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Photo-Deformation of Syndiotactic Polystyrene Gels

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Summary: We report a usual and novel phenomenon that an excitation light beam of a spectrofluorometer produced a black mark in gels of syndiotactic polystyrene (SPS). This mark whose shape is identical with that of an excitation light beam was found to appear in SPS/chloroform gel just after only irradiation at 260 nm for 5 to 10 min. The heating of the gel with the mark at 80°C diminished the mark and recovered uniformly the gel to be as it had been before irradiation. We discuss what the black mark is and why it is produced by light irradiation.

Keywords: gels; light irradiation; networks; polymer-solvent compounds; sols

Introduction

Syndiotactic polystyrene (SPS) is known to form thermoreversible gels, and more than 60 papers on SPS gels have been published so far since Kobayashi et al[1]. SPS chains forming network in a gel state (Figure 1) are already established to have a structure of polymer-solvent compounds[2,3] and/or clathrate crystal structures.[4,5]

In order to monitor free volume among SPS chains in gel form, we applied the fluorescence probe method to SPS gel systems in the same method as we did for isotactic polystyrene gel systems[6,7]: we dispersed naphthalene (NP), 1-methylnaphthalene (MN), 1,5-dimethylnaphthalene (DMN), and anthracene (A) in the SPS gels and examined in detail their fluorescence anisotropy values while changing the concentration of SPS. During these studies, we found the novel phenomenon that an excitation light beam of a spectrofluorometer can make a black mark in gels of SPS (Figure 2), although the excitation light beam is weak. When the total time of the measurements was short, the mark looked like a black line. However, the shape of the black mark was found to be identical with that of an excitation light beam, when the measurement time was long.

The objective of the present work is to clarify (i) what the black mark observed is and (ii) why this black mark is produced by the irradiation of weak light source.

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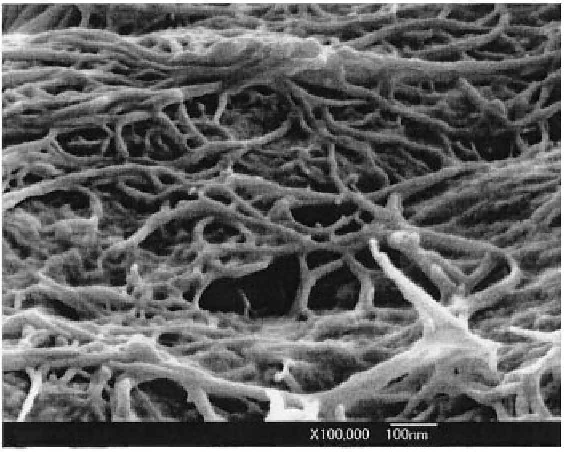

Figure 1. Scanning electron microscopy pictures of SPS/chloroform gel. The bar indicates 100 nm.

Experimental

The SPS sample used in the present study was kindly provided by Idemitsu Oil Co.: the weight average molecular weight is 1.52×10^5 (Mw/Mn=1.9). Chloroform, bromoform, and toluene were used as solvents. NP, MN, DMN, and A were used without further purification. All the gels used for the light irradiation were directly prepared in hermetically sealed quartz cells with optical path length of 1 mm and 1 cm by heating solvents and SPS until they became complete solutions and then cooling them at 4°C for 1 day. The gels were irradiated by either the light source of spectrofluorometer (resolved by slits: 5.9×10^{16} s^{-1} at 260 nm) or 500 W xenon light (resolved by interference filters: 1.6×10^{18} s^{-1} at 263 nm): the infrared light of the xenon lamp was removed by using mirrors.

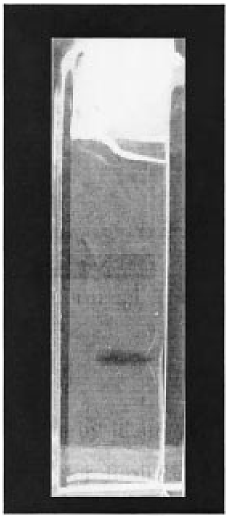

Figure 2. SPS/chloroform gel prepared in a quartz cell after the fluorescence measurements.

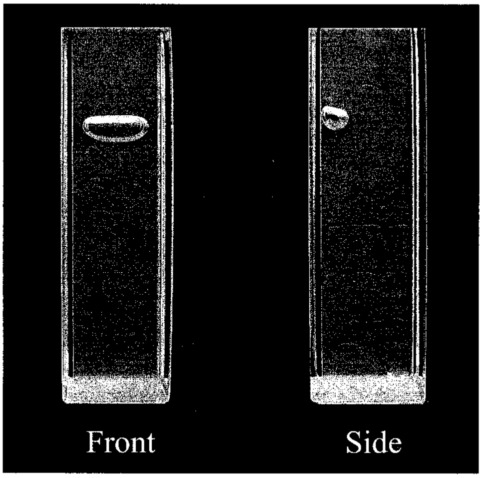

Figure 3. The front and side views of the 0.87%(wt/wt) SPS/ chloroform gel prepared in a 1 cm × 1 cm quartz cell after being irradiated at 263 nm for 4 hours and left at -25°C overnight.

Results and discussion

In order to clarify what the black mark produced in SPS gels after the fluorescence measurements is (Figure 2), we irradiated an SPS/chloroform gel for a longer time with a stronger light source. Figure 3 shows the SPS/chloroform gel that was irradiated for 4 hrs at 263 nm (1.6×10^{18}quanta/sec) using a 500 W xenon lamp and kept at -25°C overnight. It clearly demonstrates that a hole was formed in the SPS/ chloroform gel by light irradiation. Bubbles sometimes came out during keeping the gels in a freezer, but did not always appear. Consequently, the mark in an SPS gel produced by the irradiation turned out to be a hole, namely of SPS solution form. Since the infrared beams of the xenon lamp were cut thoroughly, this phenomenon was not induced by thermal heating.

The heating of the gel at 80°C diminished the hole, and the perfect gel was reformed when cooled down. We do not claim strongly that this would be efficient as a memory, but we can repeatedly write something onto SPS/chloroform gels by using uv light and reset it by heating them.

Next we examined the best condition to produce holes in SPS gels in order to clarify the process to give a sol form only by irradiation of weak light. We changed the conditions to prepare SPS gels such as concentration of SPS, additives of fluorescent probe molecules, solvents of gelation, and also changed the conditions to irradiate gels such as excitation

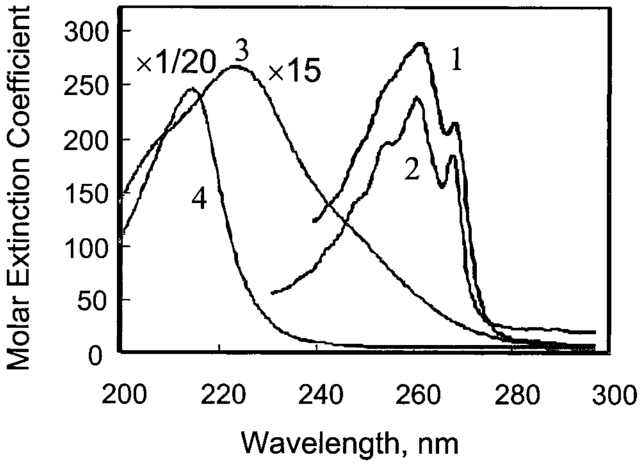

Figure 4. Uv absorption spectra of SPS/chloroform gel (1), toluene in cyclohexane (CH) (2), bromoform in CH (3), and chloroform in CH (4).

wavelength, intensities of excitation beam and irradiation time.

Because this unusual phenomenon was observed first for SPS/chloroform gels containing fluorescent probe molecules such as NP and MN, the influence of the addiives was examined in detail. However, in the long run, holes were formed more quickly and efficiently in the SPS/chloroform gels without any additives. Concerning the solvents of SPS gels, chloroform, bromoform, and toluene were examined whether they can form gels giving birth to holes when irradiated. Among three solvents, only chloroform gives a gel forming holes by uv light irradiation. Moreover, in the case of SPS/chloroform gels prepared in a quartz cell with optical path length of 1 mm, holes appeared at SPS concentrations being lower than 4 %(wt/wt): namely the concentration of SPS should not be too thick in order to produce holes when irradiated.

These experimental results clearly suggest that the formation of holes strongly depends on how much phenyl groups of SPS can absorb photons without being interfered with other molecules. Figure 4 shows the uv spectrum of SPS/chloroform gel together with the spectra of three compounds used as solvents. The solvents whose absorption is overlapping with the spectrum of SPS are found not to give SPS gels producing a hole when irradiated. Only chloroform has almost no absorbance in the wavelength range where phenyl groups of SPS have higher absorption. When the concentration of SPS is high, the light is considered unable to go into the inside of the gels, and the hole is not produced.

In order to make sure that light absorption of phenyl groups of SPS is most important for forming a hole at irradiation, we examined the dependence of excitation wavelength on formation of holes in 0.4 %(wt/wt) SPS/chloroform gels prepared in quartz cells with optical path length of 1 mm by using xenon lamp resolved by interference filters. Finally the hole was formed most quickly and sharply when the gel was excited at 263 nm, which is the peak wavelength of SPS absorption. When the gel was excited at 260 and 270 nm, the formation of a hole was also efficient. However, when the excitation wavelengths are 280 and 290 nm, it took quite a long time to form a hole, and at wavelengths higher than 300 nm, no holes were observed even after irradiation for 8 hours. In summary, the efficiency of forming a hole in an SPS gel corresponds to the absorption spectrum of SPS (Figure 4). Finally, the present novel process was concluded to start with the uv light absorption by side-chain phenyl groups of SPS.

How does this process take place after the excitation of phenyl groups of SPS gels? When a side-chain phenyl group is excited, three processes are possible: (i) the excited phenyl group deactivates by emitting fluorescence, (ii) it deactivates nonradiatively by vibrational motion, and (iii) it is photodegraded into a non-aromatic compound.

In the case of (i), the excitation energy released from SPS cannot be absorbed by chloroform, a solvent molecule, since the absorption spectrum of chloroform does not overlap with the fluorescence spectrum of SPS. Accordingly, nothing is expected to happen. However, the process of (ii) and (iii) should affect a polymer-solvent compound of SPS gel. The excitation energy of a side-chain phenyl group taking part in a polymer-solvent compound would be transferred to a chloroform molecule in the molecular compound by way of vibrational motion. This energy would urge the motion of the chloroform and may dissociate the polymer-solvent compound partly. If an excited phenyl group is degraded (process (iii)), the adjacent chloroform in the same polymer-solvent compound would become mobile because the degraded phenyl group could never keep the chloroform molecule fixed in this molecular compound any more.

Figure 5 shows the initial change of the uv spectra of 0.40% SPS/chloroform gel when it was irradiated at 263 nm. It is clear that photodegradation occurs a bit, but the decrease of phenyl groups due to the degradation is not so much. Nevertheless, the formation of a hole took place within 5 min. Thus, the process (ii) is more probable.

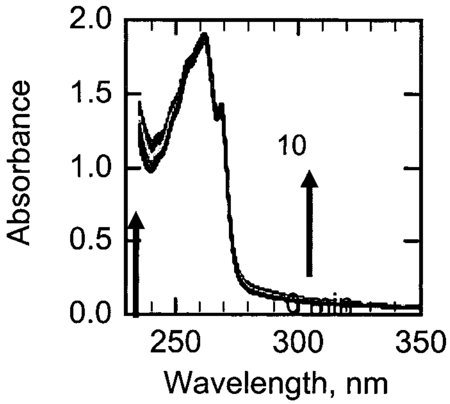

Figure 5. Change of uv spectra of 0.40% SPS/chloroform gel with an increase of irradiation time (every each 1 min from 0 to 10 min). The cross section part of the gel was perfectly the same for both irradiation at 263 nm and measurements of uv spectra.

So far no other similar phenomena induced by light irradiation have been published, but Ramzi et al. reported that agarose aggregates in water/DMSO underwent disruption while performing electric birefringence experiments[8]. It is probable that the electric field or the heat perturbs the molecular organization between solvent and polymer within the physical junctions by disorienting solvent molecules, resulting in destabilizing the organization.

Conclusion

A novel phenomenon was discovered that a hole is produced in SPS/chloroform gels by uv light irradiation. The heat released by nonradiative deactivation of excited side-chain phenyl groups of SPS is assumed to accelerate the motion of the adjacent solvent molecule in the polymer-solvent compound. This motion is concluded to urge the dissociation of the polymer-solvent compound. It would loosen and untie several networks and make the part of gels irradiated to be in sol form , followed by the destruction of the gel structure.

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