Aligning Polymer Main Chain by Pendent Chromophore Alignment: Optical and Electrical Methods

Tong Kun Lim,* Seung Ho Hong, Mi Yun Jeong, and Geon Joon Lee†

Department of Physics, Korea University, Seoul 136-701, Korea

Jung-Il Jin* and Hyung Yun Oh

Department of Chemistry and Center for Electro- and Photo-Responsive Molecules, Korea University, Seoul 136-701, Korea

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ABSTRACT: We have studied whether the main chain can be aligned by alignment of attached chromophores using two types of polymethacrylates carrying side-on attached and end-on attached chromophores. To align chromophores, nonpolar alignment by optical pumping and polar alignment by the corona poling method were used. To verify the alignment of the polymer main chain, we measured infrared wave absorption for the characteristic vibration mode. The photoalignment of side-on attached chromophore gave better aligning of the main chains. The degree of photoalignment of main chains depended on the main chain conformation as well as on the temperature at which samples were aligned. The degrees of alignment for main chains and that for the chromophores show maximum values at a temperature a little lower than the glass transition temperature. We could understand these behaviors with the free volume concept. Also, the degree of alignment for the side-on type was 2 times larger than that for the end-on type. This shows that, in the solid solution, cooperative interaction between polymer main chains and chromophores increases the rigidity and alignment of the polymer main chain. For the end-on attached chromophore, the alignments of chromophores and polymer main chains by corona poling were similar to those by optical pumping. But for the side-on attached chromophore, optical pumping was more efficient compared to the corona poling.

Introduction

Organic materials have been spotlighted as promising candidates for a wide variety of applications such as polarization holography, optical memory, integrated optical circuit, optical modulator, optical parametric oscillation, nonlinear optical generator, and surface treatment of liquid crystal display cell, etc.[1,2] However, for the realistic application, these materials have some problems in the temporal stability of aligned samples. Particularly, the aligned elements such as chromophore as well as the main chain relax back to random orientations through thermal relaxation. A lot of efforts in the field of physics and chemistry have been made toward the improvement of the drawbacks of these materials.[3−7] Not only for the application but also for understanding of the mechanism of aging process, these materials have attracted much interest. For further understanding of this problem, dynamics of the aligning processes of the polymer main chain as well as the chromophore was studied using the second harmonic generation,[8,9] electrooptical effect,[10] and photoisomerization kinetics.[11] However, these methods have been investigated by probing the dynamics of chromophores only, and the movement of the main chain could only be conjectured from the motion of chromophores.

The possibility of aligning the polymer main chain is very important for a better understanding of the characteristics of the samples. If we can align the main chain somehow, we can expect better thermal stability of the aligned sample in addition to a better ordering of the chromophore units (either side-on or end-on type) attached to the main chain. The alignment of the main chain in some direction will give strong anisotropy in the sample, which can also be utilized for the alignment of liquid crystal molecules on the surface of the sample.[12] The higher the anisotropy of the sample, the larger the anchoring energy of the liquid crystal molecules on its surface will become. It also is expected to give greater second-order nonlinear optical properties because the chromphores or other type of nonlinear optical units attached to the ordered main chains will have a higher degree of ordering. Also, the thermal stability of the sample will be improved since the orientational relaxation of the ordered main chain will be much slower when compared to that of the chromophores. Sekkat et al.[3−6] studied the effect of the glass transition temperature and the polymer molecular structure on the light-induced molecular movement for the case of end-on type attached chromophores. Although they addressed the correlation of the orientation of the polymer main chain to that of the chromophore after photo- or electro-orientation, they have not directly differentiated orientation of the main chain from that of attached chromophores. Moreover, they did not quantitatively show the influence of the orientational movement of chromophores on that of the main chain.

We believed that aligning the chromophores attached to the main chain would lead to an alignment of the polymer main chain itself. Therefore, this research was aimed at a study of the effect of chromophore alignment on the orientation of the polymer main chain, not only for the case of the main chain carrying end-on attached chromophores (Figure 1b) but also for the case of the

* Authors for correspondence. E-mails: tongklim@kuccnx.korea.ac.kr, jijin@kuccnx.korea.ac.kr.

† Present address: the Research Institute of Basic Science, Korea University, Seoul 136-701, Korea.

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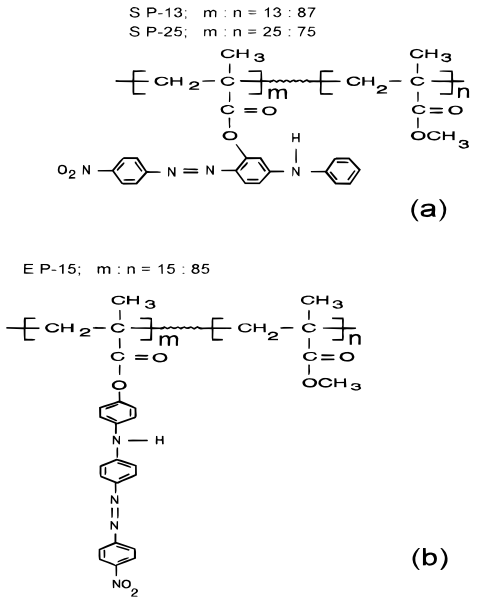

Figure 1. Structure of polymethacrylates carrying side-on attached chromophores (a) and end-on attached chromophores (b).

main chain carrying side-on attached chromophores (Figure 1a). We have used optical pumping as well as corona poling methods to align the chromophores. We used infrared (IR) absorption spectroscopy to investigate the alignment of the main chain as well as UV absorption spectroscopy to measure the orientation of the chromophore. We investigated whether there is some locomotive force that aligns the main chain when we try to align the chromophores attached to the main chain in both side-on and end-on types.

Experimental Section

Sample Preparation. Two types of polymethacrylates carrying side-on attached and end-on attached chromophores were prepared for this experiment (Figure 1).[13] It has been known[14] that the main chain becomes rather rigid when the chromophores are side-on attached. In the polymethacrylates carrying side-on attached chromophore (SP), the middle (2-hydroxy) part of the chromophore unit (2-hydroxy-4-(phenylamino)-4′-nitroazobenzene) is attached to the ester group of poly(methyl methacrylate). Two side-on type copolymers consisting of the chromophore−methacrylate and methyl methacrylate monomers were made with the chromophore content of 13 mol % (SP-13) and 25 mol % (SP-25). In the polymethacrylate carrying end-on attached chromophore (EP), the end (4-hydroxyphenyl) part of the chromophore (4-(4-hydroxyphenyl)amino-4′-nitroazobenzene) is attached to the methyl methacrylate unit. An end-on type copolymer consisting of chromophore−methacrylate and methyl methacrylate was made to contain the chromophore of 15 mol % (EP-15). The average molecular weights of these copolymers were measured to be 3800 (SP-13), 2400 (SP-25), and 27 000 (EP-15),[13] and the glass transition temperatures of these films are 117 °C (SP-13), 120 °C (SP-25), and 138 °C (EP-15), respectively. In the preparation of the films, chlorobenzene was employed as solvent for the side-on polymers and cyclopentanone for the end-on polymer. The solution was filtered using a 0.2 μm Teflon filter and then spin-coated on the plates of CaF_2 and sapphire (500 rpm, 50 s). These plates allow spectroscopic measurement of infrared region (1400−2000 cm^{-1}). These films were dried at room temperature for 12 h and then at 100 °C for 5 h under vacuum.

Photoisomerization of Attached Chromophore. To align the main chains by photoisomerization of attached chromophores, we used polarized light whose wavelength lies within the absorptive wavelength region of the original samples containing the *trans* azo groups (Figure 2). This pump light can reorientate the *trans* azo groups in the chromophores via *trans*−*cis* photoisomerization. The initially isotropically, randomly orientated *trans* chromophores are rearranged in a plane perpendicular to the direction of polarization for linearly polarized light.[15] Meanwhile, it was reported that a circularly polarized pump light forces *trans* molecules to be aligned along the propagation direction of the pump beam.[16] In our experiment, the wavelength of pump beam was 488 nm and its intensity was 300 mW/cm^2. To find the optimum condition for the alignment of main chain by pumping chromophores with the polarized light, we have performed the sample alignment at various temperatures. Samples were illuminated with polarized pump beam for 5 h at four different temperatures from 30 to 120 °C.

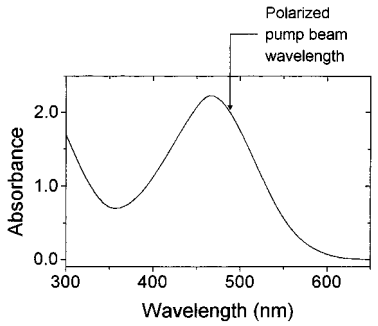

Figure 2. UV−vis absorption spectrum of the side-on polymer. The absorption spectrum of the end-on polymer is similar to that of the side-on polymer.

Corona Poling. For the electrical alignment of the chromophores, we used the corona poling method.[17] The poling voltage of 4.3 kV was applied evenly on the sample films at 90 °C for 5 h. The distance between the tungsten tip and ITO electrode was 1.5 cm.

Measurement of the Degree of Alignment of Main Chain and Chromophores. To investigate whether main chains are aligned through interaction with photoexcited chromophores, we have measured the infrared absorption spectra before and after pumping of polarized light. The FTIR spectrum was taken at room temperature after the sample was poled for 5 h followed by aging for 5 h at room temperature, which was enough for a sample to relax into thermal equilibrium. During this relaxation, the sample was kept in dark condition. The IR measurements were performed at room temperature. The degrees of alignment of main chains and chromophores were calculated from the infrared absorption change for the characteristic vibration modes. We relied our analyses on the "C=O" stretching vibration mode at 1730 cm^{-1} for the main chain and the aromatic "C=C" stretching vibration mode of para-substituted benzene rings at 1589 cm^{-1} for chromophores.

Results and Discussion

Alignment of Main Chain by Photoisomerization of Attached Chromophores. Figure 3a shows the ratio of the infrared transmission ($T_{\parallel}$) of parallely polarized wave to that ($T_{\perp}$) of perpendicularly polarized wave measured before illumination of pump light. Here, a parallel or perpendicular direction is referenced to the aligned direction of main chains when pumped by the light. As expected, unilluminated samples do not have particular peaks at 1730 and 1589 cm^{-1}. This shows that the orientational distribution of main chains as well as that of chromophores is isotropic. Figure 3b represents the infrared transmission ratio 5 h after pumping by linearly polarized light. The infrared transmission ratio spectra of the illuminated samples show two peaks; one corresponds to the characteristic vibration mode of main chain and the other to that of chromophore. The

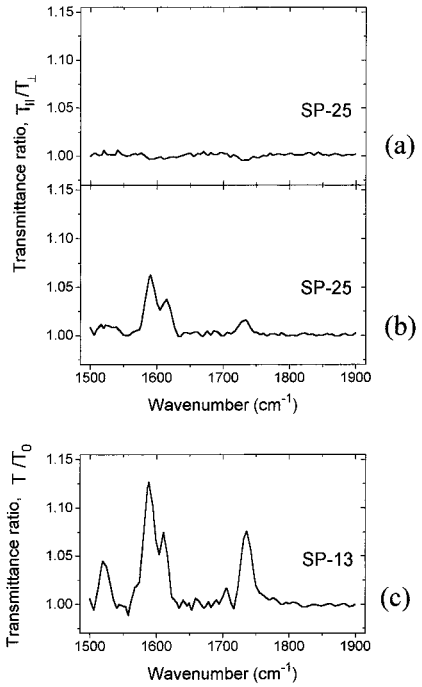

Figure 3. Infrared transmission ratio spectra before (a) and after (b) illumination of linearly polarized light. Also, (c) shows the infrared transmission ratio spectrum after illumination of circularly polarized light.

appearance of the two peaks in Figure 3b implies that the average orientation of the aromatic rings in the chromophore and that of the main chain is more or less parallel. The fact that the IR transmission ratio ($T_{\parallel}/T_{\perp}$) at 1589 cm^{-1} is greater than unity was related to the UV transmission change that was induced from pumping of linearly polarized light.[15,16] That is, *trans* chromophores absorb only the light polarized parallel to the molecular axis of chromophore. Figure 3c shows the ratio of the infrared transmission (T_0) before illumination to that (T) 5 h after illumination of circularly polarized light. The infrared transmission ratio spectra of the illuminated samples show three peaks at 1730, 1589, and 1525 cm^{-1}. Two peaks at 1730 and 1589 cm^{-1} correspond to the characteristic vibration mode of the main chain and chromophore. The additional peak at 1525 cm^{-1} corresponds the "NO_2" stretching vibration mode in the chromophore. These indicate again that the main chain as well as chromophores can be aligned by polarized pump light.

Figure 4a,b compares the degree of alignment of the main chain and chromophores vs the temperature at which samples were aligned. The degrees of alignment for the main chain and chromophores were estimated from infrared transmission ratios of the characteristic vibration modes by using the relation showing the IR extinction coefficient difference, $\Delta\alpha = 1/(\text{depth}) \times \ln(\text{transmission ratio})$. As the temperature is increased from room temperature toward the glass transition temperature, the degrees of alignment of main chains as well as chromophores are increased. This behavior can be explained with the free volume concept. It is expected that, as the temperature is increased, in addition to enhanced thermal mobility of structural components, free volume surrounding the chromophore is increased, and then the main chain as well as the chromophores can be more easily aligned due to reduction of steric hindrance. The degree of maximum alignment of polymer main chain for the side-on type is twice

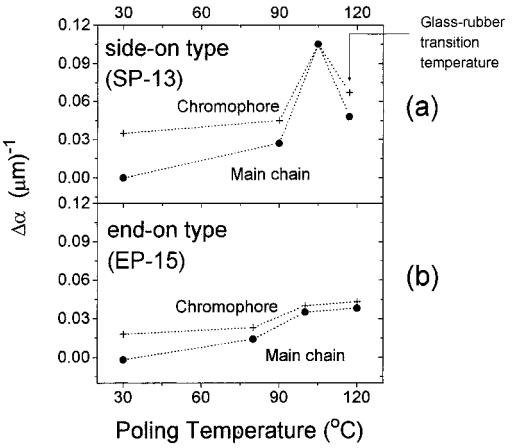

Figure 4. Temperature dependence of infrared absorption changes before and after poling with polarized light: (a) side-on polymer (T_g = 117 °C), (b) end-on polymer (T_g = 138 °C). Symbols ● and + are for the characteristic vibration modes of main chain and chromophore, respectively.

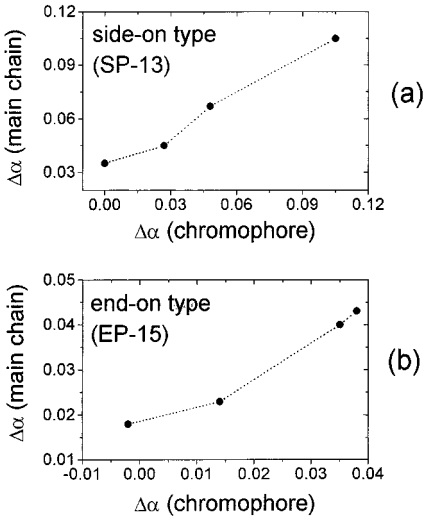

Figure 5. Main chain alignment as a function of chromophore alignment for optical pumping: (a) side-on polymer, (b) end-on polymer.

that of the end-on type (Figure 4a,b). This can be attributed to the difference of the main chain conformation in the two types of copolymers. The main chain of side-on polymers has a tendency to take a rodlike shape through the interaction with the aligned chromophores. This will lead to a higher optical anisotropy when compared to that of end-on type. This is why we attain a higher macroscopic anisotropy when the side-on polymers are photoaligned. Meanwhile, near the glass transition temperature, the degree of alignment for the main chain is decreased with an increase of temperature (Figure 4a). This can be ascribed to the fact that the thermal orientational fluctuation of main chains is large enough to override their alignments by chromophore alignment. In both cases the main chains align to some degree when the chromophores are aligned. Figure 5 clearly demonstrates that photoalignment of chromophores leads to main chain alignment, suggesting that, in the solid solution, there are cooperative interactions between polymer main chains and chromophores.

Alignment of Main Chain by Corona Poling. To study further the alignment of main chain of the present polymers, we investigated whether the main chain and chromophore can be aligned also by electrical poling.

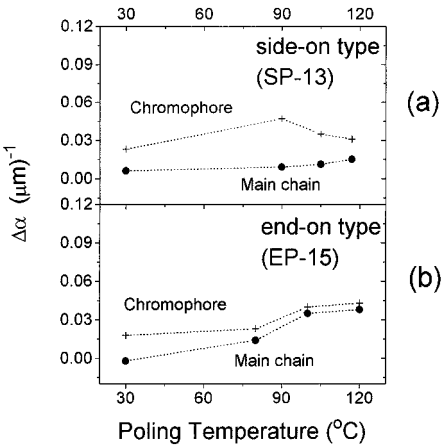

Figure 6. Temperature dependences of infrared absorption changes before and after corona poling: (a) side-on polymer, (b) end-on polymer.

Figure 6 shows poling-temperature dependency of infrared absorption changes before and after corona poling. For the end-on attached chromophore, the alignments of main chains and chromophores by corona poling are similar to those by optical pumping. But corona poling of the side-on type shows poorer alignment of the main chain when compared to that by optical pumping. The maximum value of main chain alignment by corona poling is about half of that by optical pumping. This implies that corona poling is not as efficient as optical pumping for main chain alignment of polymethacrylates carrying side-on attached chromophores.

Conclusions

For the first time, we could clearly demonstrate that alignment of the polymer main chain can be induced by alignment of attached chromophores for two types of polymethacrylates: one carrying side-on attached and the other end-on attached chromophores. Nonpolar alignment by optical pumping and polar alignment by corona poling were used for alignment of chromophores. Infrared absorption spectroscopy was used to measure the degree of alignment of the main chain. It is found that, for both types of polymers, alignment of the main chain could be induced by chromophore alignment: For the side-on type, the optical pumping was more efficient than electrical poling, but for the end-on type, the main chain alignment by optical pumping was comparable to that by electrical poling.

It was observed that the degree of alignment of the polymer main chain depends on the temperature at which samples were aligned. The degrees of alignment for main chains as well as chromophores show maximum values at a temperature a little lower than the glass transition temperature. These behaviors could be explained with the free volume concept.

We have found that attaching a chromophore to the main chain by side-on or end-on types results in different alignments of the polymer main chain. The degree of alignment of the polymer main chain for the side-on type is twice that of the end-on type. This is thought to be attributed to the fact that main chains in polymethacrylate carrying side-on attached chromophores prefer a rodlike conformation due to dipole−dipole interactions between the structural constituents, and this main chain conformation influences the alignment of polymer main chains and chromophores.

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