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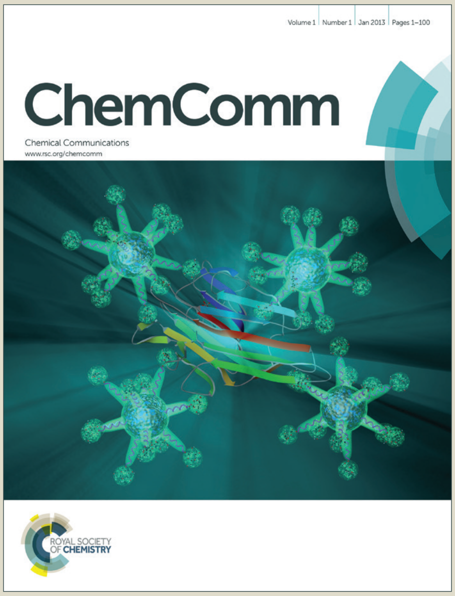

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Unprecedented colorimetric responses of polydiacetylenes driven by plasma induced polymerization and their patterning applications

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We report for the first time that polydiacetylenes (PDAs) can be alternatively prepared *via* plasma induced polymerization process. The degree of polymerization and colorimetric transitions could be manipulated by controlling the power of plasma radio frequency, exposure time and by using acrylic mask, resulting in a great potential as patterning applications.

Polydiacetylene (PDA) polymers show the blue PDAs with 640 nm maximum absorption wavelength, which can display a unique colour change to a red with 550 nm maximum absorption wavelength upon environmental stimulation.[1-5] Since this distinct change can be monitored by the naked eye, various PDA based sensors have been actively studied in recent years.[1-16] In addition, red-phase PDAs are fluorescent even though blue-phase PDAs are nonfluorescent, which enables PDAs to be not only colorimetric sensors but also fluorescent sensors. Common stimulations or anayltes have been temperature, pH, metal ions, anions, surfactants, other biologically important molecules, etc.[1-23]

On the other hand, low temperature and low pressure plasma, which contains ions, excited atoms and molecules, energetic photons, has become a popular approach especially to surface modifications for functional organic materials or inorganic materials under plasma condition.[21-24] From the plasma phase, generally, energetic ions can collide with monomers in either the solid or the liquid phase directly, and consequently the transfer of some excited species into monomers in order to initiate the polymerization process takes place at low temperature and low pressure.[24] Thus, plasma can be effectively utilized to induce the high performance functional polymer formation which is known as a quite distinct process compared to conventional polymer formations such as free radical, ionic, and radiation polymerization. During the past decades, plasma induced polymerization process has been widely recognized as a very useful technique, for applications ranging from adhesion to composite materials, protective coatings, printing, membranes, biomedical applications and so on owing to its unique surface properties with pinhole free and highly dense.[24-27] Although chemical reactions under plasma condition are still very complicated to reveal their identities and consequently are nonspecific in nature, such chemical reactions are of a great merit to realize as a special means of preparing unique polymers that cannot be made by other conventional methods.[24]

Typically, PDA polymers have been prepared by UV irradiation from self-assembled diacetylene (DA) monomers. Interestingly, it has not been reported that PDAs have been obtained from plasma induced polymerization process so far. However, it should be noticed that since some new types of DAs (diacetylene monomers) would not be appropriate to produce PDA by UV irradiation due to the structural differences of head groups of DA monomers, alternative routes could be carefully considered. For example, a new diacetylene (DA) monomer bearing hexaethylene glycol (HEG) units in this study did not undergo into blue PDAs under UV radiation in both the solution state and embedded fibre. On the other hand, we found out that it was easily polymerized to produce PDAs in the form of pure HEG embedded fibres as well as the mixture fibres between HEG and 10, 12-pentacosadiynoic acid PCDA at even very short exposure of plasma for the first time. Additionally, they displayed distinct colorimetric changes as well as fluorescence enhancements compared to the conventional PDAs originated from the typical UV exposure for initiating polymerization.

In this study, therefore, we report the first demonstration of utilizing a simple plasma process as an effective alternate to achieve PDAs with unique colorimetric responses when UV irradiation cannot initiate the polymerization of some specific DAs to produce PDAs for various applications. Furthermore, we suggest the distinct colorimetric changes of plasma induced HEG-PCDA can be applied to a potential use of coloured patterning.

For the synthesis of PCDA-HEG, oxalyl chloride was treated with 10, 12-pentacosadiynoic acid to make its acid chloride derivative, which was then reacted with hexaethylene glycol in the presence of triethylamine to give PCDA-HEG in 74 % yield after the column chromatography (Scheme S1). The detailed procedures and the ^{1}H and ^{13}C NMR spectra are explained in the Supporting Information.

The PDA-embedded polymer fibres was prepared as below and shown in Fig. 1(b).[28] A viscous solution containing PCDA, PCDA-HEG monomers and PEO as a matrix polymer were placed in a syringe and then a high voltage (4.5 kV) was applied to a conductive capillary attached to the syringe needle. This process caused a charged polymer jet to eject from the polymer solution. During fibre formation, the solvent evaporated and PCDA, PCDA-HEG self-assembly was assumed to take place because the attractive forces between the monomers were larger than those between the monomers and matrix polymers. In order to determine the effect of monomers composition on the plasma induced polymerization and their colorimetric change, fibre formation was carried out in various ratios of PCDA and PCDA-HEG.

Plasma induced polymerization for polydiacetylenes fibres was then accomplished by dielectric reactive ion etching. The process pressure was 21 mT and gas flow rates were 100 sccm. PDAs embedded fibres were placed on the water-cooled (23 ℃) bottom electrode that was powered by a 13.56 MHz rf generator, employing Ar gas (Fig. S3). In our experiments, only the exposure time or rf power was varied. For determining degree of polymerization and colour transitions, we have manipulated the molar ratio between PCDA and PCDA-HEG: 1:0, 0:1, 10:1, 5:1, 1:1, 1:5 and 1:10. The degree of polymerization was determined from the different colour change. The morphology of PCDA and PCDA-HEG embedded fibres from Scanning Electron Microscopy (SEM) images (Fig. S4) represent well defined fabric structures with the diameter of about 1 μm.

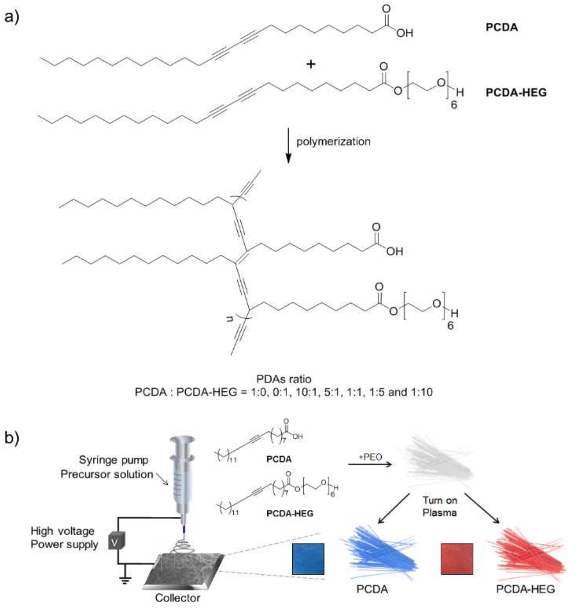

Figure 1. (a) Self-assembly and polymerization of PCDA and PCDA-HEG (b) Schematic representation of the preparation of PDAs-embedded electro-spun fibers.

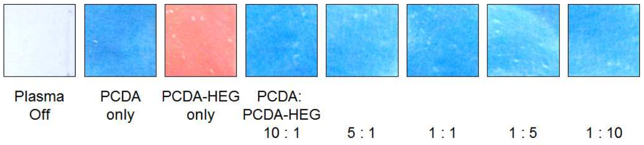

Figure 2. Plasma promoted polymerization of PDAs based electrospun fibres; PDAs with various molar ratios of PCDA and PCDA-HEG (Radio frequency powers: 5 W, Argon gas pressure: 21 mTorr, 1 sec).

In Fig. 2, the PDAs embedded fibres were exposed to the plasma for 1 sec using 5 W rf power. In spite of such a short time exposure and low rf power, all PDAs were successfully polymerized. Especially, PCDA-HEG embedded fibres directly turned to red due to the steric factors of head groups. In order to investigate colour change by plasma, we have also controlled the exposure time with various molar ratio of PCDA and PCDA-HEG using 200 W rf power (Fig. 3). Besides we also observed similar phenomenon with spin coated PDA thin films (Fig. S5). Typical blue-to-red chromic transition was observed in PCDA polymer, on the other hand, purple-to-red transition was observed in high proportion of PCDA-HEG.

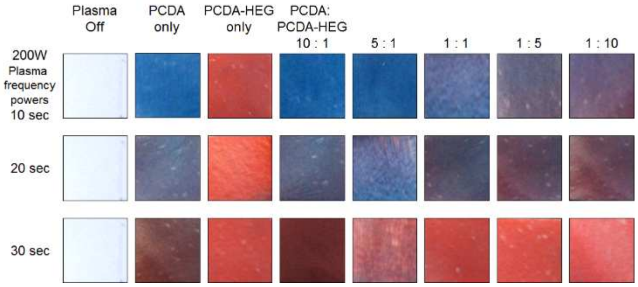

Figure 3. Time-dependent colour changes of PDAs based electrospun fibres in the presence of plasma (Radio frequency powers: 200 W, Argon gas pressure: 21 mTorr).

Besides, since plasma condition can also generate energetic photons like UV right, we fabricated a simple transparent acrylic mask in order to distinguish the effect between UV irradiation and energetic ions in the course of plasma induced polymerization. In this design, the masked parts cannot allow plasma contacts so that UV light can be only a source of polymerization. Consequently, the masked parts turned to blue phase by only UV irradiation but exposed parts turned to red phase by environmental stimulation such as plasma using 200 W rf power for 30 sec (Fig. 4).

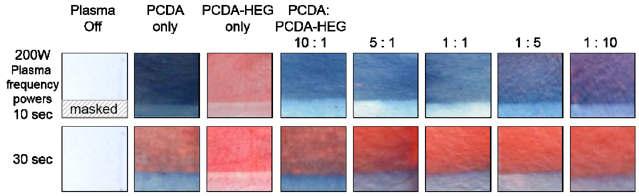

Figure 4. Time-dependent colour changes of PDAs based electrospun fibres in the presence of plasma with acrylic-mask (Radio frequency powers: 200 W, Argon gas pressure: 21 mTorr).

Then, the patterned colour and fluorescent images were obtained by using acrylic mask as illustrated in Fig. 5 (a). As shown in Fig. 5 (b), only exposed monomers (PCDA and PCDA-HEG (1:1)) were polymerized *via* plasma, turning to blue phase. By simply increasing rf power, the exposed same monomers were polymerized and turned to the red phase directly. Particularly, one of important advantages of plasma induced PDA formation is that various colour patterning could be readily controlled by adjusting ratio of monomers, rf power and exposure time. The corresponding fluorescent images for the red phase can be successfully observed as well (Fig. 5 (d)).

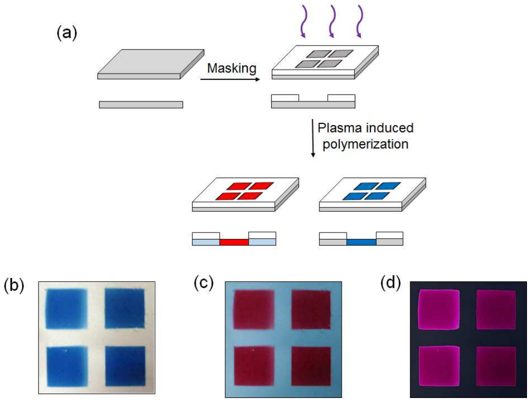

Figure 5. Patterned colour and fluorescent images obtained from acrylic-masked irradiation of immobilized PDA (PCDA : PCDA-HEG = 1:1) based electro-spun fibres (a) schematic diagram of patterning process (b) colour images obtained from using 5 W rf power for 1 sec (c) from using 200 W rf power for 30 sec (d) and its fluorescent image .

Conclusions

In conclusion, we report an efficient strategy of making new types of PDAs by the presence of plasma. In our study, energized ions from plasma condition directed on the electro-spun fibres containing pure HEG based DA monomers or mixtures with PCDA and then subsequently initiated the polymerization of DA monomers into PDAs accompanied with distinct colour changes compared to those of the conventional PDAs. We would also suggest that various patterned colorimetric and fluorometric images could be readily controlled by adjusting ratio of monomers, rf power and exposure time in the course of plasma induced polymerization. Our finding thus demonstrate not only the first example of PDA polymerization *via* plasma but also a great potential of the plasma process to be used as patterning applications with unique colour variations.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Measurement, synthesis of PCDA-HEG, preparation of PDAs embedded fibres, ^{1}H NMR and ^{13}C NMR spectra of PCDA-HEG and schematic representation of plasma induced polymerization. See DOI: 10.1039/c000000x/

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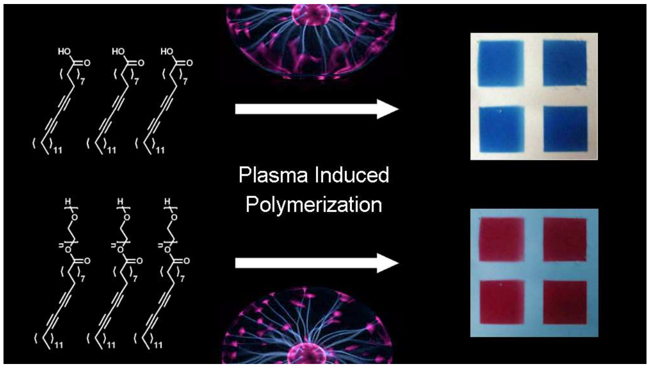

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