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Synthesis and characterization of linear diblock and triblock copolymers of 2-vinyl pyridine and ethylene oxide

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Abstract

This work describes a synthesis of linear diblock and triblock copolymers of 2-vinyl pyridine (2VP) and ethylene oxide (EO). The overall synthetic approach involved polymerization of 2VP, followed by polymerization with EO. Neutralization of the reactive end-groups of the living diblock P2VP-*b*-PEO$^{(-)}$K$^{(+)}$ produced the diblock copolymer P2VP-*b*-PEO. Reaction with dibromoxylene in the presence of CsI led to the triblock copolymer, P2VP-*b*-PEO-*b*-P2VP. The triblock copolymers were separated by fractionation at 40 °C. Copolymers were characterized by size exclusion chromatography, light scattering and nuclear magnetic resonance spectroscopy. Characterization showed that the materials have high molecular and compositional homogeneity. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Benzylpotassium; Sequential anionic polymerization; P2VP-*b*-PEO-*b*-P2VP

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1. Introduction

Polyethylene oxide (PEO), is a biocompatible, hydrophilic [1], nonionic crystalline polymer that complexes with monovalent cations [2]. Furthermore, block copolymers of PEO with hydrophobic monomers self-assemble in water and form micelles [3–7]. Because of the above properties, block copolymers of ethylene oxide (EO) are used in many commercial applications such as cosmetics, water treatment, paper and petroleum [8–11]. They are also strong candidates for technological advances in targeted drug delivery. Consequently, the synthesis of well-defined EO copolymers is highly important for designing new materials.

The synthesis of EO block copolymers using organolithium initiators suffers one disadvantage. After the addition of one EO molecule, the strong lithium alkoxide group is not capable of propagating the polymerization of EO [12]. Three different methodologies have been reported for overcoming this problem. The first involves the reaction of the living block precursor with EO, followed by neutralization of the active lithium alkoxide groups with HCl. The resulting –OH groups are reacted with an organopotassium compound to produce potassium alkoxide groups. The –OK group is reactive with EO, and the polymerization can proceed [13]. A second methodology involves transformation of the –OLi bond, by complexation of lithium with a strong base such as *tert*-butyl phosphazene (*t*-BuP$_4$), to more active species which are capable of polymerizing with EO [14]. The third strategy involves the use of an appropriate initiator, which successfully polymerizes EO and other monomers that make up targeted block copolymers [15–17].

Such an initiator is benzyl potassium (BP), introduced recently by Ekizoglou and Hadjichristidis [18]. Using this initiator, we have prepared triblock copolymers of EO and 2-vinyl pyridine (2VP) for the first time as well as selected diblock copolymers.

2. Experimental part

Purification of EO, solvents (benzene, (99%, Aldrich), THF, (99%, Aldrich)) and methanol, (99%, Aldrich) to standards required for anionic polymerization are described in detail elsewhere [19].

2-Vinyl pyridine (98%, Aldrich) was dried over CaH$_2$ overnight, exposed to Na mirror for a few minutes, and finally, distilled over trioctylaluminum. *p*-dibromoxylene (PDBX) (99%, Aldrich) and cesium iodine (CsI) (99.999%, Aldrich) was dried on a vacuum line overnight, and then dissolved in THF. *s*-BuLi was prepared from *s*-BuCl and a lithium dispersion [19]. *t*-BuOK (solution 1 M in THF, Aldrich) was used as received. Synthesis of benzyl potassium is described in detail elsewhere [18]. All

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manipulations were performed under high vacuum in 1,1-diphenyl hexyllithium (DPHL)-washed and solvent-rinsed glass reactors. Reagent addition was done through break-seals.

Size exclusion chromatography (SEC) experiments were done at 25 °C using a Waters Model 510 pump, a Waters Model 410 differential refractometer and three styragel columns having a porosity range from 10^3 to 10^6 Å. The carrier solvent was a mixture of chloroform/triethylamine (95/5, v/v) at a flow rate of 1.0 ml/min.

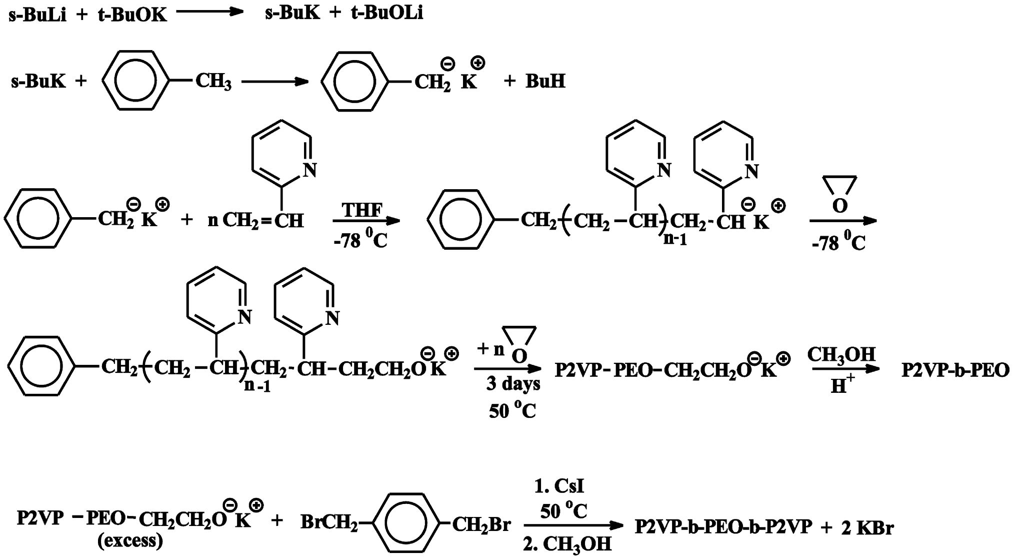
The weight-average molecular weight (M_w) of the block copolymers was measured at 25 °C with a Chromatix KMX-6 low angle laser light scattering photometer. This instrument was equipped with a helium–neon laser operating at a wavelength of 633 nm. Methanol was used as solvent, and distilled over magnesium prior to use. Refractive index increments of the copolymers, dn/dc, were measured at 25 °C in methanol with a Chromatix KMX-16 refractometer, operating at 633 nm and calibrated with NaCl solutions. M_w values were obtained from $(KC/\Delta R_\theta)^{1/2}$ vs C plots (ΔR_θ, excess Rayleigh ratio; K, combination of known optical constants) to minimize curvature due to the third virial coefficient. In all cases the correlation coefficient was better than 0.99. Nuclear magnetic resonance (NMR) spectra were generated using a Bruker 400 MHz instrument with $CDCl_3$ as solvent.

3. Synthesis of the di- and tri-block copolymers

3.1. Synthesis of linear poly(2-vinyl pyridine)-b-polyethylene oxide copolymers

Reactions used for the preparation of P2VP-*b*-PEO diblock copolymers are shown in Scheme 1.

As a typical example, the synthesis of the diblock copolymer D 30/25 (the first number indicates the approximate total molecular weight and the second the P2VP content) is given. A reactor was attached to a high vacuum line, evacuated and flame dried. Then, 1 ml of 1.6 M solution of *n*-BuLi in hexane and a slight excess of diphenylethylene (DPE) (C=C/C–Li ≈ 1.2) were added via septum to a purge section flask resulting in the formation of a deep red DPHLi solution. The septum was then removed by heat sealing the glass septum holder. One hundred milliliters of THF were distilled under vacuum in the purge section flask through the vacuum line and the whole reactor was removed from the vacuum line by heat sealing. The apparatus was thoroughly washed with DPHLi solution. The solution was then transferred back to the purge section flask and immersed in a water bath at 40 °C. The apparatus was rinsed several times by distilling THF from the purge section to the reactor under vacuum. Thus, traces of DPHLi along with impurities or reaction products were transferred to the purge section flask. Finally the solvent was distilled into the polymerization flask, frozen by liquid nitrogen, and the purge section was removed by heat sealing. The temperature of THF was lowered to −78 °C using a dry-ice/isopropanol bath. One milliliter of a 5.8×10^{-4} mol/ml solution of BP in THF was added to the reactor. Subsequently, 3.4 g of 2VP monomer was distilled into the reactor under vigorous stirring, while keeping the temperature at −78 °C. The polymerization was allowed to proceed for 15 min. Then, 0.5 g of EO was added, and the temperature was raised slowly at room temperature. 30 ml (~1 g of P2VP) of the solution was removed to a side flask by heat sealing, and quenched with degassed methanol. After addition of 7.1 g of EO, the temperature was increased to 50 °C and the solution was left undisturbed for 3 days. Thirty-five milliliters of the diblock copolymer solution were removed and quenched with methanolic HCl. The P2VP-*b*-PEO copolymer was recovered by precipitation



Scheme 1.

from a 20 ppm solution of 2,6-di-*tert*-butyl-*p*-cresol in hexane, followed by drying in the vacuum line.

3.2. Synthesis of linear poly(2-vinyl pyridine)-b-polyethylene oxide-b-poly(2-vinyl pyridine) copolymers

The reaction sequence used for the synthesis of the triblock copolymers is shown in Scheme 1. The living block copolymer D 30/25, prepared in Section 3.1, was used for the synthesis of the triblock copolymer T 60/25. The procedure, given below, is a typical example for the synthesis of the triblock copolymers. To the remainder solution (see Section 3.1), 1 ml of a 0.8×10^{-4} mol/ml of PDBX in THF was added, along with 1 ml of a 3×10^{-5} mol/ml solution of cesium iodide in THF. The linking reaction was monitored by SEC to ensure complete reaction of the linking agent. Finally, the living polymer was deactivated by addition of degassed methanol in the presence of HCl. Crude product was recovered by precipitation in hexane, followed by drying in the vacuum line.

3.3. Fractionation

Block copolymers were fractionated by using chloroform/*n*-hexane as a solvent/non-solvent system. The copolymer solution temperature was maintained higher than 40 °C to avoid crystallization of PEO, which occurs at 35 °C. The fractionation was monitored by SEC.

4. Results and discussion

The methodology used for the synthesis of the diblock copolymers can be described as a one-pot, sequential addition of two monomers. The synthesis was monitored by SEC (Fig. 1).

The molecular characteristics of the diblock and triblock copolymers, obtained by LALLS, SEC and NMR spectroscopy are given in Tables 1 and 2, respectively.

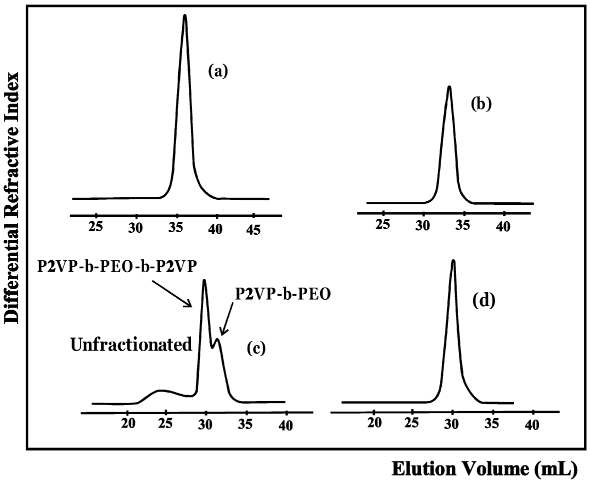


Fig. 1. Monitoring the synthesis of P2VP-*b*-PEO D 30/45 and P2VP-*b*-PEO-*b*-P2VP T 60/45 block copolymers by SEC. (a) Poly(2-vinyl pyridine) precursor, (b) Poly (2-vinyl pyridine-*b*-ethylene oxide) diblock copolymer, (c) Reaction product after the linking reaction of (b) with dibromoxylene, (d) Fractionated triblock copolymer P2VP-*b*-PEO-*b*-P2VP.

As seen in the SEC chromatograms in Fig. 1, the P2VP homopolymer, along with the final diblock and triblock copolymers, exhibit low polydispersity indices. In most cases no indication of P2VP homopolymer was found. In the case of D 200/50 approximately 10% of P2VP homopolymer was formed. This was attributed either to the incomplete purification of the EO monomer, or to reaction of the living ends with the carbon atom alpha-to the aromatic ring nitrogen of 2VP, when the temperature was raised from −78 to 25 °C. The copolymer was isolated by fractionation. For molecular weights up to 5.0×10^4, the side products were lower than 5%.

A 20% molar excess of reactive –OK end-groups over the $-CH_2Br$ groups was used to ensure complete linking. After completion of the linking reaction, in addition to the triblock copolymer and the excess of living diblock copolymer, a small amount of high molecular weight side

Table 1
Molecular characteristics of linear diblock (D) copolymers of 2-vinyl pyridine (2VP) and ethylene oxide (EO) (P2VP-*b*-PEO)

Sample[a]	M_w P2VP[b] ($\times 10^{-3}$)	Total M_w[b] ($\times 10^{-3}$)	% $P2VP_{calc}$[c] (w/w)	% P2VP[d] (w/w)	$I = M_w/M_n$[e]	dn/dc[f]
D 25/25	6.1[e]	24.3	25	24	1.05	0.157
D 30/35	9.8[e]	28.5	34	35	1.07	0.164
D 25/45	10.9[e]	23.9	46	45	1.05	0.173
D 35/40	13.2[e]	32.7	40	40	1.04	0.169
D 30/50	15.1	29.8	50	50	1.05	0.176
D 50/60	28.3	48.5	58	59	1.03	0.181
D 200/50	98.1	191.3	51	51	1.06	0.176

[a] The first number indicates the approximate total molecular weight and the second the P2VP content.

[b] Low angle laser scattering in CH_3OH at 25 °C.

[c] Calculated from the ratio of the M_w of P2VP precursor and total M_w.

[d] ^1H NMR in $CDCl_3$.

[e] Size exclusion chromatography in THF at 30 °C.

[f] Differential refractometry in CH_3OH at 25 °C.

Table 2
Molecular characteristics of linear triblock (T) copolymers of 2-vinyl pyridine (2VP) and ethylene oxide (EO) (P2VP-*b*-PEO-*b*-P2VP)

Sample	$M_{\mathrm{n\ trib}}$[a] ($\times 10^{-3}$)	2VP[b] (wt%)	$I = M_w/M_n$[c]	d*n*/d*c*[d]
T 50/25	50.6	24	1.05	0.155
T 50/45	49.1	45	1.07	0.174
T 65/40	65.8	40	1.03	0.170

The first number indicates the approximate total molecular weight and the second the P2VP content.

[a] Low angle laser light scattering in CH_3OH at 25 °C.

[b] ^1H NMR in $CDCl_3$.

[c] Size exclusion chromatography in THF at 30 °C.

[d] Differential refractometry in CH_3OH at 25 °C.

products ($\approx$ 10%) were also formed. This can be attributed to reaction of living ends with the pyridine ring, forming high molecular weight graft copolymers. A catalytic amount of CsI was used to transform the $-CH_2Br$ groups to more reactive $-CH_2I$ groups in situ. As a consequence, the linking reaction was complete within 3 h. When the reaction was done without using CsI, the linking reaction required 3 days, and the side products were significantly increased. Side products were eliminated by fractionation. The yield was ranged between 60 and 70%.

Fractionation of the copolymer was performed at 40 °C to avoid crystallization of PEO. When the fractionation was done at 25 °C, no separation between the diblock and triblock copolymers was obtained.

The apparent weight averaged molecular weights, obtained by LALLS, was expected to be close to the real ones, due to the large d*n*/d*c* value of each polymeric block and the compositional homogeneity of the copolymers. For PEO, the d*n*/d*c* value was found to be 0.136 ml/g at 25 °C and for P2VP the value was 0.220 ml/g. The measured d*n*/d*c* values of the copolymers was the weight average of the d*n*/d*c* values of the two blocks (Tables 1 and 2).

Copolymer composition was obtained from ^1H NMR spectra, using four broad peaks from the four aromatic protons of P2VP in the range of 6.3–8.4 ppm, and the single peak at 3.7 ppm from the four protons of PEO.

Combined characterization results led to the conclusion that the synthesized diblock and triblock copolymers exhibit a high degree of molecular and compositional homogeneity. This is also supported by good agreement between the composition calculated from measured molecular weights for the P2VP precursors, the final copolymers, and those obtained by NMR spectroscopy.

5. Conclusions

Linear P2VP-*b*-PEO diblock copolymers and P2VP-*b*-PEO-*b*-P2VP triblock copolymers of 2VP and EO exhibiting a high degree of molecular and compositional homogeneity were synthesized by using sequential anionic polymerization, with benzylpotassium as initiator (diblock copolymers) and dibromoxylene (triblock copolymers) in the presence of CsI as the linking agent. CsI addition was a key parameter for promotion of the linking reaction of living P2VP-*b*-PEO diblock copolymers with the linking agent. It was found that copolymer fractionation should be done at 40 °C, to avoid crystallization of PEO. In a forthcoming paper the catalytic activity of block copolymer complexes with heavy metal ions in hydrogen reactions will be reported.

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