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A facile synthesis of poly(phenylene 1,2-diphenylvinylene)

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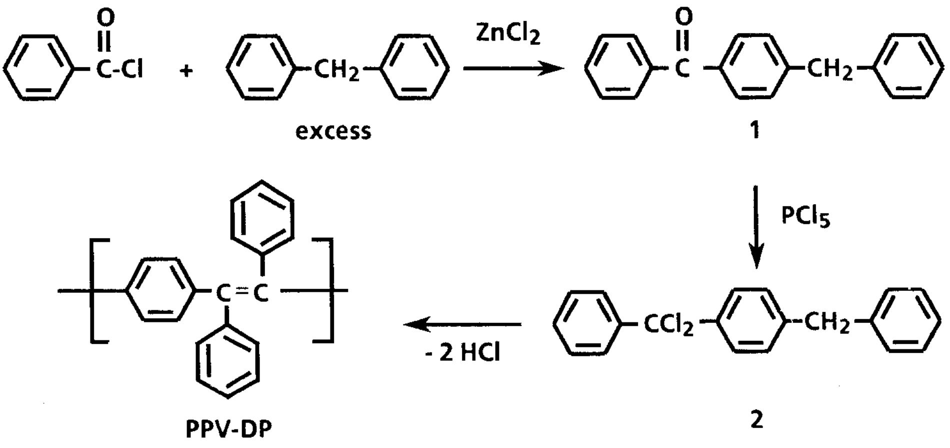
Summary

Poly(phenylene diphenyl vinylene) (PPV-DP) has been prepared by dehydrochlorination of 1-benzyl-4-(α,α-dichlorobenzyl) benzene. The polymerization process is one of the most convenient methods available.

Introduction

Extensive research activities have been devoted to poly(p-phenylene vinylene) (PPV) and its derivatives because of their novel and potentially useful properties [1-3] such as high conductivity after doping [4], photoconductivity [5], nonlinear optics [6] and electroluminescence [7], just to name a few.

Among various PPV derivatives, poly(phenylene phenyl vinylene), (PPV-P) and poly(phenylene diphenyl vinylene) (PPV-DP) are particularly attractive because they can be readily prepared and they are highly soluble in common organic solvents [1]. The synthetic routes to PPV-DP include dechlorination of bis(phenyldichloromethyl)benzene with chromium (II) acetate [1, 8] or with chromium (II) chloride [9], condensation polymerization of 4,4'-dibenzoylbiphenyl with titanium trichloride (the McMurray reaction) [10], coupling reaction of phenyl bisdiazoalkanes [11] and dehydrochlorination of phenyl xylylene dichlorides [12]. In this paper, we report a new method for the preparation of PPV-DP as shown in the following reaction sequence. The polymerization of 2 to PPV-DP is analogous to the polymerization of 4-(α,α-dichlorobenzyl) toluene to PPV-P [13, 14].



Experimental

IR spectra were recorded on a Perkin-Elmer 1750 Fourier transform spectrometer. UV-VIS spectra were recorded on a Hewlett-Packard 8451A diode array spectrophotometer. Elemental analyses were performed at Galbraith Laboratories, Inc. NMR spectra were recorded on a Bruker CXP spectrometer. GPC data were obtained from a Waters modular chromatographic system consisting of a 590 pump, 710 WISP auto-sampler, 410 refractive index detector, and 840 System Control and Data Station. The separation matrix utilized six linear, mixed bed 10 μ styrene-divinylbenzene columns at a flow rate of 1 ml/min.

4-Benzylbenzophenone (1). A mixture of diphenylmethane (400 ml), benzoyl chloride (50 g, 0.357 mol) and zinc chloride (1.4 g) was heated at 170°C for 16 h to give a black solution. After cooling, hexane (100 ml) was added and the resulting solution was extracted with 5% NaOH (150 ml x2) and water (200 ml x 2). The organic layer was dried through Na_2SO_4 and concentrated in vacuo. Most of the excess diphenylmethane was removed by vacuum distillation. The hot residue was quantitatively transferred into a 100 ml 14/20 flask and fractionally distilled in vacuum using a jacketed short path distill head with Vigreux indents (1.5 in.) from Ace Glass. The first fraction was diphenyl methane. With the help of a heating tape wrapping around the distill body, the second fraction was distilled off at 190-200°C/0.4-0.5 mm Hg (Lit. 415°C [15]) as a viscous brown oil (48 g, 50%). This was redistilled under the same condition to give a yellow fluorescent oil (45 g, 46%) which still contained a small amount of diphenylmethane, according to NMR.

1-Benzyl-4-(α,α-dichlorobenzyl) benzene (2). 1 (10.6 g, 0.04 mol) and PCl_5 (8.2 g, 0.042 mol) were heated at 100°C for 1 h and cooled. $POCl_3$ was removed in vacuo followed by pumping under high vacuum overnight to give an orange oil (12.5 g, 98%). This was used directly for polymerization.

Bulk polymerization of 2 (PPV-DP-1). 2 (3.27 g, 0.01 mol), with magnetic stirring, was heated quickly to 300°C and was kept at 290-300°C for 45 min (visible HCl evolution started at about 150°C). After cooling, benzene (15 ml) was added and stirred overnight. While stirring, the black solution was added dropwise into methanol (250 ml). The black yellow powder was further purified by precipitation into methanol and then vacuum dried to give PPV-DP-1 (2.0 g, 79%).

Solution polymerization of 2 (PPV-DP-2 and PPV-DP-3). To a solution of 2 (3.27 g, 0.01 mol) and 1,2-dichlorobenzene (3 ml) was added pyridine (1.6 g, 0.02 mol). The resulting mixture was heated quickly to 170°C (ca. 20 min). Heating was continued for 30 min and solution was then cooled. Benzene (10 ml) was added to the black reaction mixture and the resulting solution was added dropwise into methanol (250 ml) with stirring. The ochre product was collected by suction filtration and then redissolved in benzene (15 ml). The solution was then added dropwise into methanol (250 ml). The yellow precipitate was collected and vacuum dried to give PPV-DP-2 (1.6 g, 64%). PPV-DP-3 (3.0 g, 69%) was prepared similarly from 2 (5.6 g), 1,2-dichlorobenzene (5 ml) and pyridine (2.75 g). The reaction time was 1.5 h.

Results and Discussion

Four times more diphenylmethane was used, with respect to benzoyl chloride, in the preparation of 1 in order to reduce double benzoylation. One may be able to further increase the yield of 1 by increasing the amount of diphenylmethane.

According to ^{1}H NMR, 1 was contaminated with a small amount of diphenylmethane, but it should not interfere with the polymerization. Reaction of 1 with $POCl_3$ gave 2 in almost quantitative yield.

We adapted the polymerization conditions reported for the preparation of PPV-P from 4-(α,α-dichlorobenzyl) toluene [13,14] for the polymerization of 2. It is interesting to note that, during the polymerization of 2, HCl evolution took place at about 150°C which is close to that (140°C) found for the polymerization of 4-(α,α-dichlorobenzyl) toluene to give PPV-P [13, 14].

The structure of PPV-DP-1, 2 and 3 was confirmed as the expected PPV-DP by their ^{13}C NMR spectra, as exemplified by the spectrum of PPV-DP-2 shown in Fig. 1. The spectrum is identical to that reported by Hörhold for PPV-DP, prepared by dechlorination of bis(phenyldichloromethyl)benzene with chromium (II) acetate [1,8]. And, the peak assignment given in the spectrum is the assignment given by Hörhold [1,8].

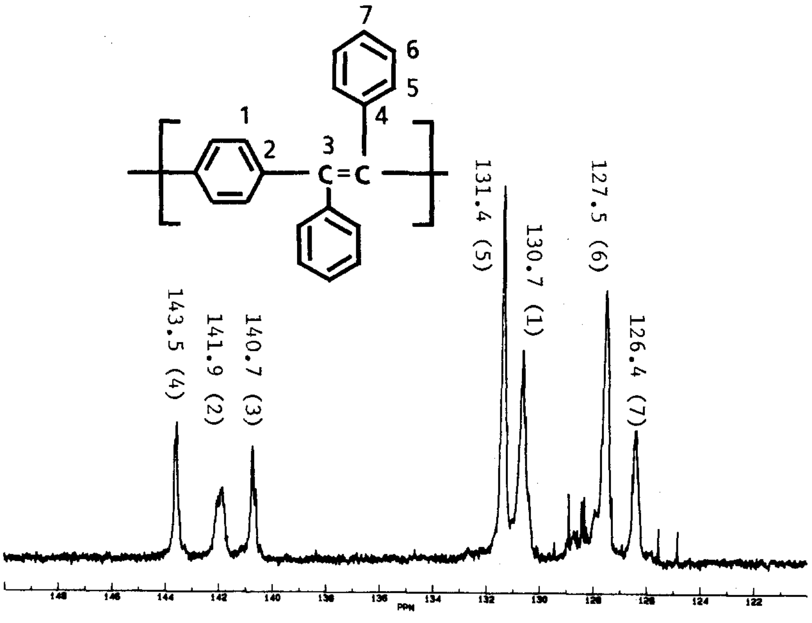
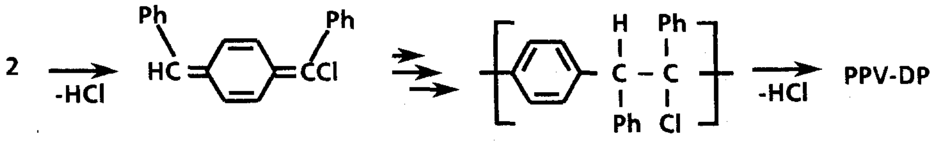


Figure 1. ^{13}C NMR spectrum of PPV-DP-2 ($CDCl_3$)

In light of the NMR result, we postulate the following polymerization mechanism (EPE-mechanism) for the formation of PPV-DPs from 2. A similar mechanism has been proposed for the polymerization of 4-(α,α-dichlorobenzyl) toluene to form PPV-P [13,14].



	PPV-DP*	PPV-DP-1	PPV-DP-2	PPV-DP-3
GPC Data**				
Mn		1900	13000	14000
Mw		7300	36000	40000
Mw/Mn		3.84	2.74	2.88
Elemental Analysis				
%C	94.49	93.65	93.31	92.78
%H	5.51	5.48	5.52	5.64
%Cl	0	0.85	1.89	1.78
Total	100	99.98	100.72	100.2

* Ideal PPV-DP. ** in THF.

The GPC and elemental analysis data for PPV-DP-1, -2 and-3 are given in the above table. PPV-DP-1, which is the bulk polymerized product has the lowest molecular weights, in agreement with that for the polymerization of 4-(α,α-dichlorobenzyl) toluene [13,14]. Longer reaction time seems to increase the molecular weight of the polymer. The molecular weights of PPV-DP-2 and -3 are higher those of PPV-P (Mn = 11900; Mw = 23000) prepared under similar conditions [14]; but they are lower than that reported for PPV-DP (Mn = 23000 by VPO) prepared by Hörhold [1,8].

In conclusion, we have found a convenient method for the preparation of PPV-DP. We are investigating the possibility of using this method for the preparation of various PPV-DP derivatives such as those reported in reference 1, in order to test its generality.

References

1. Hörhold, H. -H.; Helbig, M. *Makromol. Chem., Macromol. Symp.* **1987,** *12,* 229.
2. Mahrt, R.; Yang, J.-P.; Greiner, A.; Bassler, H.; Bradley, D. D. C. *Makromol. Chem. Rapid Commun.* **1990,** *11,* 415.
3. Kawai, T.; Iwasa, T.; Kuwabara, T.; Onoda, M.; Yoshino, K. *Jpn. J. Appl. Phys.* **1990,** *29,* 1833.
4. Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun.* **1984,** *25,* 327.
5. Takiguchi, T.; Park, D. H.; Ueno, H.; Yoshino, K. *Synth. Met.* **1987,** *17,* 657.
6. Singh, B. P.; Prasad, P. N.; Karasz, F. *Polymer* **1988,** *29,* 1940.
7. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; MacKay, K.; Friend, R. H.; Burns, P. L.; Holmes A. B. *Nature* **1990,** *347,* 539.
8. Hörhold, H. -H.; Opfermann, J.; Raabe, D.; Rathe, H.; Klee, J. *Izv. Akad. Nauk. SSSR Ser. Khim.* **1981,** (6), 23.
9. Hoyt, J. M.; Koch, K.; Sprang, C. A.; Stregevsky, S.; Frank, C. E. *Polym. Prepr.* **1964,** *5,* 680.
10. Feast, W. J.; Millichamp, I. S. *Polym. Commun.* **1983,** *24,* 102.
11. DeKoninck, L.; Smets, G. *J. Polym. Sci. Part A-1* **1969,** *7,* 3313.
12. Hörhold, H.-H.; Gottschaldt, J.; Opfermann, J. *J. Prakt. Chem.* **1977,** *319,* 611.
13. Opfermann, J.; Scherf, U.; Raabe, D.; Nowotny, J.; Hörhold, H.-H. *Angew. Makromol. Chem.* **1986,** *142,* 91.
14. Raabe, D.; Hörhold, H. -H.; Scherf, U. *Makromol. Chem., Rapid Commun.* **1986,** *7,* 613.
15. Delacre, M. *Bull. Soc. Chim. Belges* **1909,** *5,* 952 (CA 1910, 448).

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