

Preparation of New Poly(phenylene vinylene) Type Polymers by Ni-promoted Polycondensation and Their Photoluminescent Properties

Takakazu Yamamoto,* Yuqing Xu, and Hideomi Koinuma[†]

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503

[†]Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503

(Received March 2, 1998; CL-980150)

Poly(*p*-phenylene vinylene) type polymers having biphenyl-4,4'-diyl units have been prepared by organometallic polycondensation. They are photoluminescent and electrochemically active, and are considered to take a stacked and liquid crystalline structure depending on the substituent.

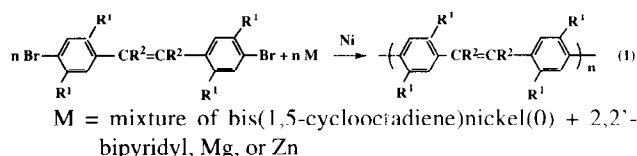
Poly(*p*-phenylene vinylene) PPV-type polymers have been the subject of recent many papers, especially in relation to its



PPV-type polymers

electrically conducting and luminescent properties.^{1,2} The polymers have usually been prepared by a precursor route involving reactions of *p*-xylylene halides and base. However, the preparation of the precursor polymers and their transformation to the PPV-type polymers are sometimes difficult, and this limitation has prevented revealing properties of the PPV-type polymers with various chemical structures.

On the other hand, recently developed Ni-promoted dehalogenation polycondensation has given various polymers,³ and herein we report the application of the dehalogenation polycondensation to the preparation of the PPV-type polymers having biphenyl-4,4'-diyl units.



The monomer was prepared by a Ti-promoted coupling reaction of the corresponding aldehyde or ketone⁴ (e.g., 2 *p*-BrC₆H₄COCH₃ + Zn → *p*-BrC₆H₄C(CH₃)=C(CH₃)C₆H₄Br; *p*; TiCl₄ promoted). The coupling reaction with ketone usually gives a *cis*-isomer, and the *cis* structure of a monomer (R¹ = H, R² = CH₃) has been confirmed by X-ray crystallography.⁵ However, crystalline products obtained from aldehydes are considered to have a *trans* structure,^{4c} since they give an IR peak at about 970 cm⁻¹ characteristic of *trans*-alkenes.

Data from elemental analysis, IR spectra, and ¹H-NMR spectra (e.g., Figure 1 for the polymer obtained in run 5) agree with the structure of the polymers. The ¹H-NMR spectra of the polymers resemble those of monomers, although *cis* to *trans* isomerization of the C=C bond partly occurs with the polymer obtained in run 5 as manifested by appearance of new peaks (e.g., a peak at δ 2.1 with the polymer obtained in run 5). The polycondensations using Mg and Zn as M in the presence of Ni catalyst (eqn. 1) also gave the polymers in high yields.

In spite of numerous examples of reported PPV-type polymers,

Table 1. Results of the polycondensation using the Ni(0) complex^a

No	R ¹	R ²	Yield/%	10 ⁻³ Mn ^b	(Mw/Mn)
1	CH ₃	H	95	5.3	3.0
2	C ₂ H ₅	H	93	2.5	1.5
3	<i>i</i> -C ₃ H ₇	H	91	2.4	1.3
4	<i>n</i> -C ₈ H ₁₇	H	90	3.8	1.7
5	H	<i>n</i> -C ₆ H ₁₃	92	2.4	1.6
6	H	<i>n</i> -C ₁₁ H ₂₃	92	3.9	1.5
7	H	C ₆ H ₅	98	3.4	2.0

^a In DMF at 60 °C for 48 h. Molar ratio of Ni(0) to the monomer: 1.2 for runs 1, 2, 4, 5, and 7 and 3.0 for runs 3 and 6; both the conditions give analogous results. ^b Determined by GPC (polystyrene standards).

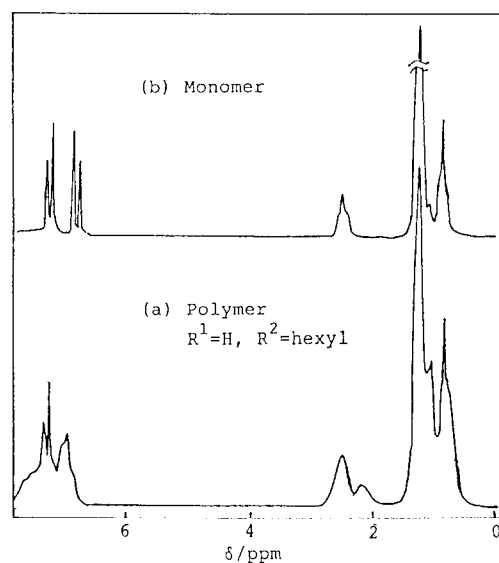


Figure 1. ¹H-NMR spectral of (a) polymer obtained in run 5 and (b) its monomer in CDCl₃.

only a few examples of the PPV type polymers with the biphenyl-4,4'-diyl unit are known.⁶ The polymers were soluble in chloroform, THF, and DMF. The polymer with a longer alkyl group had a lower melting point (M.p. = 123, 84, 48, 80, and 45 °C for the polymers obtained in runs 1, 2, 4, 5, and 6, respectively).

The polymer obtained in run 4 and having long R¹ alkyl chains gives rise to a powder X-ray diffraction pattern (Figure 2) similar to those of regioregular head-to-tail type poly(3-alkylthiophene-

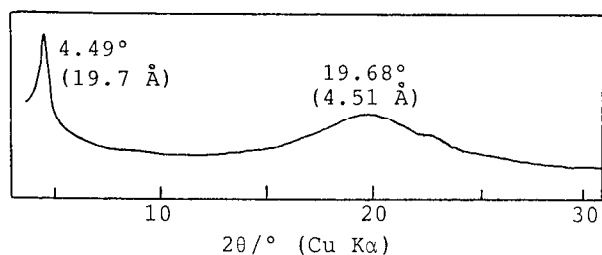


Figure 2. X-ray diffraction pattern of the polymer obtained in run 4.

2,5-diyl),⁷ HT-P3RTh, suggesting that the polymer also take a π -stacked liquid crystalline structure. The peaks at $2\theta = 19.68^\circ$ and 4.49° seem assignable to a face-to-face packing distance between the stacked planar polymer molecules and a distance between the main chains separated by the octyl group, respectively, by analogy with the case of HT-P3RTh. The d values of 4.51 \AA and 19.7 \AA are somewhat different from those (3.79 \AA and 20.1 \AA) observed with TII-P3RTh ($R = \text{octyl}$),⁷ presumably reflecting the difference in the steric effect around the biphenyl-4,4'-diyl and thiophene-2,5-diyl units having the long alkyl chain(s). DSC analysis and observation through a polarizing microscope also supports the liquid crystalline properties of the polymer.

Table 2 summarizes optical properties of the polymers. The

Table 2. UV-visible and Photoluminescence data

No.	Run No. of polymer	$\lambda_{\text{max}}/\text{nm}^a$	$\lambda_{\text{max}}(\text{PL})/\text{nm}^a$	$\Phi^b/\%$
1	1	342	408	41
2	3	320	404	18
3	4	330	404	40
4	5	282	444	5 ^c
5	7	361	477	27 ^c

^a In CHCl_3 . $\lambda_{\text{max}}(\text{PL})$ = photoluminescence peak (irradiated with light at λ_{max}) measured under N_2 . ^b Quantum yield of the photoluminescence. ^c In poly(methyl methacrylate) film.

absorption peak of the polymers appears at a longer wavelength than that of the corresponding monomers by about 30 nm due to the expansion of the π -conjugation system. The position of the absorption peak, however, locates at a shorter wavelength than that of poly(*p*-phenylene vinylene).^{1,2} This hypsochromic shift leads to emission of blue or green light (*vide infra*).

They are photoluminescent in solution, in their neat films (good films are obtained by casting from chloroform solutions), and in poly(methyl methacrylate) PMMA film, emitting blue or green

light. For the polymers having the substituent at the vinylene group, higher quantum yield is observed by dispersing the polymer in the PMMA film (e.g., $\Phi = 1.6\%$ for a neat film of the polymer obtained in run 5). This result suggests the presence of an intermolecular quenching process of the photoexcited polymer molecule (e.g., by the formation of an exciplex-type adduct) and the quenching is reduced by dispersing the polymer in the PMMA film. The quantum yield is comparable to those of reported poly(*p*-phenylene vinylene) type polymers.⁸

All of the polymers are electrochemically active and show reduction (or n-doping) peak(s) in a potential range -1.1 through -1.8 V vs Ag/Ag^+ coupled with the corresponding oxidation (or n-undoing) peak.

We are grateful to Professor T. Ikeda and Dr. A. Kanazawa of our institute for helpful discussion and experimental support. This work has been partly supported by CREST (Core Research for Evolutional Science and Technology).

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