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Suppression Effect and Coupled Two-Time Motion of the Photoisomerization in the Crosslinking Polymer System

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The photoisomerization of the crosslinked and uncrosslinked polymer-pair with azo linkages was studied by the photoinduced birefringence. The photoisomerization of azo chromophores could be controlled by crosslinking process. The inducement of birefringence in crosslinked system indicates that the photoisomerization of chromophore rearranges the orientation not only of the chromophore itself but also of polymer main chain. From the data analysis by biexponential function, it is found that there are two characteristic time scales in the photoisomerization process and they exhibit a coupled relation.

Keywords: suppression effect; crosslinked polymer; coupled relation

INTRODUCTION

In these ten years the organic polymeric materials have been heavily investigated for the potential application to nonlinear optical devices and especially polymer films containing azo dyes are considered as very promising materials for optical information storage, light switching and nonlinear devices, and liquid crystal alignment. The incorporation of a

photochromic moiety in polymers is a very attractive molecular design option due to the possibility of creating new light-sensitive materials. Even though it is known that the nature and morphology of a polymer influence both photo- and thermochroism of a chromophore in a given polymer matrix, no complete theory exists to explain how a photochromic process is linked to polymer properties. In this work, we investigate the kinetics of photoisomerization for the uncrosslinked polymer system and crosslinked polymer system.

EXPERIMENT

We employed two newly-synthesized polymer structures of the polymer-pair[1], poly [(methyl methacrylate) -co- { 4'[N -(2 - methacryoxyethyl) – N - methyl] – 2 – carboxy – 4 - nitroazobenzene}] (P(MMA-co-MMCN)(0.7:0.3)) with chromophores and Poly [(methylmetacrylate) – co - (2 -isopropenyl-2-oxazoline)] (P(MMA-co-IPO) (0.5:0.5)) without chromophores, which can be crosslinked together thermally[1]. To prepare thin films, two polymers were blended by 1:4 weight ratio and dissolved in cyclopenthanone at 10 weight %. The randomly crosslinked polymer films were prepared by keeping at 160 °C for one hour(confirmed by DSC measurement). As an optical pumping light source and probe light source, 488 nm wave and 633 nm wave were employed, respectively.

EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 1 shows the photoinduced transmittance of the crosslinked(Tg=160 °C) and uncrosslinked(Tg=120 °C) samples at several pumping powers of 488 nm beam, where the change of transmittance ratio means the degree of rearrangement of chromophores and polymer main chain[2]. Uncrosslinked chromophores show a very large difference varying pumping power. On the other hand, that of the randomly crosslinked sample increased slightly and changed a little varying power. When the photoisomerization of crosslinked azo linkage happens, it must be accompanied by the reorientation of the polymer main chain. The result of Fig. 2 gives an obvious fact that the crosslinking of chromophores to polymer main chain would suppress not

only the motion of chromophores but also the ''photoisomerization" of the completely crosslinked chromophores. All the data were fit to the

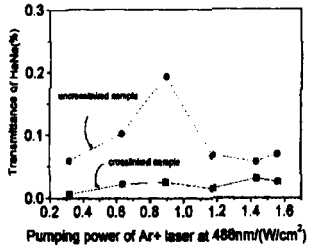

Figure 1. The photoinduced transmittance change of the crosslinked and uncrosslinked samples.

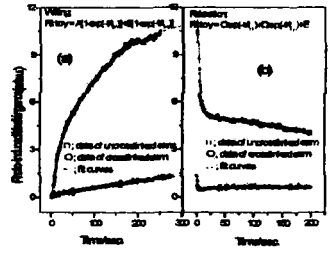

Figure 2. The experimental results and fit curves of photoinduced birefringence at the power of 0.89W.

Biexponential function of $Y=A*[1-\exp(-t/t_{w\text{-}f})]+ B*[1-\exp(-t/t_{w\text{-}s})]$ and $Y=C*\exp(-t/t_{r\text{-}f})+ D*\exp(-t/t_{r\text{-}s})+E$ for the writing process and the relaxation process, respectively[Fig. 2]. Fig. 3 and Fig. 4 show that there are two time constants of the writing and relaxation dynamics of the uncrosslinked and the crosslinked polymer systems at the various laser pumping powers. The fast time mode mainly results from the photoisomerization of the azo linkage and the slow time mode results from the reorientation of the azo linkage and polymer main chain hich is induced by the photoisomerization of azo linkage. In the writing process crosslinked the polymer system takes much longer time to achieve saturation(Fig. 2). The photoisomerization of the crosslinked system needs much larger volume than uncrosslinked polymer system and main chain will suppress the photoisomerization of azo linkage. And the quantum yield for the photoisomerization decreases when bulkier substituents are introduced on the azobenzene. In our case the crosslinked polymer is much bulkier than the uncrosslinked polymer system[1]. In the relaxation process, the greater elastic restoring force which was accumulated in the writing process of the

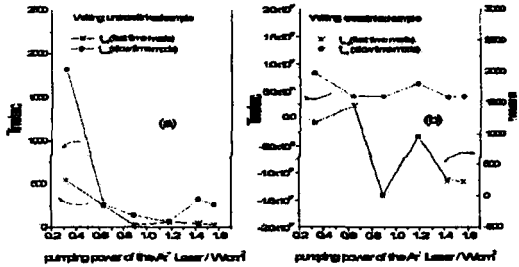

Figure 3. Two time modes in the writing process.

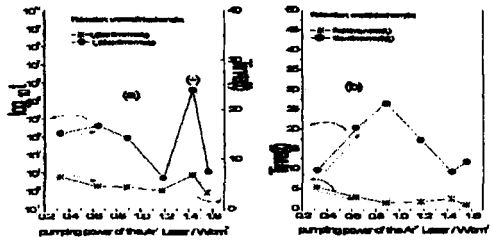

Figure 4. Two time modes in the relaxation process.

polymer main chain will act on the reorientation of trans-cis-trans of the crosslinked polymer system, since both ends of azo linkage were bonded to polymer main chain. Crosslinked azo linkage motion is strongly coupled to polymer main chain. We found that in the relaxation process (Fig. 4), if the fast mode becomes faster the slow mode becomes slower, and vice versa with laser power changing in both crosslinked and uncrosslinked systems.

Acknowledgement

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