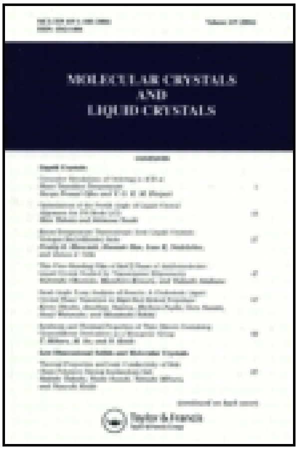


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Properties of Photoresponsive Polyacetylene Derivatives with an Azobenzene Mesogenic Moiety in the Side Group

Se Young Oh [a], Seung-Mn Hong [a] & Sung-Il Oh [a]
[a] Department of Chemical Engineering, Sogang University, Seoul, 121-742, Korea

Version of record first published: 04 Oct 2006

To cite this article: Se Young Oh, Seung-Mn Hong & Sung-Il Oh (1997): Synthesis and Properties of Photoresponsive Polyacetylene Derivatives with an Azobenzene Mesogenic Moiety in the Side Group, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 295:1, 105-108

To link to this article: http://dx.doi.org/10.1080/10587259708042807

Mol. Cryst. Liq. Cryst., 1997, Vol. 295, pp. 105–108
Reprints available directly from the publisher
Photocopying permitted by license only

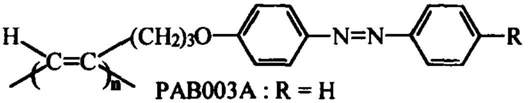
SYNTHESIS AND PROPERTIES OF PHOTORESPONSIVE POLYACETYLENE DERIVATIVES WITH AN AZOBENZENE MESOGENIC MOIETY IN THE SIDE GROUP

SE YOUNG OH , SEUNG-MIN HONG , AND SUNG-IL OH
Department of Chemical Engineering, Sogang University, Seoul 121-742, Korea

Abstract We have synthesized novel mono-substituted acetylenes with a photo-responsive azobenzene group and then polymerized them with Ziegler-Natta, metathesis, and Rh based catalysts. Especially, the Rh catalyst containing chloroform as a solvent produced a cis rich polymer with high yield of 90%. Through the measurements of DSC and polarizing microscope, polymer with a n-pentyl azobenzene group was found to show a smectic liquid crystalline phase. The reversible photoisomerization of all monomers and polymers was generated due to the irradiation of a UV(350nm) or Visible(450nm) monochromatic light.

INTRODUCTION

Mono-substituted polyacetylenes containing a functional moiety have recently attracted much considerable attention because of their electro-optical properties and good processibility.[1-3] In this study, we have attempted to synthesize polyacetylene derivatives with an azobenzene group that are photochemically switchable as shown below Scheme 1. Polymerization of two monomers, 5-[4-(4'-alkyl)phenylazo]phenoxy-1-pentyne(i.e. ABR03A, where AB, R, 0, 3, and A represent azobenzene group, number of carbon in an alkyl group, ether linkage, number of methylenic unit, and terminal acetylene, respectively) was carried out using Ziegler-Natta($Fe(acac)_3$-$AlEt_3$), metathesis($MoCl_5$-Ph_4Sn and WCl_6-Ph_4Sn), and Rh($[Rh(NBD)Cl]_2$-Et_3N) catalysts.



PAB003A : R = H
PAB503A : R = n-pentyl, where P is polymer

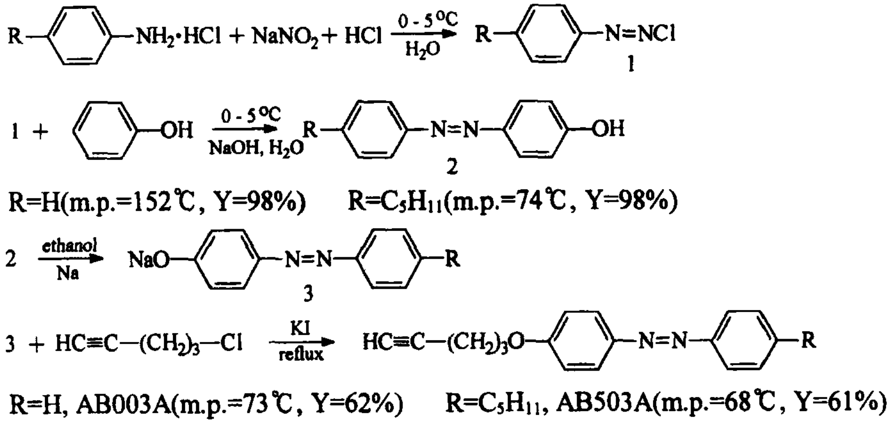
SCHEME 1 Polyacetylene derivatives.

The structure and liquid crystalline properties of all monomers and polymers were investigated by means of elemental analysis, FT-IR, UV-Visible, ^{1}H, ^{13}C-NMR, as well as DSC and polarizing microscope. The changes in polymer structure by thermal aging and photoisomerization characteristics due to the irradiation of a UV or Visible monochromatic light were also studied.

EXPERIMENTAL

Synthesis of monomers

The two steps of synthesis for ABR03A(R=H or n-pentyl) monomer are shown in Scheme 2. First, 4'-hydroxy-4-alkylazobenzene was synthesized through diazo coupling between alkylphenyldiazonium salt and phenol. Finally, ABR03A was obtained from the esterification of 4'-hydroxy-4-alkylazobenzene with 5-chloro-1-pentyne in sodium ethoxide solution using potassium iodide as a catalyst.



R=H(m.p.=152℃, Y=98%) R=C_5H_{11}(m.p.=74℃, Y=98%)

R=H, AB003A(m.p.=73℃, Y=62%) R=C_5H_{11}, AB503A(m.p.=68℃, Y=61%)

ANAL. Found for $C_{17}H_{16}N_2O$(AB003A) : C, 76.82%; H, 6.03%; N, 10.59%.
ANAL. Found for $C_{22}H_{26}N_2O$(AB503A) : C, 78.32%; H, 7.97%; N, 8.44%.

SCHEME 2 Synthesis of acetylene derivatives.

Polymerization

Polymerization was conducted at 25°C for 6h. The reaction was terminated by pouring the reaction mixture into a large amount of methanol. Polymer was filtered off and washed with methanol and then dried under vacuum. The polymer yield and molecular weight obtained from GPC measurement are summarized in Table I.

TABLE I The results of polymerization for ABR03A by Ziegler-Natta, metathesis, and Rh based catalysts.[a]

Polymer	Catalyst	Solvent	Yield(%)	M_n	M_w	M_w/M_n
PAB003A	$Fe(acac)_3$-$AlEt_3$	Toluene	44	8.2×10^3	4.2×10^5	51.2
PAB503A	$Fe(acac)_3$-$AlEt_3$	Toluene	41	1.2×10^4	1.6×10^6	133.3
PAB003A	$MoCl_5[WCl_6]$-Ph_4Sn	Toluene	-	-	-	-
PAB003A	$[Rh(NBD)Cl]_2$-Et_3N	Chloroform	90	9.0×10^3	3.0×10^4	3.3
PAB503A	$[Rh(NBD)Cl]_2$-Et_3N	Chloroform	90	1.3×10^4	3.5×10^4	2.7

[a][Monomer]/[Catalyst]=50, [Catalyst]=0.01mol/l, $[AlEt_3]/[Fe]=6$, $[Et_3N]/[Rh]=100$.

RESULTS AND DISCUSSION

Thermal history of polyacetylene derivatives

Figure 1 shows the changes in ^{1}H-NMR spectrum of PAB003A prepared by a $[Rh(NBD)Cl]_2$-Et_3N catalyst. The peak of 6.04 ppm corresponding to a cis proton was completely disappeared after thermal treatment at 180°C for 50min. This temperarure is in fair agreement with that of cis-trans isomerization obtained from DSC measurement. Especially, a significant decrease in molecular weight was observed at this temperature.[1]

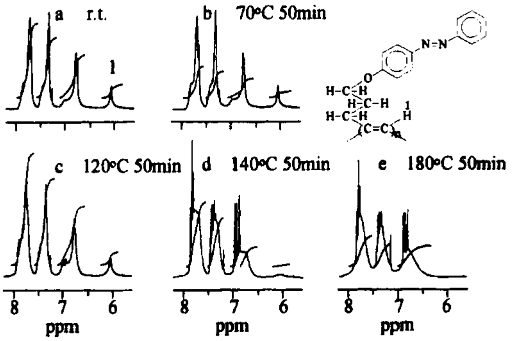


FIGURE 1 Changes in ^{1}H-NMR spectrum of the heat treated PAB003A prepared by a $[Rh(NBD)Cl]_2$-Et_3N catalyst.

Liquid crystalline properties of monomers and polymers

AB503A monomer with a pentyl group in the terminal moiety of azobenzene was found to show a nematic liquid crystalline phase, which the corresponding polymer(PAB503A) showed a smectic phase due to a higher order in molecular arrangement of mesogenic moiety generated by the polymerization.[2] Table II summarized the phase transition temperature obtained from DSC and polarizing microscope measurements.

TABLE II Phase transition temperature of AB503A monomer and PAB503A polymer[a].

Momoner or Polymer(catalyst)	first heating		first cooling	
AB503A	T_{KN}=56	T_{NI}=68	T_{IN}=64	T_{NK}=45
PAB503A(Fe)[b]	T_{KS}=166	T_{SI}=200	T_{IS}=118	-
PAB503A(Rh)[b]	T_{KS}=174	T_{SI}=186	T_{IS}=114	-

[a] K=crystalline, S=smectic A, and I=isotropic, [b] No distinct DSC peak associated with the phase transition between the crystalline phase and smectic A phase was observed.

Photoisomerization characteristics

Figure 2 shows the changes in UV-Visible spectrum of PAB003A due to the irradiation of a 350nm UV light. The UV-Visible spectrum of polymer are characterized by an maximum absorption at 337nm corresponding to trans form of the azobenzene group and a broad absorption peak at 430nm due to cis form in the dark state. The absorption intensity of trans isomer is dramatically decreased due to the irradiation of a 350nm monochromatic light, while that of cis isomer is slowly increased. When a 450nm visible light is illuminated, a reversible isomerization from cis to trans form is observed.

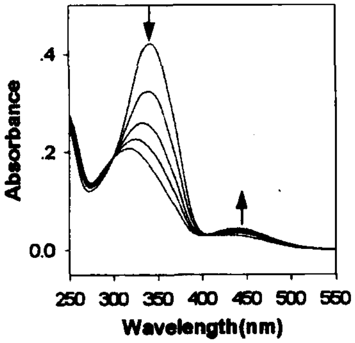


FIGURE 2 The changes of UV-Visible spectrum of PAB003A in chloroform solution during the irradiation of a 350 nm UV light.

REFERENCES

1. S. Y. Oh, Y. Ezaki, K. Akagi, and H. Shirakawa, J. Polym. Sci. Polym.Chem. Ed., 31, 2977 (1993).
2. S. Y. Oh, K. Akatgi, H. Shirakawa, and K. Araya, Macromolecules, 26, 6203 (1993).
3. K. Akagi, H. Goto, Y. Kadokura, H. Shirakawa, S. Y. Oh, and K. Araya, Synth. Met., 69, 13(1995)