

Synthesis of Multiblock Copolymers of Poly(2-vinylpyridine) and Polyoxyethylene

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ABSTRACT: Telechelic dihydroxy poly(2-vinylpyridine) (THPVP) samples with different molecular weights were synthesized by using lithium α -methylnaphthalene as an anionic initiator in mixed solvents of benzene and tetrahydrofuran (THF). Then multiblock copolymers of poly(2-vinylpyridine) (P2VP) and polyoxyethylene (PEO) were obtained by condensing THPVP and PEO with dichloromethane in the presence of potassium hydroxide. The effects of reaction time, molecular weight of PEO and THPVP, and raw material ratio PEO/THPVP (w/w) were investigated. The best conditions were found. The copolymers can be purified

by water and toluene. The purified copolymers were characterized by infrared (IR) and ^1H nuclear magnetic resonance ($^1\text{H-NMR}$). The PEO segment content was calculated from the integral curve of $^1\text{H-NMR}$ spectra. The results showed that these multiblock copolymers were connected through oxymethylene. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1632–1636, 2003

Key words: poly(2-vinylpyridine); polyoxyethylene; block copolymer; anionic polymerization

INTRODUCTION

Block copolymers with amphiphilic character, having a large solubility difference between hydrophilic and hydrophobic segments, are known to lead, in the presence of oil, water, and alcohol, to the formation of transparent phase. The copolymer chains in the dispersed phase present a micellar structure such that the hydrophobic and hydrophilic parts are solvated preferentially by oil and water, respectively.¹ Block copolymers containing hydrophilic polyoxyethylene (PEO) segments and other hydrophobic segments have attracted much attention, because PEO segments are not only hydrophilic, but also nonionic and crystalline, and can complex monovalent metallic cations.² The amphiphilic nature of these copolymers containing incompatible segments gives rise to special properties in selective solvents, at surfaces as well as in the bulk, owing to microphase separation morphologies. They have many uses including polymeric surfactants, electrostatic charge reducers, compatibilizers in polymer blending, phase transfer catalysts or solid polymer electrolytes,² and controlled release of drugs.³

After doping electron-conducting poly(2-vinylpyridine) (P2VP)^{4–8} and poly(4-vinylpyridine)^{4,6} backbones with PEO chains that can be complexed with alkali metal salts, ion-conducting polymers were ob-

tained. These mixed (electron- and ion-) conducting polymers displayed superior discharge characteristics as polymer electrodes in polymer electrolytes due to the decreased contact resistance between electrode materials and the polymer electrolyte in solid-state cells. After doping, the mixed (electron and ion) conductivity of the copolymer of EO and 4-vinylpyridine or 2-vinylpyridine was intermediate between ionic and electronic conductivity.

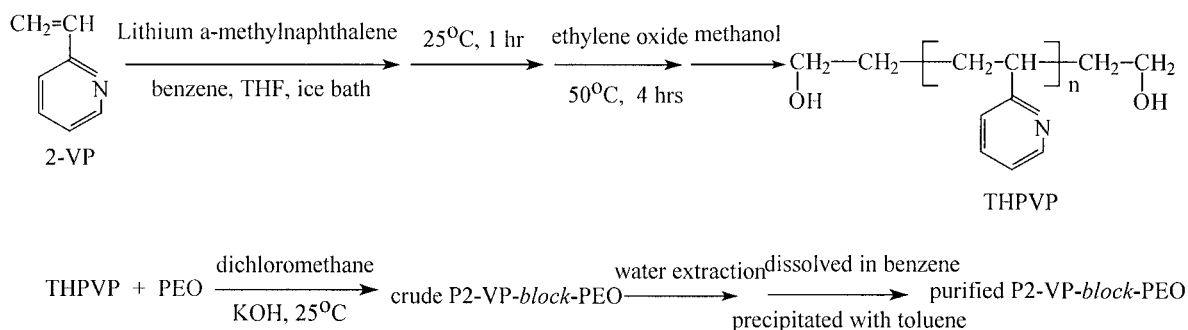
The block copolymer of poly(2-vinylpyridine) and PEO was prepared via anionic polymerization by Galot et al.⁹ But the reaction condition was very rigorous and very low temperature was required. In this article, telechelic dihydroxy poly(2-vinylpyridine) (THPVP) samples with number-average molecular weight from 2000 to 5000 were synthesized by the anionic polymerization of 2VP in the gentle conditions, using lithium α -methylnaphthalene as the initiator, benzene and tetrahydrofuran (THF) as the solvents, and EO as the hydroxylation reagent. Multiblock copolymers of P2VP and PEO were obtained by condensing THPVP and PEO with dichloromethane in the presence of potassium hydroxide.

EXPERIMENTAL

Materials

THF was distilled over CaH_2 (Aldrich). Benzene was dried overnight with 4 Å molecular sieves and distilled over CaH_2 . Dichloromethane was distilled. Commercial 2VP was distilled twice over CaH_2 before

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Scheme 1 Synthesis of THPVP and P2VP-*block*-PEO.

used. Commercial EO was treated with KOH and CaH_2 successively, then distilled into a cold trap and stored in a refrigerator. Lithium α -methyl-naphthalene was synthesized in our laboratory. PEOs (Kohjin) with molecular weights of 600, 800, 1000, and 2000 were distilled at reduced pressure in the presence of toluene in order to remove water. Other pure grade reagents were used without further purification.

Synthesis of THPVP

Under nitrogen atmosphere, a small amount of THF solution of lithium α -methyl-naphthalene was dropped into the 200 mL benzene and 50 mL THF solution with 50 mL 2VP via syringe to scavenge the impurities of the reaction system until the light yellow color ceased to disappear. The required amount of THF solution of lithium α -methyl-naphthalene was then injected by means of syringe. The reaction solution became dark red and was cooled in an ice bath for about 10 min in order to prevent an explosion. Then the reaction was maintained at 25°C for 1 h with a magnetic stir. An excess of the benzene solution of EO was injected into the reaction system, allowing it to react at 50°C for 4 h. The reaction was terminated by a small amount of methanol. The product was precipitated out and washed with ethyl ether. The precipitate was dissolved in chloroform and reprecipitated with ethyl ether, filtered, and vacuum dried to constant weight. The number-average molecular weight of the THPVP was measured with a Knauer VPO apparatus by using chloroform as the solvent.

Synthesis of multiblock copolymers of P2VP and PEO (P2VP-*block*-PEO)

Sixty milliliters of dichloromethane and 8 g KOH powder were placed into a 250 mL three-necked flask and stirred at 25°C for a half hour; then the 40 mL dichloromethane solution of total weight 20 g THPVP and PEO was added again. After a half hour, 4 g KOH powder was added, then added again every 1 h for twice. The reaction solution was continuously stirred

for 20 h. After vacuum drying to constant weight, the crude product obtained was extracted with water three times to separate out the unblocked PEO. Then the residue was dissolved in benzene and the unblocked THPVP was precipitated out by adding toluene. The block copolymer in the supernatant was obtained after evaporating off the benzene and toluene and vacuum drying at 80°C to constant weight. The weight percentage content of PEO in the block copolymer was calculated by use of the $^1\text{H-NMR}$ spectrum.

Characterization of the purified block copolymers

Infrared (IR) and ultraviolet (UV) spectra of the purified block copolymers were recorded on a Shimadzu IR 408 spectrophotometer and a Shimadzu UV 240 spectrophotometer, respectively. ^1H nuclear magnetic resonance ($^1\text{H-NMR}$) spectra of the purified block copolymers were recorded with a Bruker Ac-80 NMR spectrometer, using CDCl_3 as the solvent and tetramethylsilane (TMS) as an internal standard. The intrinsic viscosity data $[\eta]$ were obtained by using a Ubbelohde viscometer at 30°C and dimethylformamide (DMF) was the solvent.

RESULTS AND DISCUSSION

Synthesis of THPVP

THPVP is synthesized by the anionic polymerization of 2VP, as in Scheme 1, using benzene and THF as the solvents and EO as the hydroxylation reagent. Lithium α -methyl-naphthalene is used as the anionic initiator because of its advantages: (1) lithium α -methyl-naphthalene is liquid in the room temperature and (2) lithium α -methyl-naphthalene is soluble in both polar and nonpolar organic solvents. The concentration of lithium α -methyl-naphthalene in THF obtained in our laboratory is about 1 mol/L.

In order to obtain THPVP with the high molecular weight, the reaction time in 50°C should be prolonged. In this work, five THPVP samples with different mo-

TABLE I
Effect of Reaction Time

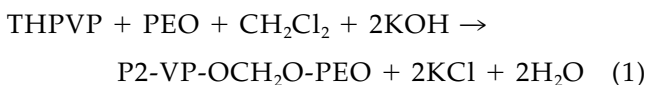
Reaction time (h)	$[\eta]$ (dL/g)	Yield (%)	PEO (wt %)
8	1.27	25.0	24.0
13	1.28	30.5	25.4
20.5	1.31	38.0	30.2
23.5	1.31	37.8	35.5

Conditions: M_n of THPVP is 3900; M_n of PEO is 600; raw meal ratio PEO/THPVP = 6/4 (w/w); reaction temperature is 25°C.

molecular weight of 2400, 3900, 4600, 5000, and 5400, respectively, were synthesized.

Synthesis of P2VP-*block*-PEO

THPVP and PEO can be connected together with dichloromethane in the presence of potassium hydroxide as in Scheme 1. The reaction equation is as below:



The crude reaction product, containing the homopolymer of P2VP and PEO, unreacted THPVP and PEO, and the block copolymer, is purified according to the same method as that of the graft copolymer of P2VP and PEO.⁸ The unreacted PEO and its homopolymer can be separated from the graft copolymer by water extractions. Hence, this water solution was dried and dissolved in benzene, followed by precipitation with a large excess of toluene. A UV spectrum showed that there is no P2P at 264 nm in the supernatant, and the precipitate is the block copolymer. After extraction in water, the product containing the homopolymer of P2VP and the block copolymer is dissolved in benzene, and this solution is precipitated with toluene (6 times the volume of benzene). The block copolymer is in the supernatant, and the precipitate is the homopolymer of P2VP. The supernatant is dried to constant weight. The efficiency of purification was determined by extraction of a mixture of PEO and THPVP in the same way. However, when the composition of PEO in the block copolymer is higher than 40 wt %, some block copolymer will be extracted by water.

The effect of the reaction time on this reaction was investigated by the measurement of the yield of P2VP-*block*-PEO, $[\eta]$ and the weight percentage content of PEO in the block copolymer. The results are listed in Table I. From Table I, we can see that the yield of the block copolymers increases from 25 to 38% with the increase of the reaction time from 8 to 20.5 h and has no obvious change with the further increase of the reaction time. In the initial stage of this reaction, increasing the reaction time, more THPVP and PEO are connected with dichloromethane and the yield in-

creases. In the latter stage of this reaction, the reaction system becomes increasingly viscous due to the formation of a large number of P2VP-*block*-PEO. THPVP and PEO themselves are macromolecules and the molecular chains move with difficulty in the viscous system, so the activity of THPVP and PEO decreases, and the yield increases no longer.

The effect of the reaction time on $[\eta]$ of P2VP-*block*-PEO is very small. The cause is that the increase of $[\eta]$ of P2VP-*block*-PEO mainly depends on P2VP segments because the molecular weight of THPVP is 3920, much bigger than that of PEO, which is 600 in this research section, and moreover, the pyridine ring in P2VP segments is rigid. With the progress of the reaction, the amount of THPVP molecules decreases and the viscosity of the reaction system increases. The low activity allows THPVP to participate in P2VP-*block*-PEO no longer. The increase of the yield this time is because of the participation of PEO, which can be testified to from the experimental result that the weight percentage content of PEO in the block copolymer increases with increasing reaction time, as showed in Table I. From the above discussion, we know that the best reaction time is about 20 h.

Table II shows the effect of molecular weight of PEO from 600 to 2000 for this reaction. With the increase of molecular weight of PEO, $[\eta]$ of the resulted P2VP-*block*-PEO first increases then decreases, and the yield first is constant then decreases; the weight percentage content of PEO in the block copolymer decreases all along. The increase of molecular weight of PEO weakens the activity of PEO and the amount of PEO participated in the block copolymer decreases, i.e., the weight percentage content of PEO in the block copolymer decreases. At the same time, the increase of molecular weight of PEO up to 1000 or more will enhance the viscosity of the reaction system and the weak activity of PEO and THPVP, especially PEO, results in the sharp decrease of the yield of the block copolymer from 41 to 17.2 and to 8.0%. The increase of $[\eta]$ of P2-VP*block*-PEO results from the increase of the weight percentage content of P2VP in the block copolymer because of the rigidity of the pyridine ring. It is surprising that $[\eta]$ abruptly decreases down to 0.60 when the molecular weight of PEO is 2000. The possible cause is that the weak activity of THPVP and

TABLE II
Effect of Molecular Weight of PEO

M_n (PEO)	$[\eta]$ (dL/g)	Yield (%)	PEO (wt %)
600	1.05	41.0	40.0
800	1.29	41.2	27.1
1000	1.44	17.2	24.7
2000	0.60	8.0	13.1

Conditions: M_n of THPVP is 4600; reaction time is 20 h; other conditions as in Table I.

TABLE III
Effect of Molecular Weight of THPVP

M_n (THPVP)	$[\eta]$ (dL/g)	Yield (%)	PEO (wt %)
2400	1.40	37.2	20.4
3900	1.27	38.0	30.2
4600	1.05	41.0	40.0
5000	0.99	46.0	32.8

Conditions: M_n of PEO is 600; other conditions as in Table II.

PEO results in the small molecular weight of P2VP-*block*-PEO. As known from the results of the yield, $[\eta]$, and the weight percentage content of PEO of the block copolymer, the molecular weight of PEO has a large effect on this reaction and PEO of molecular weight 600 is most favor.

In Table III, the effect of molecular weight of THPVP from 2400 to 5000 in this reaction is investigated. With the increase of molecular weight of THPVP, $[\eta]$ of P2VP-*block*-PEO decreases and the yield increases slowly all along; the weight percentage content of PEO in the block copolymer first increases and then decreases. The increase of molecular weight of THPVP weakens the activity of THPVP and the amount of THPVP participated in the block copolymer decreases, i.e., the weight percentage content of PEO in the block copolymer increases, which is the cause of the decrease of $[\eta]$ of the block copolymer. It is inexplicable that the yield increases with the increase of molecular weight of THPVP. We do not know the cause now. But from the experimental results, we consider that THPVP of molecular weight about 4600 is more favorable to this reaction.

Table IV illuminates the effect of raw meal ratio PEO/THPVP (w/w) on this reaction. With the increase of PEO/THPVP, the yield and the weight percentage content of PEO in the block copolymer increases sharply.

Characterization of P2VP-*block*-PEO

The IR spectrum of the purified P2VP-*block*-PEO copolymer is shown in Figure 1. There are characteristic peaks at 1060–1150 cm^{-1} for the C—O—C ether group, peaks at 2850–2960 cm^{-1} for the —CH₂— and

TABLE IV
Effect of Raw Meal Ratio PEO/THPVP

PEO/THPVP (w/w)	$[\eta]$ (dL/g)	Yield (%)	PEO (wt%)
8/2	0.86	63.5	75.0
7/3	0.83	62.0	46.1
6/4	0.84	44.5	30.4
5/5	2.23	27.5	22.0

Conditions: M_n of THPVP is 5400; other conditions as in Table III.

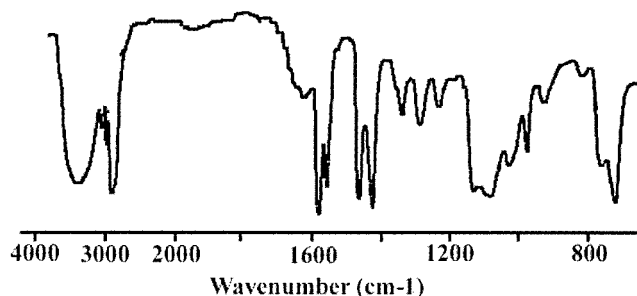


Figure 1 IR spectrum of P2VP-*block*-PEO.

—CH— groups, peaks at 1440, 1475, 1570, and 1590 cm^{-1} for the C=C and C=N groups in the pyridine ring, and peaks at 740 and 780 cm^{-1} for the C—H of the pyridine. These indicate that the copolymers are composed of EO and 2VP units.

Chart 1 shows the schematic representation of P2VP-*block*-PEO copolymer and Figure 2 is the ¹H-NMR spectrum of the multiblock copolymer. The peaks at 6.3–7.3 and 8.3 ppm are the protons of pyridine ring, the peaks at 3.5–3.9 ppm are the protons of —CH₂CH₂O—, the peaks at 1.8 and 2.7 ppm are the protons of —CH₂CH(C)— in P2VP, and the peak at 4.7 ppm is the protons of —OCH₂O—, which is the block point of P2VP and PEO. Comparison with the spectra of P2VP and PEO also indicates that the copolymers are composed of EO and 2VP units, and P2VP and PEO are connected through oxymethylene.

The PEO segment content can be calculated from the integral curve of ¹H-NMR spectra. We suppose that *A* is the peaks area of 1.8 and 2.7 ppm for —CH₂CH(C)— in the P2VP segment and *B* is the peaks area of 3.5–3.9 ppm for —CH₂CH₂O— in then PEO segment, and then

$$\frac{A}{B} = \frac{3m}{4n} \quad m = \frac{4A}{3B}n \quad (2)$$

where *m* is the repeat unit number of 2VP in P2VP segment and *n* is the repeat unit number of EO in PEO segment. The weight percentage content of PEO in the block copolymer can be obtained from the equation below:

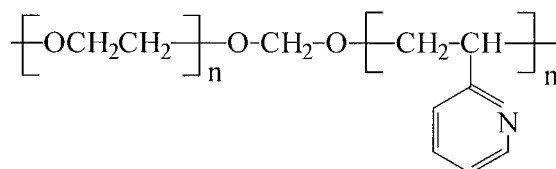


Chart 1 Schematic representation of P2VP-*block*-PEO copolymer.

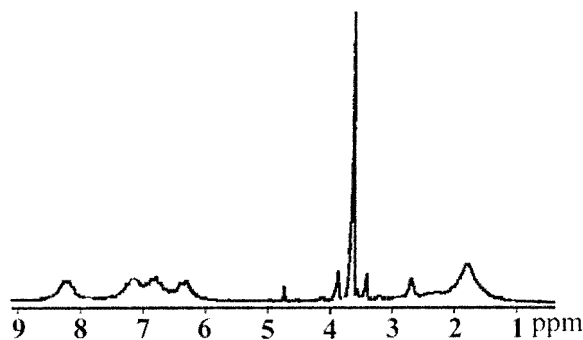


Figure 2 $^1\text{H-NMR}$ spectrum of P2VP-*block*-PEO.

$$\begin{aligned} \text{PEO wt \%} &= \frac{\text{PEO}}{\text{P2VP} + \text{PEO}} = \frac{44.05n}{105m + 44.05n} \\ &= \frac{132.15B}{420A + 132.15B} \quad (3) \end{aligned}$$

In Figure 2, $A = 0.8$ and $B = 0.55$, so PEO wt % = 17.8%.

CONCLUSION

THPVP samples were synthesized by the anionic polymerization of 2-vinylpyridine. Multiblock copolymers of poly(2-vinylpyridine) and polyoxyethylene were obtained by condensing THPVP and PEO with

dichloromethane in the presence of potassium hydroxide. The best reaction conditions are that the reaction time is 20 h, the molecular weight of PEO is 600, and the molecular weight of THPVP is 4600. The copolymers can be purified by water and toluene. The purified products were characterized by IR and $^1\text{H-NMR}$, and the PEO segment content was calculated from the integral curve of $^1\text{H-NMR}$ spectra. The results show that these multiblock copolymers were connected through oxymethylene.

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