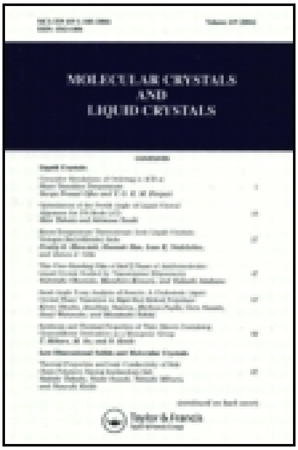

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Synthesis and Properties of Polyacetylene Copolymer with Liquid Crystal and Stable Radical Substituents

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Synthesis and Properties of Polyacetylene Copolymer with Liquid Crystal and Stable Radical Substituents

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We synthesized the polyacetylene copolymers consisting of acetylene segments with a liquid crystal and stable radical group for magnetic polymer. The copolymers show liquid crystallinity in both the heating and cooling processes. The ESR measurement of the copolymer revealed an orientational behavior of the copolymer for alignment of the liquid crystalline (LC) substituents and spin species.

Keywords: polyacetylene copolymer; magnetism; ESR; conjugated polymer

INTRODUCTION

Magnetic polymers with stable radical group have been investigated so far, mainly in the amorphous state. Up to now, the intrachain spin alignment has been achieved in the conjugated polymer with stable radical groups[1]. However, no macroscopic spin alignment has been succeeded, giving no ferromagnetic polymer in bulk. The problem can be solved with liquid crystalline polymers[2]. For these polymers, the spins in the polymer align along the liquid crystalline order. However, there is no reported magnetic LC polymer which polymer's backbone is consisting of conjugated polymer main chain, except a study of *di*-substituted polyacetylene derivative with LC and

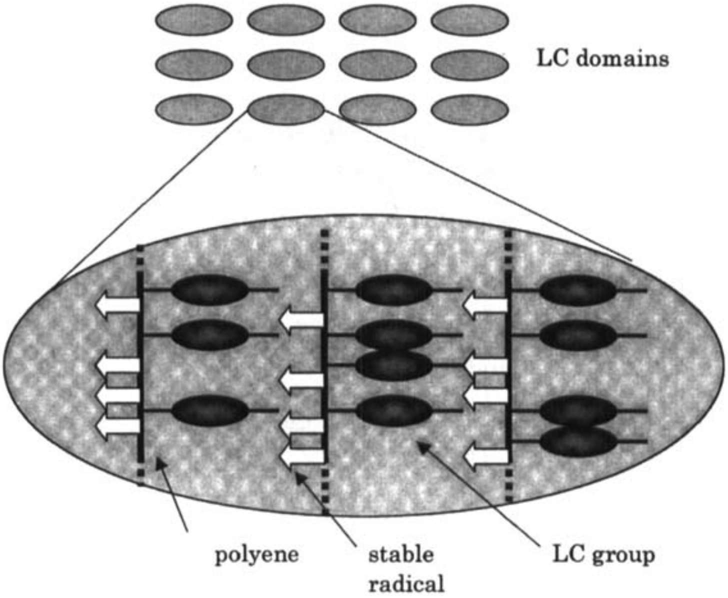


FIGURE 1 Schematic illustration of the conjugated copolymer with liquid crystal and stable radical group.

stable radical group[3]. In the present study, we synthesized conjugated copolymers bearing LC and stable radical groups to afford a spin alignment with aid of spontaneous orientation by LC side chains as illustrated in Figure 1. The copolymer is consisting of polyacetylene as main chain, stable phenoxy radical as spin unit and LC group as substituent. The phase transition behavior and the magnetic properties of the copolymers are discussed.

EXPERIMENTAL

Synthesis

Copolymerization of **Ac-*dt*-BPHA** (3,5-di-*tert*-butyl-4-acetoxyphenylacetylene) with **PCH503A** (5-*p*-*trans*-pentylcyclohexylphenoxy-1-pentyne) were carried out using rhodium complex catalyst in tetrahydrofuran (THF) under basic condition at room temperature. The monomer ratio of **Ac-*d*-*t*BPHA / PCH503A** was changed from 0.06 to 0.11 in the copolymerization, as shown in Scheme 1. After the polymerization, the acetoxy-protected moiety of the copolymer was removed using $LiAlH_4$ in THF to give a hydroxyl group. The hydroxyl group was oxidized with PbO_2 in benzene to obtain radical group. All of copolymers were soluble in good organic solvents such as $CHCl_3$, and THF. Number-averaged polymer weights (M_n) of the copolymers were from 6,500 to 12,000, according to polystyrene standard.

RESULTS AND DISCUSSION

IR absorptions of **Ac-*dt*-BPHA, 2, 2', and 2"** were summarized in Table I. **Ac-*dt*BPHA** showed absorptions due to HC≡, C≡C stretching vibration at 3286 and 2102 cm^{-1}, respectively. These peaks were disappeared after the polymerization. The IR spectra of **2'** and **2"** show no absorptions at 1760 cm^{-1} characteristic to C=O stretching vibration of the acetoxy group. The IR spectra of **1, 1', 1", 3, 3'**, and **3"** were obtained which similar to these results. The CH_3 signal in the terminal alkyl group of the polymers appeared at 0.87 ppm in ^{1}H-NMR spectrum,. The proton of the methylene spacer and cyclohexyl moiety were appeared between 1.03 and 2.40 ppm, respectively.

The signal of the CH_3 neighboring to the OPh of **2** appeared at 3.90 ppm. Overall, the IR and ^{1}H-NMR spectra of the copolymers were very good agreement with the proposed structure.

TABLE I Assignment of the IR spectra[a] of **Ac-*dt*BPHA, 2, 2', and 2"**.

compound	ν_{OH}	$\nu_{HC\equiv}$	ν_{CH2}	$\nu_{C\equiv C}$	$\nu_{C=O}$	$\nu_{C=C}$ (ph)
Ac-*dt*BPHA	—[b]	3286	3006-2875	2102	1764	1610
PCH503A	—[b]	3310	2925-2850	2120	—[b]	1612
2	—[b]	—[b]	2920-2850	—[b]	1762	1612
2'	3445	—[b]	2957-2851	—[b]	—[b]	1612
2"	3423	—[b]	2954-2851	—[b]	—[b]	1612

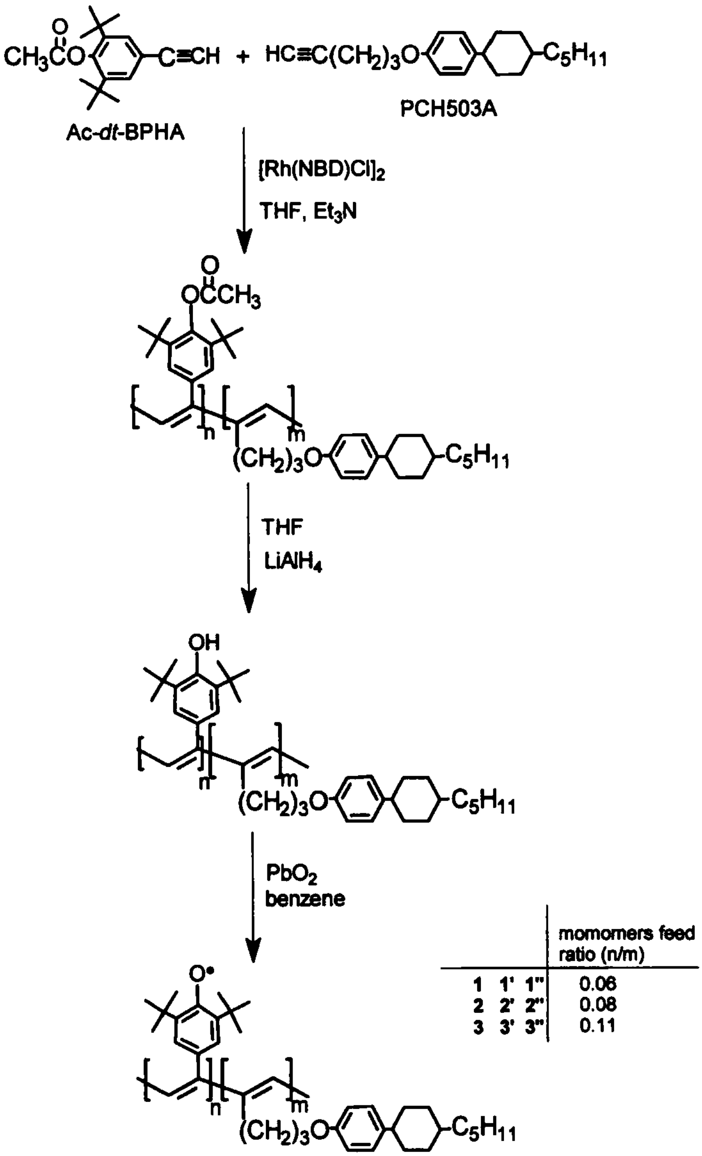
[a] KBr, in cm^{-1}

[b] no absorption

TABLE II Phase transition temperatures of the copolymers

copolymer	phase transition temperatures (°C)[a]	
	heating process	cooling process
1	G 60 S_X 150 I	G 58 S_X 139 I
1'	G 59 S_X 150 I	G 56 S_X 144 I
2	G 60 S_X 145 I	G 57 S_X 135 I
2'	G 58 S_X 134 I	G 55 S_X 130 I
3	—[b]	—[b]
3'	—[b]	—[b]

[a] determined by DSC; G: glassy state, Sx: smectic X, I: isotropic, [b] no LC



			momomers feed ratio (n/m)
1	1'	1''	0.06
2	2'	2''	0.08
3	3'	3''	0.11

SCHEME 1 Copolymerizations.

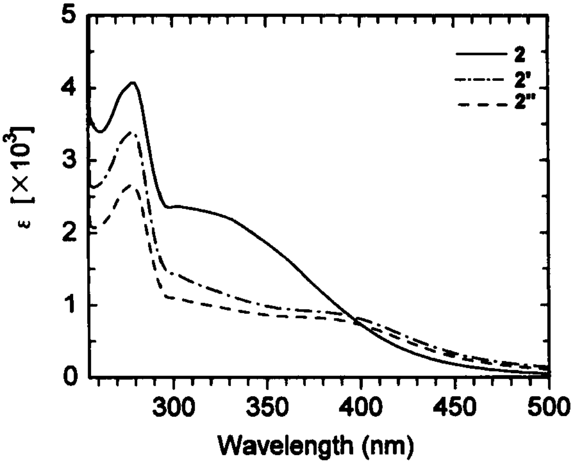


FIGURE 2 UV-Vis spectra of **2**, **2'** and **2"** in THF.

Liquid crystallinity was examined through polarizing optical microscopy observations and differential scanning calorimeter (DSC) measurements. **1**, **1'**, **2** and **2'** show mesophase. **3** and **3'** of high proportion of 2,6-*di*-*tert*-butylphenoxy units in the copolymer showed no mesophase. The transition temperatures of the polymers were summarized in Table II. **PPCH503A** showed typical fan-shaped texture, indicating a smectic LC. **1'** and **2'** showed battonet texture in LC temperature range, which was assigned to smectic phase. However, detailed liquid crystallinity is unknown. This may be due to the bulky 2,6-*di*-*tert*-butylphenoxy groups suppressing their liquid crystallinity. The UV-Vis absorption spectra of **2**, **2'** and **2"** are shown in Figure 2. The absorption at 280 nm is due to the mono-substituted

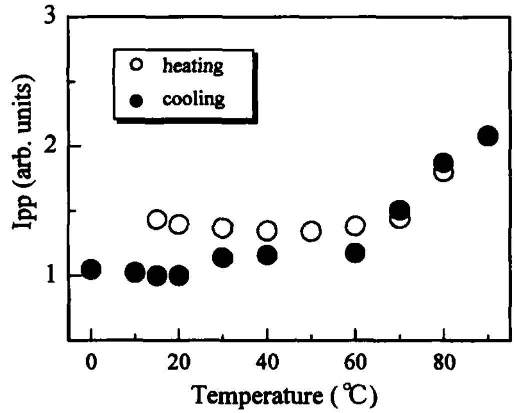


FIGURE 3 Temperature dependence of the ESR signal intensity of **2"**.

phenylene ring in the mesogenic group. The absorption at 304 nm is due to the $\pi \rightarrow \pi^*$ transition of the polymer main chain.

The phenoxy radical is decomposed with temperature, and its ESR signal gradually disappears around 100℃. Hence the ESR measurements of **1"** and **2"** were carried out in the temperature range from r.t. to 90 ℃. The polymers were first melted by heating under helium atmosphere, and it was gradually cooled to room temperature. The polymers were solidified at the glass transition temperature, and can remain unchanged at lower temperature. Figure 3 shows temperature dependence of the ESR signal intensity of the polymers. In the heating process, the intensity of the ESR signal increased at LC temperature around 60℃, despite an ordinary compounds having radical group decrease their intensity in the ESR with temperature due to an increase of entropy of molecule. This result indicates that the LC substituents of the polymers align in macroscopic region, and a formation of spin alignment accompanied with the LC.

CONCLUSION

Conjugated copolymers having stable radical and LC substituents were synthesized from copolymerization of the corresponding monomers using rhodium complex catalyst. The ESR measurements evaluated that phenoxy radicals on the copolymer as spin species were aligned in the LC temperature range. The LC polyradicals are expected to be a potential candidate as a magnetically condensed material.

Acknowledgments

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