

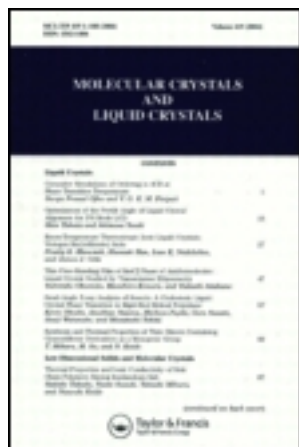
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Photoswitching Properties of Polyacetylene Derivatives with a Photoinduced Azobenzene Moiety in the Side Group

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Photoswitching Properties of Polyacetylene Derivatives with a Photoinduced Azobenzene Moiety in the Side Group

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We report on the photoswitching properties of novel mono-substituted polyacetylene derivatives with various azobenzene moieties that are photochemically reactive in the side group. Polymerization of the polyacetylene derivatives were carried out with Ziegler-Natta, metathesis, and Rh complex catalysts. When exposed with 350 nm UV or 450 nm visible monochromatic light, the azobenzene side groups in the polyacetylene derivatives undergo *trans*→*cis* reversible photoisomerization process. The photoisomerization rate of polyacetylene derivatives having a long alkyl chain in the azobenzene terminal group was more effective due to the providing of enough intermolecular free volume.

Keywords : polyacetylene derivatives; Rh complex catalyst; azobenzene; photoswitching; photoisomerization

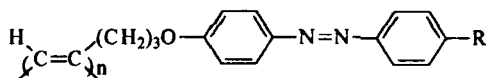
INTRODUCTION

Azobenzene compound is characterized by reversible transformation from more stable *trans* form to the less stable *cis* form upon irradiation with UV or visible light. Thus, polymers with an azobenzene moiety in the side chain have been widely investigated to use as a photoswitching device^[1].

In the previous work, we have reported on the synthesis of polyacetylene derivatives, Poly[5-(4'-alkyl)phenylazo]phenoxy-1-pentyne (i.e. PABR03A, where AB, R, 0, 3, and A represent azobenzene mesogenic

moiety, number of carbon in an alkyl group attached to the azobenzene group, ether linkage, number of methylenic unit in the spacer between azobenzene and acetylenic group, terminal acetylene, respectively and the first P means polymer) as shown in SCHEME 1, and their basic photoresponsive characteristics^[2].

In the present study, we report on the synthesis and properties of polyacetylene derivatives with a cyano(nitrile) or methoxy group in the azobenzene terminal moiety. Especially, we discuss in detail the photochemically and thermally induced reaction kinetics according to the species of azobenzene terminal moiety.



R = H, PAB003A

R = n-pentyl, PAB503A

R = cyano, PABC03A

R = methoxy, PABM03A

SCHEME 1. Polyacetylene derivatives

EXPERIMENTAL

Synthesis of monomers having cyano and methoxy groups in the azobenzene terminal moiety was carried out by the synthetic route of AB003A monomer reported previously. ABR03A(R=H, pentyl, cyano, and methoxy) monomers were polymerized by Ziegler-Natta($\text{Fe}(\text{acac})_3\text{-AlEt}_3$, acac=acetylacetonate), metathesis($\text{MoCl}_5\text{-Ph}_4\text{Sn}$, $\text{WCl}_5\text{-Ph}_4\text{Sn}$), and Rh complex($[\text{Rh}(\text{NBD})\text{Cl}]_2\text{-Et}_3\text{N}$, NBD=norbornadene) and its results are summarized in TABLE I.

The molecular weight and structure of these polymers and monomers were investigated by GPC, FT-IR, ^1H , ^{13}C -NMR, and UV-Visible spectroscopic measurements. The photoresponsive characteristics due to the irradiation of UV(350 nm) or Visible(450 nm) monochromatic light with a 450 W Xenon lamp were studied by UV-Visible spectroscopic measurement in toluene solution.

TABLE 1. Polymerization of ABR03A by Ziegler-Natta, metathesis, and Rh complex catalysts.

| Polymer | Catalyst ^a | Solvent | Yield(%) | M_n | M_w | M_w/M_n |
|---------|-----------------------|------------|----------|-------------------|-------------------|-----------|
| PAB003A | Fe | Toluene | 44 | 8.2×10^3 | 4.2×10^3 | 51.2 |
| PAB503A | Fe | Toluene | 41 | 1.2×10^3 | 1.6×10^6 | 133.3 |
| PAB003A | Mo | Toluene | trace | - | - | - |
| PAB003A | W | Toluene | trace | - | - | - |
| PAB003A | Rh | Chloroform | 90 | 9.0×10^3 | 3.0×10^4 | 3.3 |
| PAB503A | Rh | Chloroform | 90 | 1.3×10^3 | 3.5×10^4 | 2.7 |
| PABC03A | Rh | Chloroform | 22 | 5.1×10^3 | 1.3×10^4 | 2.6 |
| PABM03A | Rh | Chloroform | 85 | 3.8×10^3 | 1.4×10^4 | 3.8 |

^a Fe-Fe(acac)₃-AlEt₃, Mo-MoCl₅-Ph₃Sn, W-WCl₆-Ph₃Sn, and Rh-[Rh(NBD)Cl]₂-Et₃N
 Polymerized for 6 hours at room temperature. [monomer]/[catalyst]=50, [catalyst]=0.01 mole/L

RESULTS AND DISCUSSION

The reversible photoisomerization of monomers and polymers was investigated by UV-Visible measurements. The absorption intensity of trans isomer is dramatically decreased due to the irradiation of 350 nm monochromatic light, while that of cis isomer is slowly increased. When a 450 nm visible light is illuminated, a reversible isomerization from cis to trans form is observed. The trans-cis photoisomerization rate of polyacetylene derivatives was obtained from the UV-Visible spectra characterized by maximum absorption peak of trans isomer at 337 nm and a

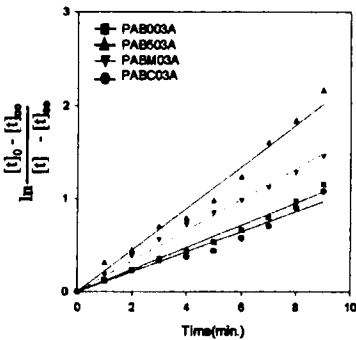


FIGURE 1. plots for the trans→cis photoisomerization kinetics of PABR03A.

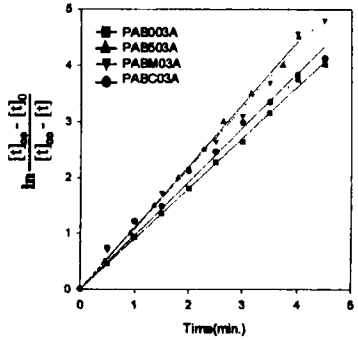


FIGURE 2. Plots for the cis→trans photoisomerization kinetics of PABR03A.

broad absorption peak of *cis* isomer at 430 nm.

The plots for *trans*→*cis* photoisomerization of PABR03A(R=H, pentyl, methoxy, and cyano group) are shown in FIGURE 1. The reaction of all polymers proceeds in the first order in toluene solution. The difference in slopes is mainly due to the difference in intermolecular free volume between polymer backbones necessary for the reaction occurring according to the molecular species of azobenzene terminal moiety. On the other hand, the rate of *cis*→*trans* isomerization is 2 times higher than that of *trans*→*cis* isomerization owing to the difference in quantum yield, and is independent of the azobenzene terminal moiety as shown in FIGURE 2. FIGURE 3. shows the typical switching characteristics of PAB503A casting film and its solution state. While the switching time of the casting film was longer than that of solution state, the switching behavior itself was reversible and highly reproducible.

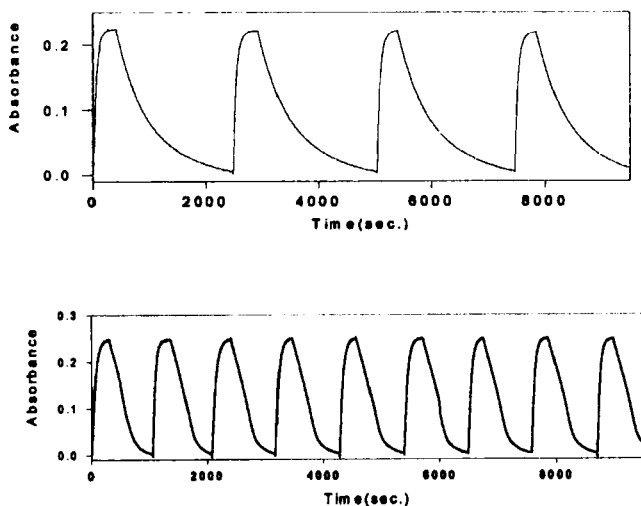


FIGURE 3. Optical switching of PAB503A in casting film(upper) and toluene solution(bottom).

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