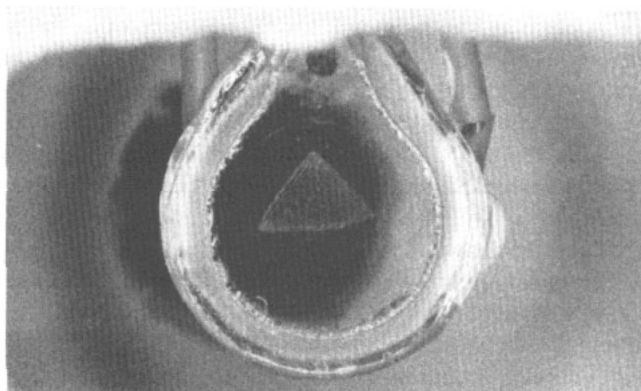


Figure 14. Pattern in the laser-illuminated triangular area of liquid sulphur at 130 °C during repeated illumination with a pulsed laser with a intensity of 30 mJ/pulse.

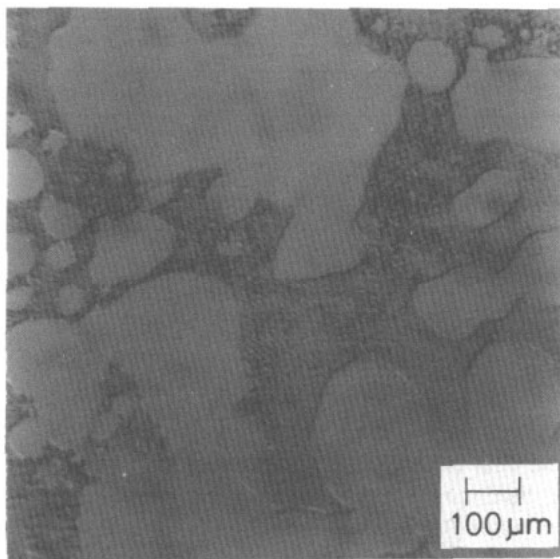


Figure 15. Picture of an opalescent part in the triangular area shown in figure 14 with a 120 times enlarged scale. Since stopping the illumination with the laser 10 seconds have passed.

Figure 14 shows the pattern appearing in the laser-illuminated triangular area of liquid sulphur at 130 °C during repeated illumination with a pulsed laser with a intensity of 30 mJ/pulse. We have found that the triangular area changed from transparent to opalescent immediately after the illumination. We have also observed a rainbow-colour after stopping the illumination. The transparent initial state comes back again after 30–60 seconds. Figure 15 shows the 120 times enlarged picture of a opalescent part in the triangular area shown in figure 14 which was obtained by using a stereoscopic microscope at 10 seconds after stopping the pulsed laser. There are two different regions, homogeneous and

inhomogeneous regions. The inhomogeneous region resembles islands linked together and the homogeneous an inland sea. The inhomogeneous region shrinks and the homogeneous region extends. After 30–60 seconds the whole area is covered by the homogeneous region. The homogeneous region is transparent, but the inhomogeneous one is coloured. The colour changes from place to place and with time. It should be noticed that there appear parallel lines in the inhomogeneous region. The distance between lines is found to be about $10\ \mu\text{m}$. It seems that the giant molecules with colloidal form lie on parallel lines. Such an interesting pattern was observed when the quartz cell with 1.0 or $0.3\ \mu\text{m}$ thick sample space was used but never observed with a $7\ \mu\text{m}$ thick sample space. Therefore, the appearance of the pattern must be strongly connected with the restricted geometry. In fact the length of one random chain [23] containing 10^{5-6} sulphur atoms is estimated to be $0.1-0.3\ \mu\text{m}$, assuming that the bond length and the amplitudes of bond angle and dihedral angle are the same as those of the S_8 ring but only the sign of the dihedral angle along the chain changes randomly. So it is not so unreasonable to consider that a thickness of 1.0 or $0.3\ \mu\text{m}$ gives a two-dimensional restriction to the random chain. A kind of structural change from the random chain structure to a densely packed one may be induced by the geometrical restriction resulting in the generation of colloids. The pattern suggests that these colloids come together to have a macroscopically ordered structure.

Table 1. Summary of photoinduced phenomena in liquid sulphur below T_p on changing the intensity of the laser.

	<0.07 mJ/pulse	0.07–10 mJ/pulse	10–20 mJ/pulse	>20 mJ/pulse
Single pulse	Charge transfer complex		Polymer	Giant molecules with colloidal form using the cell with 0.3 and $1\ \mu\text{m}$ thick sample space
Repeating illumination	Charge transfer complex	Polymer		

4. Conclusion

We have measured for the first time the transient absorption spectra for liquid sulphur below and above T_p after illuminating with a pulsed laser. For the measurement we have developed a specially designed optical cell made of quartz which enabled us to measure the change of optical absorption spectra in the high-absorption region accompanying the polymerization. We have found that the photoinduced polymerization clearly occurs below T_p . On changing the intensity of the pulsed laser three different photoinduced phenomena have been found, which are summarized in table 1. It will be necessary to study the structural and electronic properties of long-lived products in order to examine whether the charge transfer complex really exists or not. The charge transfer complex must play an important role for the occurrence of the temperature-induced polymerization. Our studies suggest that the polymerization in liquid sulphur occurs when the concentration of charge transfer complexes increases up to the critical value, and charge transfer complexes become unstable due to the short-range interaction between them. The generation of giant molecules with colloidal form might be specifically interesting when considered in connection with polymer science and the new phenomena will give an insight for common problems in

range from the microscopic to the macroscopic scale and the phenomena can be controlled by changing the intensity of the laser and the repeating time.

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