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Corona poling of liquid crystalline polymers with nitroazobenzene side chains

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Summary

The orientational behavior of liquid crystalline polymers with para-nitro azobenzene as side chains under electric field was studied by UV-visible spectroscopy. The results showed that λ_{max} of the poled polymer films was around 394nm, compared to that of the unpoled films, the absorption decreased due to poling. The orientational parameters increased linearly with the increase of the electric field. The temporal stability of the poled polymer film is good at room temperature. This kind of materials showed promise application as nonlinear optical component in photorefractive polymers

Introduction

Recent advances in optical communication have created intense interest in nonlinear optical materials [1,2]. Poled polymers are considered as the most potential nonlinear optical materials due to their ease of processability, low dielectric constant etc. and they are suggested to be used in high frequency optical modulators, integrated semiconductors [3,4]. Different kinds of polymer with electron donor-acceptor substituted benzenes, stilbenzenes, azobenzenes, bezylidene or tolanes chromophore were synthesized to satisfy the requirement of NLO polymers. Among them, high temporal stability, large electro-optical coefficients (r_{33}) and low optical loss are the most desired.

Inspirited by the early work of D. J. Williams[5] who examined SHG of the DANS dispersed in a liquid crystalline side chain polymer host, and the results showed that its SHG intensity is 100 folds higher than that of it in amorphous PMMA due to the guest-host correlation, we incorporated azobenzene derivative containing electron donor and acceptor groups which is used as mesogenic and chromophore groups to a polymer backbone and hope that the liquid crystallinity could improve the second -order nonlinear optical property.

Our present paper reported the orientational behavior of this side chain liquid crystalline polymer under electric field. The materials reported here might also be used in optical storage, electro-optic modulations and optical switching[6] even as photorefractive materials due to the existing of azobenzene structure.

Experimental

Synthesis of polymer

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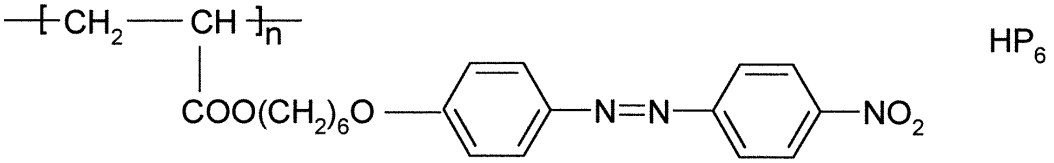
The side chain liquid crystalline polymer was synthesized by free radical polymerization using AIBN as initiator, chlorobenzene as solvent at 60°C for 48 hr. Detailed description could be found in our previous publication[7]. The molecular structure of the polymer studied is given in figure 1



Tg 308.9K T_{KN} 344.2KT_{NI} 401K

Figure 1 Molecular structure and phase behavior of HP6

Methods

Film preparation

The polymer was dissolved in chloroform, thus obtained solution was filtrated and films were prepared by spin-coating the solution onto ITO glasses. The films thus obtained were dried overnight at room temperature under vacuum to remove the residual solvent.

Corona poling

Corona poling with a needle top electrode which was placed 1 cm above the film surface was employed to pole the polymer film. The film was poled under a certain electric field at a certain temperature for 30 min. and then the temperature was lowered to room temperature while the voltage hold constant.

Measurement

UV-visible spectra were recorded on a VU_2 UV-visible spectrometer (Zeiss, Germany).

Results and discussion

Phase behavior of HP6

The phase behavior of HP6 was reported in our previous paper and the results showed that its Tg is 308.9K, melting temperature 344.2K and the clearing point 401K. The texture observation and WAXD suggested nematic phase existed in polymer HP6 in the course of heating.

Optical property of HP6

UV-visible spectra of the poled and unpoled polymer HP6 are given in figure 2. It can be seen that the maximum absorption wavelength was 394 nm, while the value for the commonly used Dispersed Red 1 was 460 nm. That is to say, the NLO materials we synthesized shows great value in frequency doubling applications.

The noncentrosymmetric alignment of chromophores was achieved by corona poling. It can be seen from figure 2 that the chromophores aligned along the poling field, the absorption of the poled polymer film decreased compared to that of the unpoled one. The order parameter (ϕ) of the poled polymer film could be determined by the following equation[8]

$$\phi = 1 - A_{\perp}/A_0 \qquad (1)$$

Where A_0 is the absorption of the unpoled polymer films and, $A_{\perp}$ is the absorption of the poled polymer film with the electric field of light perpendicular to the poling direction.

According to equation (1), the order parameter of the poled polymer film given in figure 2 is 0.41.

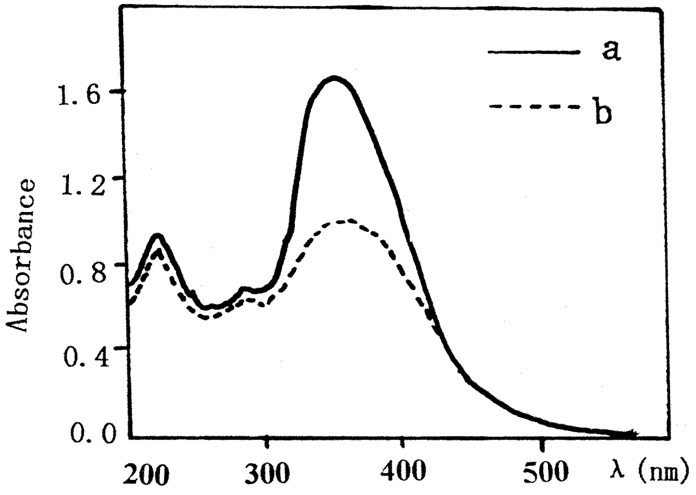
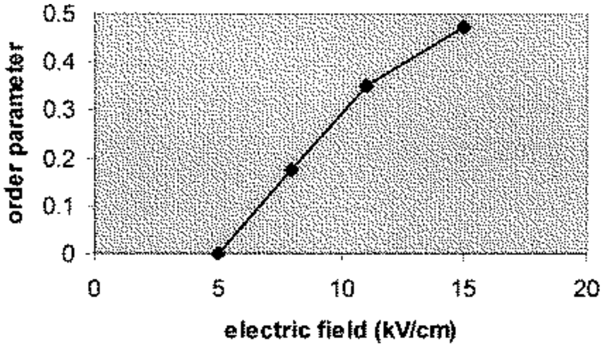
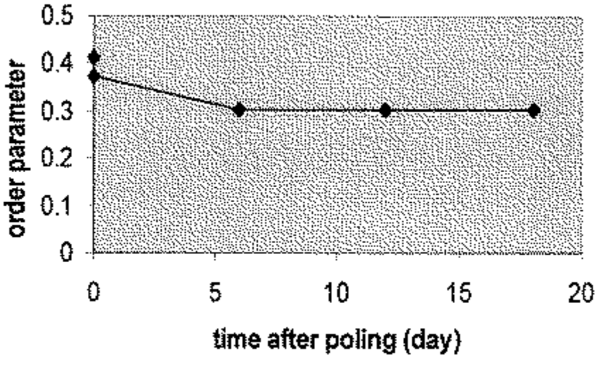


Figure 2 UV-visible spectra of HP6 films. a. before poling b. after poling
poling conditions: 11kV, 356 K, 30 min.

Table I is the order parameter of the films poled at different temperatures. It can be seen that the order parameter is the lowest when the film was poled in its isotropic states, while ϕ had the same value either it was poled in amorphouse or in liquid crystalline states. As we know that for ordinary materilas, the higher the poling temperature, the lower the ϕ value. Our results showed that the order parameter was relative high although it was poled at 383 K. This might be due to the self-assembly property of the mesogens.





Figurc3 Plot of order parameter of the poled films versus electric field (383K, 30 min.)

Figure 4 Plot of order parameters of HP6 films versus time (15 kV, 358K 30 min.)

Table I Order parameter of the oriented HP6 films poled at different temperatures (10 kV, 20min.)

T(K)	360	383	420
ϕ	0.36	0.36	0.09

Figure 3 shows the plot of order parameter of the HP6 film versus poling electric field. As can be seen that the order parameter increased linearly with the increased of poling field.

Temporal stability of the poled polymer film at room temperature are given in Figure 4. As can be found that the order parameter decreased largely from 0.414 to 0.374 when it was held for two hours at room temperature after poling, it changed to 0.302 after being held for 6 days at room temperature and then ϕ remained almost unchanged within 6 months. The above results showed that the poled polymer films exhibited good stability at room temperature.

Some further measurement and modification of the polymer by crosslinking to increase its stability are in progress.

Conclusion

The orientational behavior of the nematic side chain liquid crystalline polyacrylate with para-nitroazobenzene mesogens under corona poling was studied by UV-visible spectroscopy. The results showed that the mesogens could be aligned by poling and showed good stability at room temperature.

Acknowledgement

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References

1. Prasad P, Williams D(1991) Nonlinear Optical Effects in Molecules and Polymers, John Wiley and Sons, New York.
2. Zyss J(1987), Molecular Nonlinear Optics, Materials, Physics and Devices, Academic Press, Orlando, FL, P1994.
3. Dalton L R, Harper A W, Ghosn F, Steier W H, Ziari M, Fetterman H, Shi Y, Mustacich R V, Ten A K Y, Shea K J (1995) Chem Mater **7**: 1060
4. Dalton L R, Harper A W, Wu B, Ghosn R, Laquindanum J, Liang Z, Hubbel A, Xu C (1995) Chem Mater **7**: 519
5. Meredith G R, VanDusen J G, Williams D J(1982), Macromolecules **15**: 1385
6. Xie S, Natansohn, Rochon P (1993) Chem Mater **5**: 403
7. Li M, Zhou E, Xu J, Yang C, Tang X (1995) Polym Bull **35**: 65
8. Mortazavi M, knoesen A, Kowel S, Higgins B, Dienes A (1989) J Opt Soc Am B **6**: 733