

Synthesis and Properties of Alkyl-Substituted Poly(1,4-phenylenevinylene) Derivatives

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ABSTRACT: The luminescent poly(2-dodecyl-5-methyl-1,4-phenylenevinylene) was synthesized with a new synthetic route. The structure and properties of the polymers were characterized by IR, UV-vis, luminescent spectra, GPC, and both thermal and elemental analysis. The glass-transition temperature increases and the photoluminescent relative quantum yield decreases with the increase of the conjugation extent of the polymer. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1299–1304, 2001

Key words: alkyl-poly(1,4-phenylenevinylene); synthetic route; FTIR; glass-transition temperature; UV-vis absorption spectra; photoluminescent relative quantum yield

INTRODUCTION

Polymer light-emitting devices have attracted intensive research because of their potential applications.^{1–4} The luminescent polymers used in the devices are mainly poly(1,4-phenylenevinylene) (PPV) and its soluble derivatives, because PPV and its derivatives have good thermal stability and luminescent property and can form good-quality films. Different kinds of PPV derivatives have been synthesized,^{5–9} and the performance of light-emitting devices has been improved dramatically in recent years.

PPV is insoluble and nonmeltable, but we can get its soluble derivatives by the polymerization of a monomer containing soluble substituents or side groups. Usually the side groups are either alkoxy or alkyl substituents. Intensive studies have focused on alkoxy-PPVs, which emit red or

yellow light, whereas studies on alkyl-PPVs, which emit green light and are the most suitable for display applications, are only rarely studied.^{10,11} A possible reason is that the synthesis of the monomers of alkyl-PPVs is much more difficult than that of the monomers of alkoxy-PPVs. To our knowledge, only two synthesis methods of alkyl-PPV have been reported.^{12,13} The yields are low and there are some limitations in the methods. In this study, a new synthesis method for monomers of alkyl-PPVs is reported, and the thermal and luminescent properties of the polymers are characterized.

EXPERIMENTAL

1-Dodecyl-4-methylbenzene (compound A) was synthesized by the procedure shown in Figure 1. Under N₂, Mg (7.3g, 0.3 mol) and 30 mL of dry THF were added into a 500-mL flask. The solution of *p*-bromotoluene (50 g, 0.29 mol) in 150 mL of THF was added dropwise into the flask. The mixture was kept slightly boiling, then refluxed for 3 h. Cooled to room temperature, the mixture

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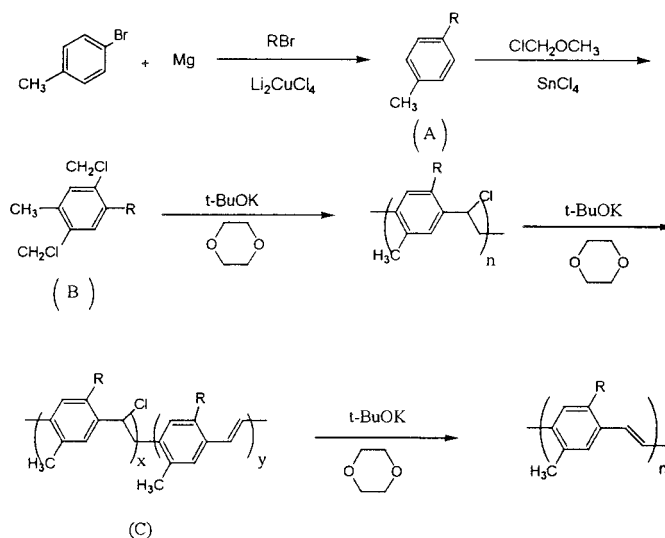


Figure 1 Synthesis route of alkyl-PPV.

was filtered under N_2 . To the mixture, kept at 0°C , was added $\text{C}_{12}\text{H}_{25}\text{Br}$ (67 g, 0.27 mol) and 10 mL of 0.1M Li_2CuCl_4 ¹⁴ THF solution, and was stirred for 6 h. Dilute sulfuric acid (100 mL) was added to the solution to quench the reaction. The organic layer was separated and washed twice with 50 mL of water, and the water layer was extracted with ether. The two organic layers were mixed and dried with CaCl_2 . The solvent was distilled and distillation under reduced pressure (140–142°C/2 mmHg) afforded 48 g of product (yield was 68%).

$^1\text{H-NMR}$ [CDCl_3 , tetramethylsilane (TMS)] δ : 7.04 (4 h, s), 2.58 (2 h, t), 2.30 (3 h, s), 1.60 (2 h, m), 1.30 (18 h, m), 0.90 (3 h, t).

The Li_2CuCl_4 THF solution (0.1M) was prepared by reacting lithium chloride (0.2 mol) and copper(II)-chloride (0.1 mol) in tetrahydrofuran (1000 mL).

1,4-Bis(chloromethyl)-2-dodecyl-5-methyl-benzene (compound B) was synthesized by the following procedure. $\text{ClCH}_2\text{OCH}_3$ (14 g, 0.17 mol)¹⁵ and compound A (10.4 g, 0.04 mol) were added into CS_2 (60 mL). The mixture was cooled to -7°C and stirred. SnCl_4 (9 mL) was added dropwise into the mixture kept at -5°C , stirred for 3 h, then poured on ice. The CS_2 was removed and the aqueous phase was extracted with 40 mL of CS_2 . The combined CS_2 solutions were dried over CaCl_2 and the solvent was removed on a steam bath. Recrystallization of the residue from ethanol gave 11.3 g of product (yield was 79%).

$^1\text{H-NMR}$ (CDCl_3 , TMS) δ : 7.18 (2 h, d), 4.60 (4 h, d), 2.68 (2 h, t), 2.40 (3 h, s), 1.70 (2 h, m), 1.30 (18 h, m), 0.90 (3 h, t).

$\text{ClCH}_2\text{OCH}_3$ was synthesized as follows. In a 2-L round-bottom flask fitted with a stopper, which carried a reflux condenser and a glass tube reaching nearly to the bottom of the flask, were placed 350 g of methyl alcohol and 620 mL of 38% formaldehyde solution. A rapid stream of hydrogen chloride was run into the mixture, which was cooled with running water. After about 6 h, the organic layer was separated. The water layer was saturated with CaCl_2 , and more ether separated. The two organic layers were combined and dried over CaCl_2 and fractionally distilled. The yield of the product boiling at $55\text{--}60^\circ\text{C}$ was about 500 g.

Poly(2-dodecyl-5-methyl-1,4-phenylenevinylene) [polymer (C)] was obtained by the method according to the reported route.¹⁶ Under N_2 , a solution of potassium *tert*-butoxide (1.3 g, 11.2 mmol) in 20 mL of 1,4-dioxane and 20 mL of THF was added dropwise to the solution of the monomer (compound B; 2 g, 5.6 mmol) in 100 mL of 1,4-dioxane. The mixture was stirred at about 100°C overnight and precipitated with 150 mL of ethanol to afford crude polymer (about 1.3 g). The polymer was purified by dissolving it in 50 mL of THF, filtering the solution, and precipitating it by addition of 150 mL of ethanol. After washing with ethanol (100 mL), ethanol/water (50/50 mL), and ethanol (100 mL), respectively, the polymer was dried at room temperature under reduced pressure. The product was a yellow fibrous polymer. The yield was about 30%. GPC gave $M_w = 12.3 \times 10^4$, $M_z = 32.3 \times 10^4$, $d = 2.6$.

$^1\text{H-NMR}$ (CDCl_3) δ : 7.39 (s, 1 h), 7.18 (s, 1 h), 6.85 (m, 1 h), 5.28 (s, 0.7 h), 3.20–3.50 (s, 1.5 h), 2.20–2.65 (m, 5 h), 1.20–1.85 (m, 20 h), 0.90 (t,

3 h). ELEM. ANAL. showed that this polymer had 7% Cl.

The UV-vis absorption spectra were obtained from Hitachi U-3010 spectrometer in air. The photoluminescence spectra were obtained on the Hitachi F-4500 spectrometer in air. The FTIR spectrum was obtained from PE-2000 FTIR. The thermal properties of the polymers were measured by Perkin-Elmer 7 Thermal Analysis System (Perkin-Elmer, Foster City, CA). All chemicals used were analytical grade.

RESULTS AND DISCUSSION

Synthesis Route

There are two methods reported to introduce long-chained alkyl substituents to the benzene ring of alkyl-PPVs.^{12,13} One is to acylate toluene and, then, reduce the product to obtain a dialkylbenzene derivative.¹² The yield of the dialkylbenzene derivative is low and it is difficult to separate the isomers by this method. The other method is to use a kind of Ni catalyst named *dppp* as catalyst to catalyze cross-coupling of alkyl grignard reagent with aryl halides.¹³ By this method, the yield of the product is good, but it is difficult to synthesize asymmetrically substituted dialkylbenzene derivatives,¹⁷ which lead to higher solubility of the resulting alkyl-PPV. We use Li_2CuCl_4 to catalyze cross-coupling aryl grignard reagent with alkyl halides and get good yield. There is another method to introduce long-chained alkyl

substituents to benzene ring¹⁸ using cross-coupling of aryl lithium with alkyl halides. The yield by this method is about the same as that we get, although lithium is much more expensive than Mg. To bischloromethylate dialkylbenzene derivatives, Starring et al.¹² used $\text{CH}_2\text{O}/\text{HCl}$ and the yield was poor (about 15%). Sonoda et al.¹³ used $\text{ClCH}_2\text{OCH}_3/\text{fuming H}_2\text{SO}_4$. The yield was low (about 42%) and some by-products were developed by this method.¹⁹ Using $\text{ClH}_2\text{COCH}_3/\text{SnCl}_4$, the method that we adopted, is one of the best ways to chloromethylate alkylbenzene derivatives. The yield can be as high as 90%.²⁰ This reaction must be performed in a nonpolar solvent such as CS_2 . In a polar solvent such as CH_2Cl_2 , the product is not the bischloromethylated one but rather some polymers with low molecular weights.

To polymerize the monomer, we used the Gilch route. We controlled the content of chlorine in the polymer by adding different amounts of *t*-BuOK solution to the reaction system. We found it difficult to eliminate all the chlorine in the polymer. When the content of chlorine in the polymer is lower than 1%, the solubility is poor, which perhaps results from the crystallization of the polymer. Using branched substituents could perhaps increase the solubility. In the polymerization, many insoluble parts were formed. We think they were polymers with excessively large molecular weights, perhaps formed by crosslinking.²¹ To resolve this problem, we used monofunctional monomers such as benzyl bromide and benzyl

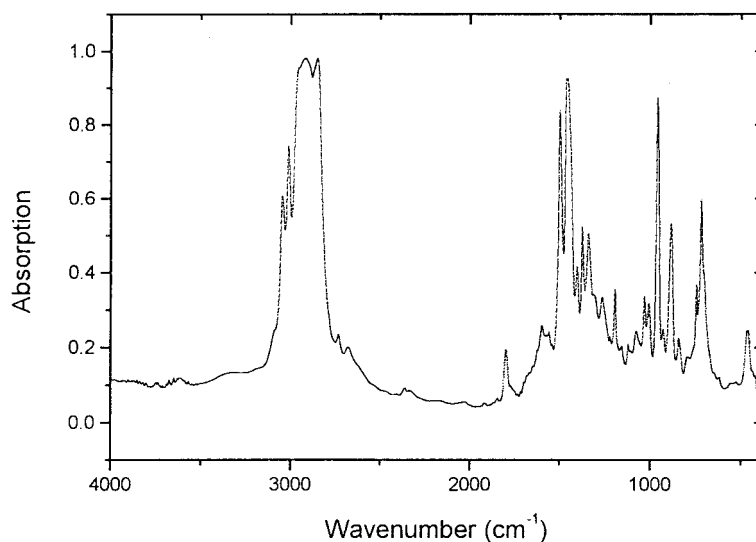


Figure 2 FTIR spectrum of a film of polymer (C).

Table I T_g and Pyrolysis Temperatures (T_1 , T_2 , T_3) of Polymer (C) Containing Different Content of Chlorine

Cl %	T_g (°C)	T_1 (°C)	T_2 (°C)	T_3 (°C)
1.33	—	194	—	—
2.26	155.79	191	436	610
4.15	149.37	200	439	—
7.00	98.27	210	450	631
9.35	85.36	180	451	640
11.04	72.63	180	473	—

The heating rate in the thermal analysis is 20°C/min.

chloride to lower the molecular weight of the polymer, but got little effect. It seems that the activity of the bifunctional monomer is much higher than that of the monofunctional monomers.

Figure 2 shows the Fourier transform infrared (FTIR) spectrum of a film of polymer (C). The absorption peaks are at 3013, 2919, 2852, 1502, 1464, 1377, 961, 887, and 721 cm^{-1} . The strong peak at 961 cm^{-1} is assigned to *trans* double bonds. The absorption at 3013, 2919, and 2852 cm^{-1} is ascribed to the C—H stretching vibration of the methyl and methylene groups. The peak at 721 cm^{-1} is the result of the wagging vibration of the methylene groups. The peaks at 1377, 1464, and 1502 cm^{-1} result from the skeletal vibration of a 1,2,4,5-tetrasubstituted benzene ring. The C—H out-of-plane vibration is observed at 887 cm^{-1} . The peak near 1700 cm^{-1} means that the polymer is oxidized somewhat to form C=O.

Solubility

Polymer (C) [poly(2-dodecyl-5-methyl-1,4-phenylenevinylene)] ($M_w = 90,000\text{--}150,000$) is soluble in xylene, THF, CHCl_3 , and toluene; slightly soluble in DMF and cyclohexanone; and insoluble in ether and ethanol.

Thermal Properties

We measured the pyrolysis temperatures (T_1 , T_2 , T_3) and glass-transition temperature (T_g) of polymer (C) as listed in Table I. The contents of chlorine listed in Table I were given by elemental analysis. The pyrolysis temperatures here are the initial temperatures of the weight loss of polymer (C) in pyrolysis.

We find that the weight loss at about 200°C is much the same as the chlorine content given by elemental analysis, so we conclude that T_1 is the temperature of losing HCl. T_2 and T_3 are the pyrolysis temperatures of the main chain and side chain, respectively. They are not affected by the conjugation extent of the polymer, whereas the glass-transition temperature of the polymer is considerably affected. We can see from Table I that the higher the conjugation extent, the higher the glass-transition temperature. This is because the more conjugated the polymer is, the more rigid it is.

UV-Vis Absorption and Luminescence Properties

Figure 3 shows the UV-vis absorption and photoluminescence spectra of the dilute solution of

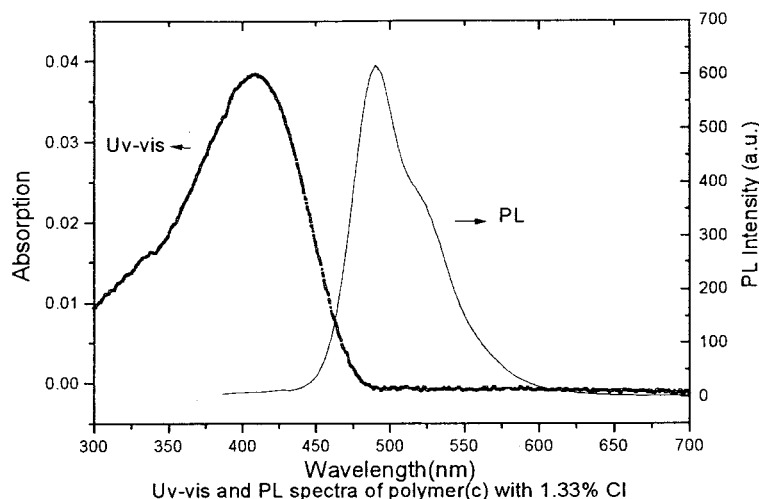


Figure 3 UV-vis and photoluminescent spectra of dilute solution of polymer (C) with 1.33% Cl.

Table II Photoluminescent Emission Peak λ and Relative Quantum Yield of Dilute Solution of Polymer (C) with Different Chlorine Content

Cl %	λ (nm)	Φ (%)
1.33	491	38
2.26	490	43
4.15	489	52
7.00	483	59
9.35	482	78
11.04	484	77

polymer (C) in THF. The exciting wavelength in the photoluminescence measurements was 380 nm, and all the measurements were carried out in air. The emission peak of the dilute solution of polymer (C) moves slightly to longer wavelength when the chlorine content of the polymer decreases, as listed in Table II, whereas that of the thin film moves significantly. This phenomenon means that the conjugation extent of the polymer increases with the reduction of chlorine content in the polymer. Comparing Table I with Table II, we can find that the emission peak of the thin film is obviously in longer wavelength than that of the solution of the polymer with the same chlorine content. This is a normal phenomenon.²²

Table II shows the effect of the conjugation extent on the relative photoluminescent quantum yield (Φ) of the dilute solution of polymer (C). We used the following equation²¹ to calculate the relative photoluminescent quantum yield:

$$\Phi = \Phi_s \times S/S_s \times A_s/A \times n_s^2/n^2$$

where Φ_s , S_s , A_s , and n_s are the photoluminescent quantum yield, area of luminescence spectrum,

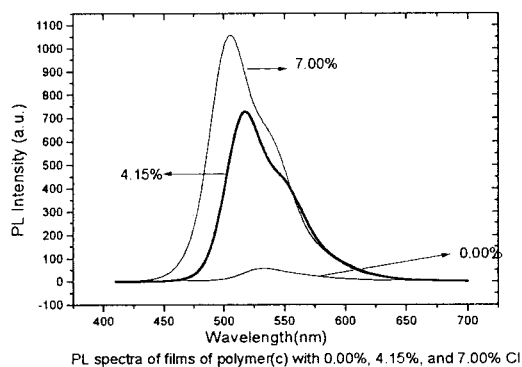

Figure 4 Photoluminescent spectra of thin films of polymer (C) with different chlorine contents.

Table III Photoluminescent Emission Peak λ of Thin Films of Polymer (C) with Different Chlorine Content

Cl %	7.00	4.15	0.00
λ (nm)	504.8	517.2	533.0

absorption at exciting wavelength, and the refractive index of the solvent of the standard sample, respectively. Φ , S , A , and n belong to the sample measured. The standard sample we used was the dilute solution of 9,10-diphenylanthracene in cyclohexane and its quantum yield is 1.00.²³

Compared with the low efficiency (about 15%) of the most popular alkoxy-PPV derivatives (such as MEH-PPV¹⁰ or OC1C10-PPV²⁴), the efficiency of the polymer we synthesized is quite high (the lowest is 38%, from Table II). The relative photoluminescent quantum yield of the dilute solution decreases markedly with the increase of the conjugation extent. This is very much the same as that of the thin film.^{12,25} To explain this phenomenon, Samuel et al.²⁵ said that the migration of excitons to quenching sites would be faster in more-conjugated material, so the nonradiative decay increased and the radiative decay decreased.

Figure 4 shows the PL spectra of the films of polymer (C). The emission peak of the films shifts to longer wavelength more obviously with the decrease of the Cl content [i.e., with the increase of the conjugation extent of polymer (C)], as listed in Table III.

CONCLUSIONS

A highly efficient method to synthesize alkyl-PPV monomers was designed. An alkyl-PPV, poly(2-dodecyl-5-methyl-1,4-phenylenevinylene), was synthesized with this method. The glass-transition temperature increases and the relative photoluminescent quantum yield of the dilute solution decreases with the increase of the conjugation extent of the polymer. The relative photoluminescent quantum yield of the polymer is much higher than that of the alkoxy-PPVs.

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