Laser-induced Pattern Formation of Polymeric Sulphur

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イオウは融点（113℃:斜方晶系）直上では八員環分子からなる分子性液体であるが、159℃で鎖状高分子と八員環分子との混合液体へと重合転移を起こすことが古くから知られている。我々は最近、この重合転移を、転移温度以下の温度においても光を照射することによって起こすことができることを明らかにした。そしてさらに、強力なパルスレーザー光を照射することによって、マクロなパターンの形成を伴った新しい高分子相が出現することを見出した。本講演では、試料厚みを詳細に変えてこのマクロなパターンの生成から消滅に至るまでの過程を顕微鏡観察した結果を報告し、イオウ高分子がマクロなスケールで示す多様な振る舞いを紹介する。

It is well known that liquid sulphur, which consists of 8-membered puckered rings, changes to have long polymeric chains around 159℃ accompanied by rapid colour change from light yellow to red. Recently we have found that such polymerization transition can be induced by a laser-illumination on liquid sulphur kept below polymerization temperature [1]. This means that the content of polymers in liquid sulphur can be controlled by changing the intensity of the laser-illumination. Therefore, it is expected that the illumination of a strong pulsed laser produces extremely dense polymers and creates a new situation, which has never been observed in the "thermally" polymerized system. Based on this idea, we made the strong pulsed laser with the intensity more than 70 mJ/cm^2 illuminate liquid sulphur and we have found that the strongly illuminated area changes to have colours like rainbow [1]. This change is observed with naked eyes as shown in Figure 1. Such macroscopic change is considered to be caused by the photo-generated giant molecules.

Figure 2 shows the micrograph of the photo-generated pattern which was observed with a microscope. There are two different regions in the illuminated area; the inhomogeneous region like islands and homogeneous region like sea. The inhomogeneous region colours like rainbow while the homogeneous region is transparent [2]. The rainbow-coloured region grows for the repeated illumination of the pulsed laser having a clear boundary with the transparent region. This aspect reminds us two phase separation. According to the observation with a polari-microscope for the quenched sample, both of the regions are made of polymers. The polymers in the transparent region are supposed to have the same structure as that of thermally-generated polymers, which extend freely in the liquid composed of S_8-rings. On the other hand, the polymers in rainbow-coloured region are supposed to have different structure, which is highly ordered, and make up a

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new phase, which has never been observed for changing temperatures and pressures. It should be noticed that there are stripes in the inhomogeneous region. The interval is about 10μm. It is quite interesting that such ordered structure is generated by a laser-illumination in random system of liquid. It is considered that the macroscopic order is related to the structure of photo-generated giant molecules. For example, the order can be explained by assuming the arranged particles about 10μm in diameter, which are created by photo-generated colloidal polymers.

Detailed studies of the photo-generated patterns with changing the sample thickness revealed that the pattern with rainbow-colour is remarkable for the thin samples with the thickness of sub-micron and it is not observed for thicker samples. This suggests that the spatial constraint plays an important role on the generation of the new phase. For the thick sample with the thickness of 2mm, another type of pattern was observed. The pattern is completely different from those in thin samples and seems wrinkles fluctuating with time. The mechanism of the pattern formation for both thin and thick liquid samples is discussed.

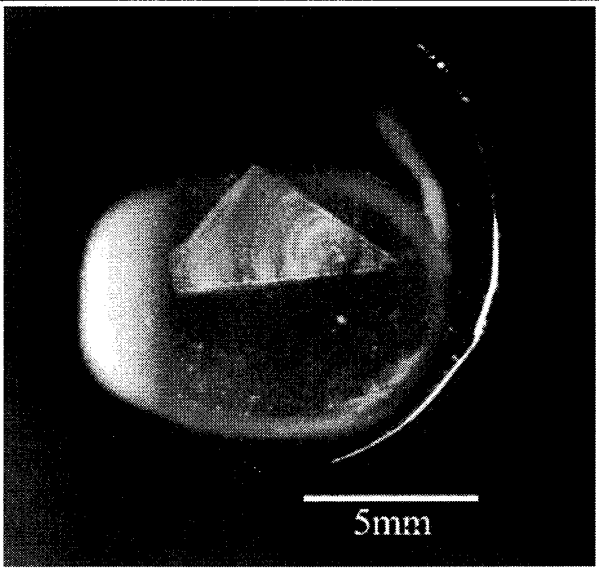

Figure 1: The pattern formed on liquid sulphur, which is generated by strong illumination of pulsed laser. The laser illuminated liquid sulphur inside the triangle.

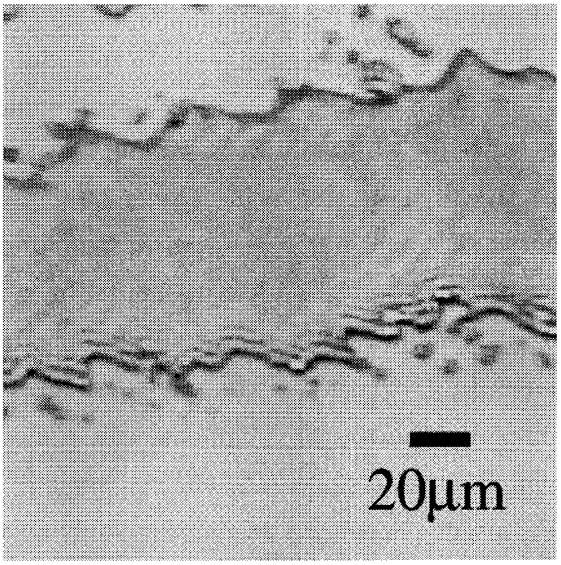

Figure2: Micrograph of the photo-generated pattern.

References

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