to consider that the change of $a_{^{13}\mathrm{C}}$ is mainly due to the variation of the spin density rather than of the polar and geometric effects.

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Topochemical Photodimerization in Polymer Liquid Crystals

A topochemical reaction was first demonstrated by Schmidt and co-workers for crystals of cinnamic acid derivatives.[2] The C═C bonds adjacent to the carbonyl group in these compounds dimerize to give cyclobutane rings on photoirradiation with ~300-nm light. The efficiency of the photodimerization was strongly dependent on the structure of crystal forms. In addition, the mode of addition was also influenced by the crystal forms (head-to-head, head-to-tail, and so forth). The idea of topochemical reactions was later developed and applied to photopolymerization by Hasegawa.[3]

If such a topochemical reaction could be applied to polymer systems, two-dimensional reinforced polymer materials might be obtained. For two-dimensional strengthening, biaxial orientation is a possible approach, although it cannot provide polymer materials with ultimate reinforcement. Several attempts have been reported regarding the concept of introducing interpolymer bonding after orientation of the reactive chromophores.[4,5] Bimolecular reaction under restricted molecular motion is a contradicting requirement. Topochemical photoreaction in polymer liquid crystals may allow the formation of two-dimensional reinforced polymer materials.

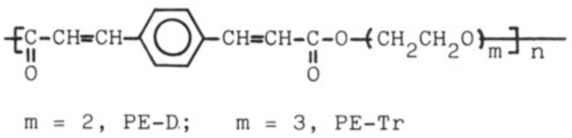

Figure 1. Structure and abbreviations of polyesters used in this study.

In Figure 1 the structure of polymers used in this study as well as their abbreviations is shown. *p*-Phenylenediacrylic acid (PDA) and its ethyl ester were synthesized by the method reported previously.[6] Number-averaged molecular weights (M_n) of PE-D and PE-Tr were determined as 7000 (PE-D) and 7200 (PE-Tr) by gel permeation chromatography (GPC) calibrated with standard polystyrene samples. In order to explore the effect of M_n on the photochemical reactivity, the samples of PE-D and PE-Tr were subjected to fractionation by a preparative GPC using chloroform as eluent.

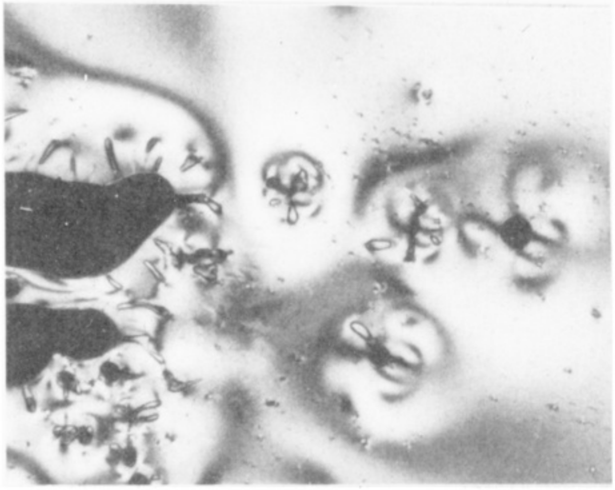

Figure 2. Photograph of texture observed for PE-D under crossed polarizers at 50 °C.

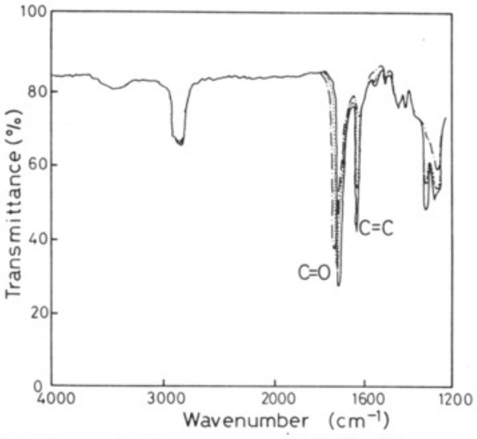

Figure 3. Change in IR spectrum of PE-Tr film on photoirradiation. λ_{ex} = 313 nm: (—) before irradiation; (···) 5 min of irradiation; (–·–) 100 min of irradiation.

Figure 2 shows a typical example of the texture of a polymer film of PE-D observed on a polarizing microscope through a pair of crossed polarizers. The temperature of the sample was controlled within ±0.1 °C with the aid of a Mettler hot stage (FP-80 and FP-82). The texture seen was very similar to that of the schlieren phase, so that PE-D is considered to form a nematic phase. The schlieren-like texture was also observed in the polymer film of PE-Tr, indicating that PE-Tr also forms a nematic phase. Differential scanning calorimetry (DSC) showed that both PE-D and PE-Tr exhibited two endothermic events which corresponded to the glass transition of the polymers (T_g) and to the liquid crystal to isotropic phase transitions (T_{NI}). T_g and T_{NI} of the unfractionated polymers (UF) were T_g = 30 (PE-D) and 14 °C (PE-Tr) and T_{NI} = 87 (PE-D) and 122 °C (PE-Tr). It seems quite reasonable that T_g of PE-Tr is lower than that of PE-D since PE-Tr possessed longer flexible spacers between PDA moieties in the main chain. The higher T_{NI} of PE-Tr may be attributed to the odd-numbered units of spacers between the PDA moieties (odd–even effect).[7]

Unlike low molecular weight liquid crystals, annealing of the polymer films was essential to obtain reproducible results. The polymer films were prepared by casting the polymer solution in chloroform onto glass plates and by evaporating the solvent under reduced pressure. After drying completely, the films were subjected to aging in a thermostat at 70 °C for 5 h. By this procedure, the polymer films always exhibited the same texture as seen

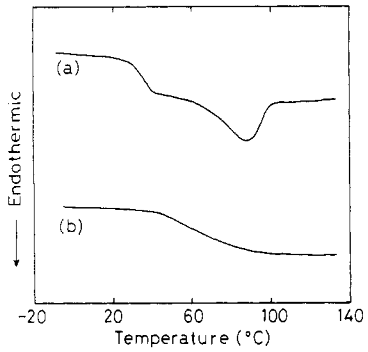

Figure 4. DSC thermograms of PE-D film before and after photoirradiation: (a) before irradiation; (b) after irradiation at 313 nm for 5 h.

in the polarizing microscope.

Change in IR spectra of the PE-Tr film on photoirradiation with a monochromatic light of 313 nm is shown in Figure 3. Photoirradiation was performed in air at 35 °C, where PE-Tr exhibited liquid crystal (LC) phase behavior. Before irradiation, a peak at 1710 cm^{-1}, assigned to C=O stretching mode, and a peak at 1635 cm^{-1} assigned to C=C stretching mode, were clearly observed. After irradiation, the peak intensity at 1635 cm^{-1} decreased, and the peak due to the C=O stretching mode was shifted to higher wavenumbers. After 100 min of irradiation, the C=O stretching peak was shifted to 1720 cm^{-1}, and the peak at 1635 cm^{-1} almost disappeared. This means that the C=C bonds in PE-Tr react on photoirradiation.

Solid-state ^{13}C NMR (^{13}C CP/MAS) spectra of the irradiated samples of PE-Tr were also measured. A peak at 165 ppm which could be assigned to the C=C bond disappeared after 5 h of irradiation, and two new peaks were observed around 0 and 50 ppm, which could be assigned to cyclobutane ring formed on photoirradiation. This result as well as the result obtained by IR spectroscopy clearly indicates that the C=C bonds in the PDA moieties of the polyesters photodimerize to give cyclobutane units as in the case of cinnamic acid derivatives with low molecular weight.[3,6] Since the PDA moieties are present in the main chain of the polymers, the cyclobutane formation between the PDA moieties of different polymer chains leads to cross-linking between the polymer chains. Support of this view was provided by other experimental results. Both PE-D and PE-Tr were very soluble in chloroform regardless of M_n before photoirradiation. However, after 5 min of photoirradiation of the polymer films, the polymers became completely insoluble in chloroform. This indicates occurrence of cross-linking between the polymer chains. Further support for the occurrence of the cross-linking was obtained from DSC measurements of the irradiated polymer films. Figure 4 shows DSC thermograms of the PE-D films before and after photoirradiation. As described above, two endothermic processes were seen before photoirradiation. However, the irradiated sample exhibited only one endothermic process which corresponds to the glass transition. It is clear that T_g of the irradiated sample is shifted to a higher temperature indicative of cross-linking and that the N → I phase transition disappeared.

A remarkably large temperature dependence of the photochemical reactivity was observed for both PE-D and PE-Tr, and the results are shown in Figure 5. The photochemical reactivity was evaluated by measuring the decrease in absorbance at 1635 cm^{-1} (A_{1635}) relative to the absorbance at 2950 cm^{-1} (A_{2950}) which remained unchanged on photoreaction. In Figure 5 the relative photochemical reactivity, $1 - (A_t/A_0)$, is plotted as a function of temperature in the case of PE-D, where $A_t = A_{1635}/A_{2950}$ at $t = 5$ min and A_0 is A_t at $t = 0$. Figure 5 also shows the effect of M_n on the photoreactivity where two fractionated samples of PE-D with $M_n = 14000$ (HMW) and 2600 (LMW) were examined on their reactivity at various temperatures. The most prominent feature seen in the figure is that the photoreactivity is higher in the temperature range where PE-D exhibited the LC phase ($T_g < T < T_{NI}$). In the LC phase, the PDA chromophores are expected to be aligned in one direction and the mobility of the PDA chromophores is high enough to enable them to approach each other so as to attain the appropriate orientation for topochemical reaction. Below T_g, segmental mobility is frozen in, so photoreactivity is quite low. Above T_{NI}, while the segmental mobility is high, orientation of the PDA chromophores is random, as in the case of isotropic solution, and overall reactivity is lower than that in the LC phase.

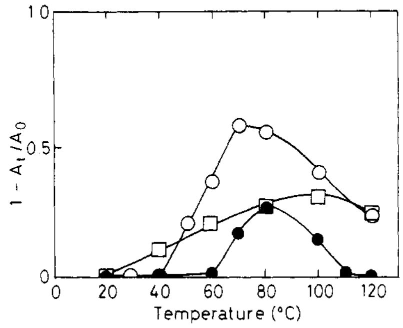

Figure 5. Temperature dependence of topochemical photodimerization in PE-D: (●) HMW; (□) LMW; (○) UF.

Another interesting feature is the effect of molecular weight. The temperature effect on the photoreactivity is sharper in HMW than in LMW; however, the reactivity is highest over nearly the whole temperature range for the unfractionated sample (UF). A similar temperature profile was also obtained for PE-Tr. As described previously, the photoreactivity is affected by orientation as well as by mobility of the chromophores. In HMW, orientation may be favored while mobility is restricted. On the other hand, in LMW the regular orientation may not be achieved as with HMW, but the mobility is much favored. The unfractionated sample possesses both fractions which may contribute in a complementary manner to the higher reactivity observed.

Registry No. PE-D (copolymer), 117371-38-7; PE-D (SRU), 117371-39-8; PE-Tr (copolymer), 99763-73-2; PE-Tr (SRU), 99763-64-1.

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