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## COMMUNICATION

## Effect of Solvent Vapour Annealing on Polymer Thin Films and the Application on Nonlinear Optical Fields

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**Solvent vapour annealed (SVA) technique was successfully used on controlling the morphology of the polymer thin film blending with low molecular weight chromophoric (LMWC) molecules. And it was studied by XRD, UV-vis, AFM and TEM. Outstanding electro-optical signal was detected on the films prepared by SVA method, confirming that it can be widely applied on the nonlinear optical fields.**

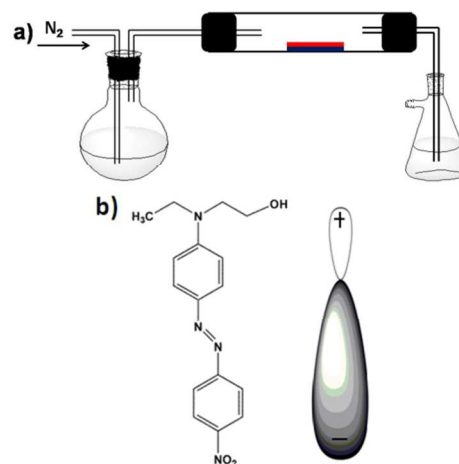
Organic polymeric second-order nonlinear optical (SONLO) materials have attracted steady attention for many years because of their tremendous potential applications in optical telecommunication devices and electro-optical (EO) devices.<sup>1</sup> As we all known, so far, poled polymer is the most typical and promising organic SONLO material, which have been studied widely in the past few years.<sup>2</sup> The treatments at high temperature and high voltage are the inevitable processes for the preparation of poled polymer films. However, electro-optic coefficient will always be declined due to the partly decomposition of the low molecular weight chromophoric (LMWC) molecules in polymer films at high temperature during the process of polarization.<sup>3</sup> The shortcomings above have limited the developments and applications of poled polymer seriously.<sup>4</sup>

Solvent vapour annealing (SVA) has been widely used in improving the photoelectric conversion efficiency of organic polymer solar cells,<sup>5</sup> organic thin film transistors and other optoelectronic devices by controlling the morphology of conjugated polymer films.<sup>6</sup> SVA technique has many advantages, such as convenient, high efficiency and environmental protection, et al.

In this work, through building specific device, SVA technique was expanded to the field of nonlinear optics. LMWC molecules in polymer films could be oriented consistently under the effect of solvent vapour, SONLO films would be prepared by SVA technique without the heating processes, avoiding the decomposition of LMWC molecules compared with poled polymer.

A typical LMWC molecule of N-Ethyl-N-(2-hydroxyethyl)-4-(4-nitrophenylazo) aniline (DR1) and poly (methyl methacrylate) (PMMA) were used in this study. All the reagents and materials were analytical reagent grade and purchased from Aldrich Company. The processes for investigating the effect of SVA on the polymer thin films were shown in scheme 1 (a). Solvent vapour was brought

about under the driving of pure nitrogen (N<sub>2</sub>), and the concentration of the vapour could be effectively controlled through the flow velocity and the acting time of N<sub>2</sub>, which would be closely saturated after a certain time. The molecular structure of DR1 and the schematic representation of its electron cloud distribution (dipoles) were as shown as in scheme 1 (b).

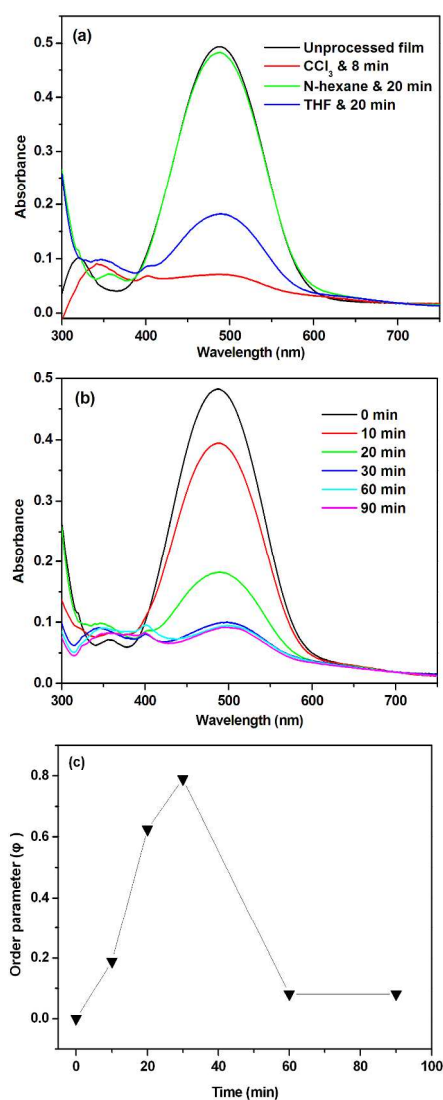


**Scheme 1.** (a) Schematic representation of the processes of the polymer thin films under SVA method; (b) Molecular structure of DR1 and the corresponding schematic diagram of the electron cloud distribution.

The noncentrosymmetric alignment of DR1 in DR1/PMMA blend film before and after SVA process was confirmed and evaluated by UV-Vis spectra. As shown in Fig.1, the absorption peak at 486 nm was attributed to the absorption of azo phenyl groups in DR1.<sup>7</sup> The order parameter  $\phi$  ( $\phi = 1 - A_1/A_0$ ) has been used to estimate the degree of the orientation of chromophore, where  $A_1$  and  $A_0$  are the UV-vis absorbance of the processed and unprocessed film, respectively.<sup>8</sup>

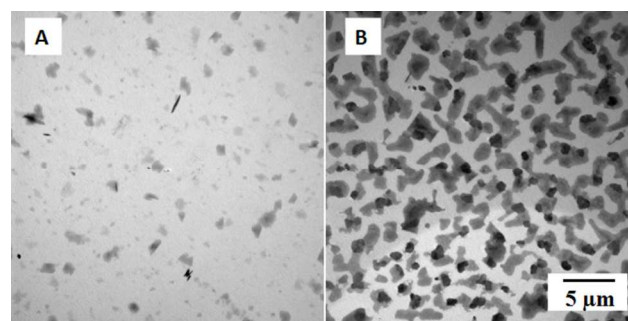
It can be seen that the order parameter of DR1/PMMA blend film treated under tetrahydrofuran (THF) vapour was increased gradually with the increasing of the processing time until it reached 30 min, which was calculated to be 0.37 (Fig. 1b and 1c), meanwhile, it was

easy to operate and repeat the results above with the method in such a long time. The variations of UV-vis absorption spectra of the blend film under different solvent vapour were compared as shown as in Fig.1a, the order parameter of hybrid film under the chloroform ( $\text{CHCl}_3$ ) vapor for 8 min was calculated to be 0.42, which was higher than the one under THF and n-hexane vapour ( $\phi=0.06$ ) for 20 min, but the surface of the film have been bleached and destroyed partly because of the strong solubility. The results above illustrated that appropriate polarity of solvent was necessary for the orientation of LMWC and high-quality polymer films during the SVA process of the hybrid films. THF was just a suitable solvent for DR1/PMMA blending films in SVA method. In addition, polymer films with large amount of LMWC molecules oriented consistently should exhibit nonlinear optical properties, which was usually measured by way of a simple reflection technique.<sup>9</sup> Obvious electro-optic signal was detected on the DR1/PMMA film fabricated by THF vapour above, the electro-optic coefficient ( $r_{33}$ ) was calculated to be 7.5 pm/v, which was a considerable value with the nonlinear optical films fabricated by electric-field poling technique.<sup>10</sup>



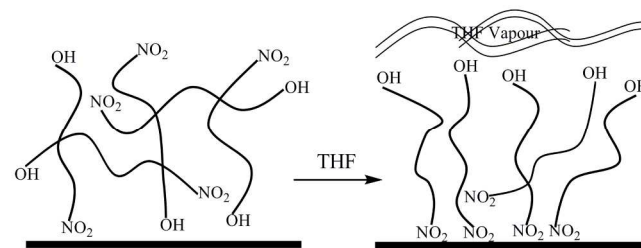
**Fig 1.** (a) UV-Vis absorption spectra of DR1/PMMA films with different solvents vapour and (b) different processing time under THF vapour and (c) the variation of the corresponding order parameter ( $\phi$ ).

The corresponding transmission electron microscopy (TEM) images of DR1/PMMA films before and after SVA treatment were shown in Fig.2. It can be seen that azobenzene molecules were reunited together evenly under the effect of THF vapour. The size of the aggregation of azobenzene molecules was basically at about 1 micron, which was less than the wavelength of incident light on the application (1.03  $\mu\text{m}$  and 1.55  $\mu\text{m}$ ), so the morphology was beneficial to the propagation of light and photoelectric effect. TEM images of the films shown in Fig.2 are not of high quality probably due to the instability of the PMMA polymer under the electronic beam, but the results are consistent with the varieties of UV-vis absorption spectrum.



**Fig 2.** Transmission electron microscopy (TEM) images of DR1/PMMA films before (A) and after (B) the treatment by THF vapour.

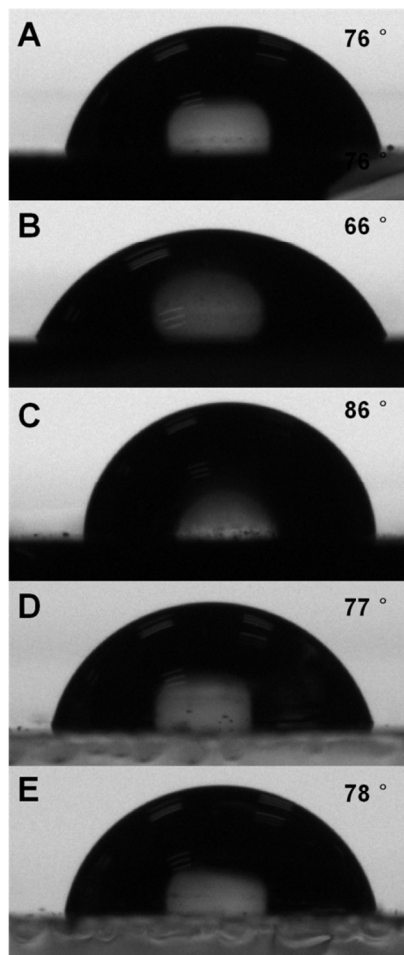
From the experiments and results above, we can deduce that the aggregation and orientation of LMWC molecules in the blending films fabricated by SVA technique are depended on the molecular structure of LMWC molecule and the polarity of solvent, which can be described by scheme 2, the hydroxyl group and nitro group in DR1 are typical hydrophilic group and hydrophobic group respectively, so the hydroxyl group and THF vapour will attract each other when they contact with each other, and the effect of nitro group is opposite.<sup>11</sup> It eventually led to the orientation consistent and aggregation of DR1 in DR1/PMMA films in a particular time. The test method and the mechanism mentioned above is universal and can be widely used in the morphology control of blending film containing chromophoric molecule with polar groups.



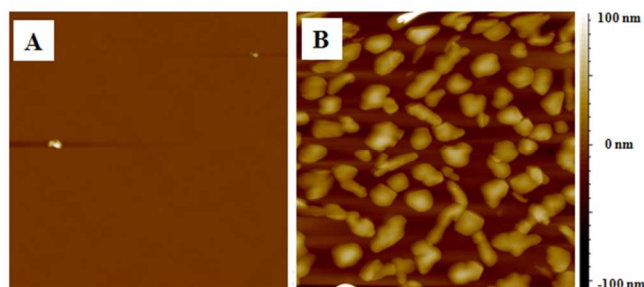
**Scheme 2.** Schematic diagram of the distribution of LMWC molecules in blend film after processing under THF vapour for 30 min.

In order to confirm the inference mentioned above further, contact angle measurement has been used to illustrate the action process (as shown in Fig 3). Contact angle of DR1/PMMA film without any treatment was 76°, the value was 66° and 86° after the treatment under THF vapor and  $\text{CHCl}_3$  vapor respectively. It can be inferred from the results that the hydroxyl groups were toward the surface of

the film under the THF vapor, and the nitro-groups were toward the surface of the film under the CHCl<sub>3</sub> vapor. It was confirmed that the aggregation and orientation of LMWC molecules in the blending films fabricated by SVA technique were depended on the molecular structure of LMWC molecule and the polarity of the solvent. In addition, the contact angle of the pure PMMA film has not obvious variation, which can be sure that the variation of the contact angle of the blend film under organic vapor was due to the orientation of LMWC molecule

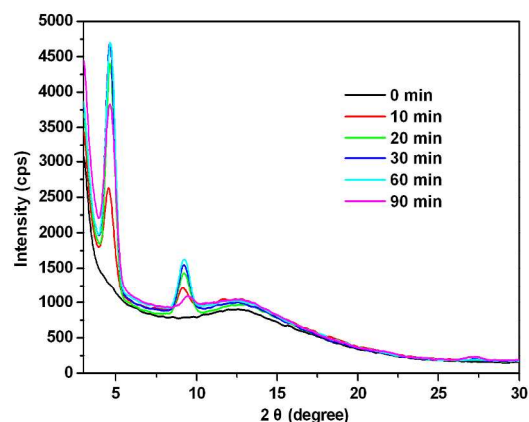


**Fig 3.** Contact angle values of DR1/PMMA film (A), DR1/PMMA film under THF vapor (B), DR1/PMMA film under CHCl<sub>3</sub> film (C), PMMA film (D) and PMMA film under THF vapor (E).



**Fig 4.** Atomic force microscope (AFM) images on tapping mode at 20×20μm<sup>2</sup> areas of DR1/PMMA films before and after the treatment by THF vapour.

Atomic force microscopic (AFM) had been further used to characterize the morphology and the quality of the blend films, as shown as in Fig.4. Uniform molecular reorganization can be observed from the AFM images, which were consistent with the results of TEM examination. The surface roughness (RMS) of the test samples can reach 5.5 nm, which was smooth enough to fabricate corresponding devices.



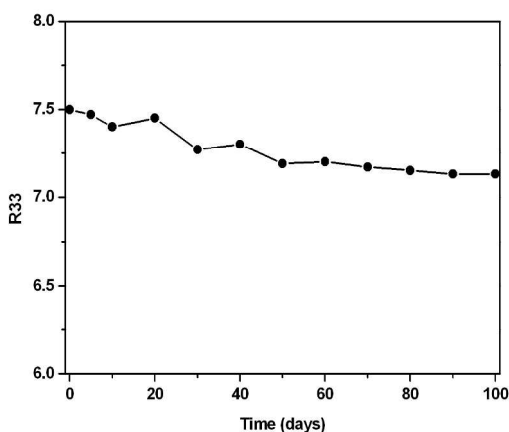
**Fig 5.** X-ray diffraction (XRD) profiles of DR1/PMMA films with different processing time under THF vapour.

In addition, the kinds of nanostructures of the aggregation in the films had been determined by means of X-ray diffraction (XRD). The results are shown in Fig.5, compared with the spectrum of unprocessed film, there was an obvious characteristic peak centered at 4.58° ( $d = 19.277 \text{ \AA}$ ) attributed to the films after THF vapour treatment. Meanwhile, it was interesting to note that by far another diffraction of all the films was located at  $2\theta = 9^\circ$ , corresponding to an distance of 9.8 Å, which was tantalizingly close to the length of trans-azo-benzene molecule (9 Å).<sup>8</sup> Furthermore, the intensities of diffraction peaks at 4.58° and 9.8 Å were increased linearly with the increases of processing time of THF vapour, which were no longer increased linearly so much as decreased until 30 min. The varieties of X-ray diffraction data are consistent with the varieties of UV-Vis absorption spectrum.

The electro-optic coefficients were measured by way of a simple reflection technique proposed by Teng et al.<sup>9</sup> The electric-optic coefficient ( $r_{33}$ ) can be calculated using the following equation:

$$r_{33} = \frac{3\lambda I_m (n^2 - \sin^2 \theta)^{\frac{1}{2}}}{4\pi V_m I n^2 \sin^2 \theta} = \frac{R I_m}{V_m I_e} \quad (\theta = 45^\circ, \lambda = 1.3 \mu\text{m})$$

Where  $I_m$  is the amplitude of modulation,  $V_m$  is the modulating voltage applied to the sample, and  $I_e$  is the half the maximum intensity of modulation,  $n$  is the refractive indices of the new sol-gel films and  $R$  is constant. The values of electro-optic coefficient  $r_{33}$  of the DR1/PMMA film prepared by SVA technique was 7.5 pm/v. And as shown as in Fig.6,  $r_{33}$  could be retained to around 95% at room temperature for 100 days. It exhibited high temporal stability which was a good candidate material for applying to electro-optic modulators.



**Fig 6.** Temporal stabilities of DR1/PMMA films prepared by SVA method.

## Conclusions

In summary, SVA method has been successfully used in controlling the morphology of polymer films with LMWC molecules in this paper. Appropriate aggregation and consistent orientation of DR1 in DR1/PMMA hybrid film has been demonstrated successfully under THF vapor, and outstanding electro-optical signal has been obviously detected. It can be confirmed that the technique can widely applied on the fabrication of second-order nonlinear optical materials. The test method and the mechanism mentioned above is universal and can be widely used in the morphology control of blending film containing chromophoric molecule with polar groups. The hybrid films blending with LMWC molecules with specific morphology fabricated in this article will be widely applied on photoelectric switches, organic thin film transistor and photorefractive materials.

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## Notes and references

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