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SYNTHESIS, CHARACTERIZATION, AND CONDUCTIVITIES OF POLY(2-VINYLPYRIDINE)-*graft*-POLYOXYETHYLENE USING A MACROMER TECHNIQUE

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ABSTRACT

Poly(2-vinylpyridine) (P2-VP) with uniform polyoxyethylene (PEO) grafts was synthesized using a macromer technique. 2-Vinylpyridine was copolymerized with PEO macromer in solution by using azobisisobutyronitrile (AIBN) as the initiator. The effects of the amount of AIBN, the concentrations of 2-vinylpyridine and macromer, the number-average molecular weight of macromer, and the charging ratio of macromer to 2-vinylpyridine in the copolymerization were studied. The copolymerization rate of the PEO macromer with 2-vinylpyridine was also investigated. The grafting efficiency reached about 56%. The crude graft copolymer was purified by extraction and precipitation, and it was characterized by IR, ^{1}H-NMR, and Bruss membrane osmometry. The PEO grafts were doped with $LiClO_4$ and showed ionic conductivity around 4.10×10^{-6} S·cm^{-1} at 25°C whereas the P2-VP main chains were complexed with TCNQ to obtain electronic conductivity around 5.50×10^{-6} S·cm^{-1} at 25°C. The mixed (ionic and electronic) conductivity of the doped copolymer could reach about 5.40×10^{-5} S·cm^{-1} at 25°C and showed a synergistic effect.

INTRODUCTION

Since Milkovich [1] demonstrated the synthesis and applications of a variety of macromers, it has been established that the macromer technique is one of the best methods for the preparation of well-defined graft copolymers. Xie et al. [2] reported the synthesis of polyoxyethylene (PEO) macromers through the anionic polymerization of ethylene oxide (EO) in DMSO by using potassium napthalide in tetrahydrofuran as the initiator and methacryloyl chloride as the terminating agent.

Recently, some interesting novel polymers, such as poly[*N*-(3,6,9-trioxadecyl)pyrrole [3], poly[(2,5,8,11,14,17,20,23-octaoxapentacosyl methacrylate)-*block*-poly(4-vinylpyridine)] [4], and poly[3-methyl thiophene-*block*-ω-methoxyocta(oxyethylene)methacrylate] [5], have been reported. After doping an electron-conducting polypyrrole, poly(4-vinylpyridine) and poly(3-methylthiophene) backbones with short oligo(oxyethylene) side chains which can be complexed with alkali metal salts to get ion-conducting were obtained. 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 (ionic and electronic) conductivity [4] of the copolymer of EO and 4-vinylpyridine was intermediate between ionic and electronic conductivity. However, the DP of ethylene oxide in these copolymers was 8, and the synthesis should be carried out at −60°C. This paper deals with the synthesis of poly(2-vinylpyridine)-*graft*-PEO using PEO macromers whose number-average molecular weight varied from 3000 to 9000 in order to obtain a higher mixed (electronic and ionic) conducting copolymer. Synthesis of the graft copolymer is easy to accomplish by using AIBN as the initiator at 60°C. It is not necessary to proceed at a very low temperature. The ionic, electronic, and mixed (ionic and electronic) conductivities of these graft copolymers were studied.

EXPERIMENTAL

Materials

A.R. dimethylsulfoxide (DMSO) was dried with CaH_2 for 48 hours and distilled under nitrogen; the distillate was collected at 85–87°C/25 mmHg. Commercial ethylene oxide (EO) was treated with KOH and CaH_2 successively, then distilled into a cold trap and stored in a refrigerator. A.R. tetrahydrofuran (THF) was distilled over CaH_2. Commercial 2-vinylpyridine (2-VP) was distilled twice over CaH_2 before use. C.P. benzene was dried overnight with 4A Molecular Sieves and distilled over CaH_2. C.P. azobisisobutyronitrile (AIBN) was recrystallized from ethanol.

Synthesis of PEO Macromers [2]

Under nitrogen atmosphere, the THF solution of potassium napthalide was dropped into the DMSO solution of EO 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 potassium napthalide was then injected by means of a syringe. The mixture was cooled in an ice bath in order to keep the reaction temperature below 30°C for 2 hours so as to prevent an explosion. Then the reaction was maintained at 30°C for 6 hours. The reaction solution became dark yellow. The reaction was terminated by injecting an excess of α-methacryloyl chloride into the reaction system and allowing it to react at 30°C for 4 hours. 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 weight of the macromer ($\overline{M}_{ng}$) was measured with a Knauer VPO apparatus by using chloroform as the solvent.

Copolymerization of the PEO Macromer with 2-VP and Purification of Graft Copolymer

A certain amount of the dried macromer was dissolved in THF or benzene, and 2-VP and AIBN were added. Copolymerization was carried out at 60°C under nitrogen atmosphere with stirring for 24 hours. Then a small amount of hydroquinone was added to terminate the copolymerization. After vacuum drying to constant weight, the crude product obtained was extracted with water three times to separate out the ungrafted PEO macromer. Then the residue was dissolved in benzene and the homopolymer of 2-VP was precipitated out by adding toluene. The graft copolymer in the supernatant was obtained after evaporating off the benzene and toluene and vacuum drying at 80°C to constant weight. Conversion of 2-VP and the grafting efficiency (G.E.) can be calculated with the following equations:

$$\text{G.E.,\%} = \frac{(\text{macromer charged}) - (\text{macromer ungrafted})}{\text{macromer charged}} \times 100$$

$$\text{\% Conversion of 2-VP} = \frac{(\text{crude product}) - (\text{macromer charged})}{\text{2-VP}} \times 100$$

Characterization of the Purified Graft Copolymer

IR and UV spectra were recorded on a Shimadzu IR 408 spectrophotometer and a Shimadzu UV 240 spectrophotometer, respectively. The number-average molecular weights of the copolymers were determined by using a Bruss membrane osmometer with DMF as the solvent. The ^{1}H-NMR spectra were recorded with a Bruker Ac-80 NMR spectrometer, using $CDCl_3$ as the solvent and TMS as an internal standard.

Preparation of Complexes

The graft copolymer/$LiClO_4$ complex was prepared by evaporating a mixture of graft copolymer/benzene and $LiClO_4$/ethanol. The graft copolymer/TCNQ complex was prepared as follows: The graft copolymer was dissolved in distilled DMF, then TCNQ/DMF was added to the solution with stirring for 5 hours. The solvent was then evaporated. The graft copolymer/$LiClO_4$/TCNQ complex was prepared by a similar procedure. $LiClO_4$/ethanol was added with vigorous stirring to a DMF solution of TCNQ and graft copolymer. All complexes were dried thoroughly in a vacuum oven.

Measurement of Conductivities

Conductivities of the polymer complexes were measured with a DDS-11A conductometer operating at 1100–1200 Hz and 1.5 V.

RESULTS AND DISCUSSION

Effect of Total Concentrations of 2-VP and Macromer on Copolymerization

Figure 1 shows the effect of total concentrations of 2-VP and macromer on the copolymerization. With an increase of the total concentrations of 2-VP and macromer, the grafting efficiency gradually increased. This result can be explained as follows: The increase of concentrations enhances the collision probability of the macromer, thus increasing the grafting efficiency. At lower concentrations, more impurities are present in the copolymerization system, thereby inducing more termination of the active chain and reducing the grafting efficiency. Figure 1 also shows that the molecular weight of the copolymer increases with concentration. This result is expected since the kinetic chain length is usually proportional to the monomer concentration.

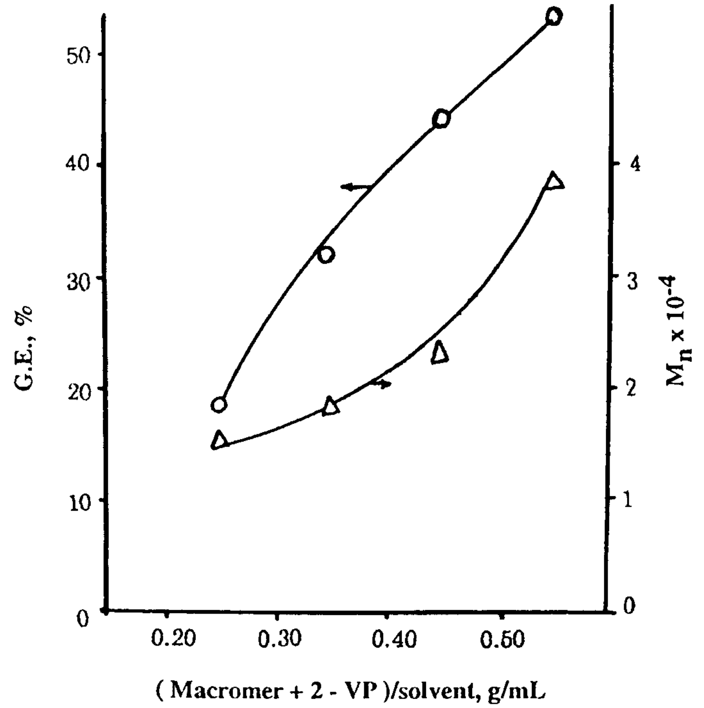

FIG. 1. Effect of total concentrations of 2-VP and macromer on the grafting efficiency (○) and molecular weight (△) of the copolymer (macromer/2-VP = 3/7 w/w).

Effect of Amount of Initiator on Copolymerization

The effect of the amount of initiator on the grafting efficiency and molecular weight of the copolymer is illustrated in Figure 2. The grafting efficiency increases and the molecular weight of the copolymer decreases with an increase in the amount of AIBN used. This is simply due to the fact that the concentration of active centers increases with an increase in AIBN, resulting in a decrease in the molecular weight of the copolymer and the viscosity of the solution. The latter helps the increase of grafting efficiency.

Effect of Molecular Weight of Macromer ($\overline{M}_{ng}$) on Copolymerization

Table 1 shows the effect of molecular weight of macromer ($\overline{M}_{ng}$) on the grafting efficiency and molecular weight of the copolymer. There are maxima value in both the grafting efficiency and molecular weight of copolymer with the increase of $\overline{M}_{ng}$. These may be explained as follows: If the $\overline{M}_{ng}$ is too small, the ability of homopolymerization of macromer is high (the homopolymer of PEO macromer is soluble in water), hence reducing the grafting efficiency and molecular weight of

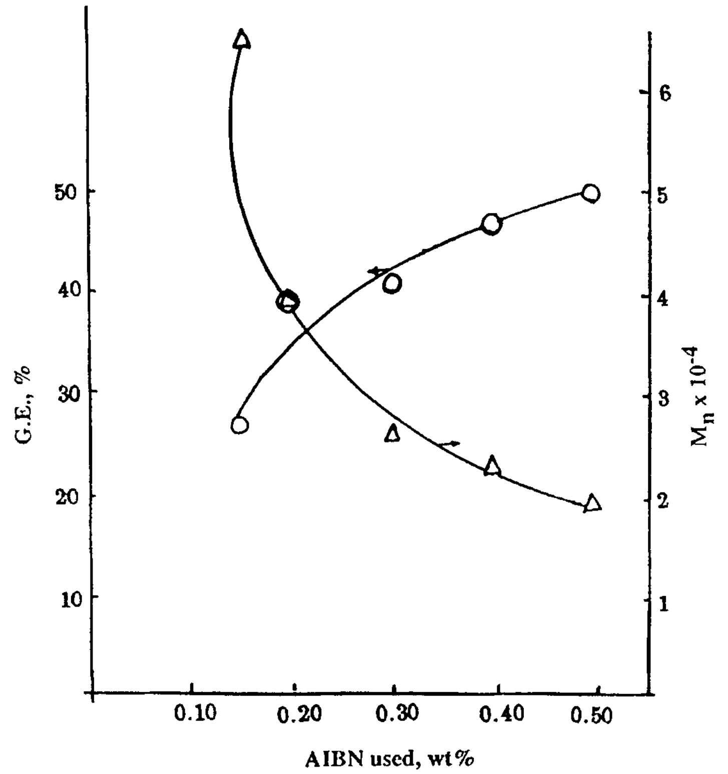

FIG. 2. Effect of amount of initiator on the grafting efficiency (○) and molecular weight (△) of the copolymer [macromer/2-VP = 3/7 w/w, 0.45 g (2-VP + macromer)/mL solvent].

TABLE 1. Effect of Molecular Weight of PEO Macromer ($\overline{M}_{ng}$) on the Grafting Efficiency and Molecular Weight of the Copolymer ($\overline{M}_{nc}$)[a]

	$\overline{M}_{ng}$				
	3203	4909	5504	6378	8971
G.E. (%)	40.0	49.3	53.0	51.6	35.3
$\overline{M}_{nc}$ ($\times 10^{-4}$)	1.33	1.46	2.51	3.83	2.66

[a] Polymerization conditions: macromer/2-VP = 3/7 (w/w), 60°C, 24 hours, THF, AIBN 0.4 wt%, 0.45 g (2-VP + macromer)/mL solvent.

copolymer. However, if the $\overline{M}_{ng}$ is too large, the active chain groups are less, thus decreasing the reactivity of macromer and reducing the grafting efficiency and molecular weight of copolymer.

Copolymerization Rate of the Macromer with 2-VP

Figure 3 shows the copolymerization rates of the macromer and 2-VP. Initially, the conversion rate of the macromer was higher than that of 2-VP, but after 8 hours the conversion of macromer increased slightly and the conversion of 2-VP exceeded that of the macromer. This is due to the higher reactivity of the methacryloyl group of the macromer than that of the vinyl group of 2-VP at the beginning of the reaction. With an increase in conversion, the viscosity of the polymerization solution gradually increases, resulting in decreased diffusion of the macromer.

Effect of Charging Ratio of PEO Macromer/2-VP on Copolymerization

The effect of charging ratio of PEO macromer/2-VP on the grafting efficiency and molecular weight of the copolymer is shown in Fig. 4. An increase in the macromer/2-VP ratio causes the viscosity of the system to increase, resulting in a decrease in the grafting efficiency. Figure 4 also shows a minimum in molecular weight. This may be explained as follows: The increase of viscosity may decrease the probability of molecule collisions, thus making chain propagation difficult, leading to the lowering of molecular weight. This may also make chain termination difficult, resulting in the increase of molecular weight. When the macromer/2-VP ratio is lower, the former effect is dominant. When the ratio is higher, the latter is dominant. The competition between the two effects causes a minimum in molecular weight.

Purification and Characterization of the Graft Copolymer

The crude reaction product contains the homopolymer of 2-VP, unreacted PEO macromer, the homopolymer of PEO, and the graft copolymer. The unreacted PEO macromer and its homopolymer can be separated from the graft copolymer by

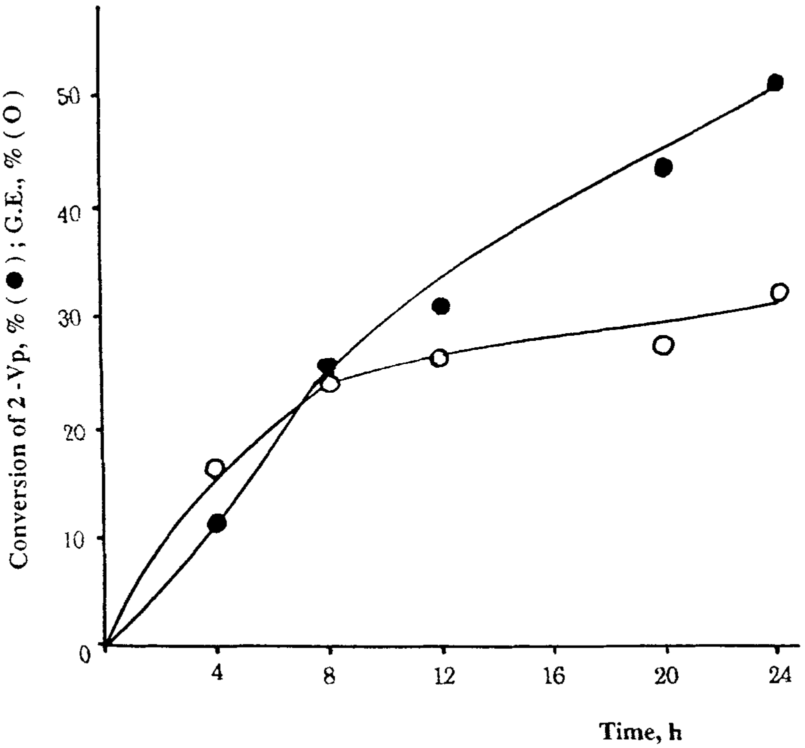

FIG. 3. Conversion of 2-VP (●) and macromer (○) versus copolymerization time [macromer/2-VP = 3/7 w/w, 0.25 g (2-VP + macromer)/mL solvent].

water extractions, but when the composition of PEO macromer in the graft copolymer is higher than 40 wt%, some graft copolymer will be extracted by water. Hence, this water solution was dried and dissolved in benzene, followed by precipitation with a large excess of toluene. UV spectrum showed that there is no P2-VP at 264 nm in the supernatant, and the precipitate is the graft copolymer. After extraction in water, the product containing the homopolymer of 2-VP and the graft copolymer is dissolved in benzene, and this solution is precipitated with toluene (6 times the volume of benzene). The graft copolymer is in the supernatant, and the precipitate is the homopolymer of 2-VP. The supernatant is dried to constant weight. The efficiency of purification was determined by extraction of a mixture of PEO macromer and poly(2-vinylpyridine) in the same way.

The IR spectrum of the purified P2-VP-*graft*-PEO copolymer is shown in Fig. 5. There is a characteristic peak at 1110 cm^{-1} for the C—O—C ether group, peaks at 2880 and 1440 cm^{-1} for the methylene group, peaks at 1590 and 1470 cm^{-1} for the C=C and C=N groups in the pyridine ring, and a peak at 740 cm^{-1} for the C—H of the pyridine. These indicate that the copolymers are composed of EO and 2-VP units. Figure 6 shows the ^{1}H-NMR spectrum of P2-VP-*graft*-PEO. The peaks at 6.3, 7.3, and 8.2 ppm are the protons of pyridine, the peak at 3.7 ppm is the proton of $-CH_2CH_2O-$, and the peaks at 1.8 and 2.7 ppm are the protons of

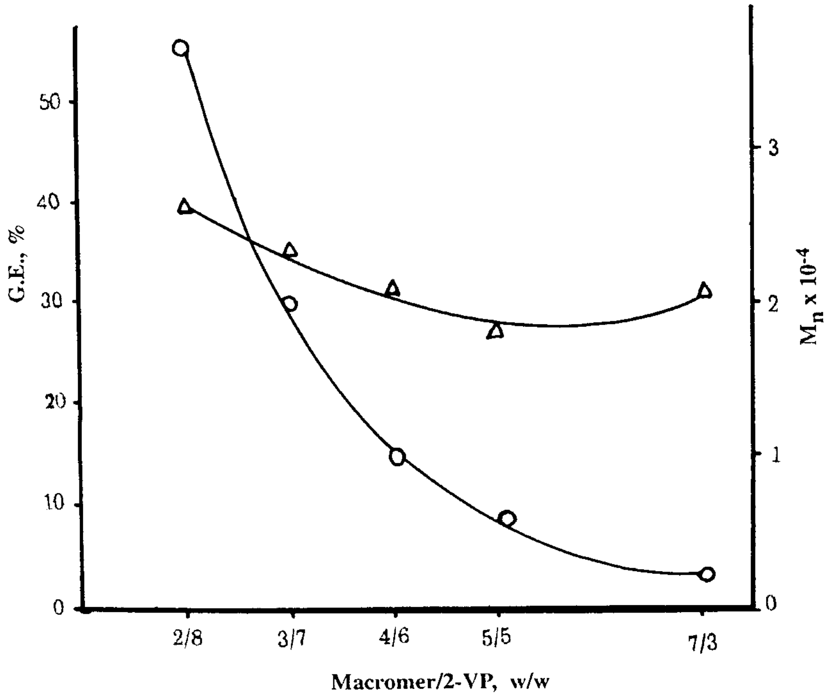

FIG. 4. Effect of charging ratio of macromer/2-VP (w/w) on the grafting efficiency (○) and molecular weight (△) of the copolymer [0.45 g (2-VP + macromer)/mL solvent].

—CH$_2$— and —CH— in P2-VP. Comparison with the spectra of P2-VP and PEO also indicates that the copolymers are composed of EO and 2-VP units. The number-average molecular weight of the graft copolymer was measured by a Bruss membrane osmometer with DMF as the solvent.

Conductivities of the Graft Copolymer Complexes

As is well known, PEO can be complexed with $LiClO_4$ to form ion-conducting materials, whereas P2-VP can be complexed with TCNQ to form electron-conducting materials due to charge transfer. When the graft copolymer was complexed with $LiClO_4$, TCNQ, or both $LiClO_4$ and TCNQ, it showed ionic conductivity, electronic conductivity, or mixed conductivity, respectively. Figure 7 indicates that the log σ plot versus $1/T$ follows the Arrhenius equation quite well. Table 2 lists the different conductivity values of the graft copolymer at 25 and 60°C. It can be seen that at 25°C the graft copolymer exhibited ionic conductivity, electronic conductivity, and mixed conductivity at 4.10×10^{-6}, 5.50×10^{-6}, and 5.40×10^{-5} S/cm, respectively. It is of interest to note that the mixed conductivity is higher than the sum of the ionic conductivity and electronic conductivity, i.e., a synergistic effect occurs.

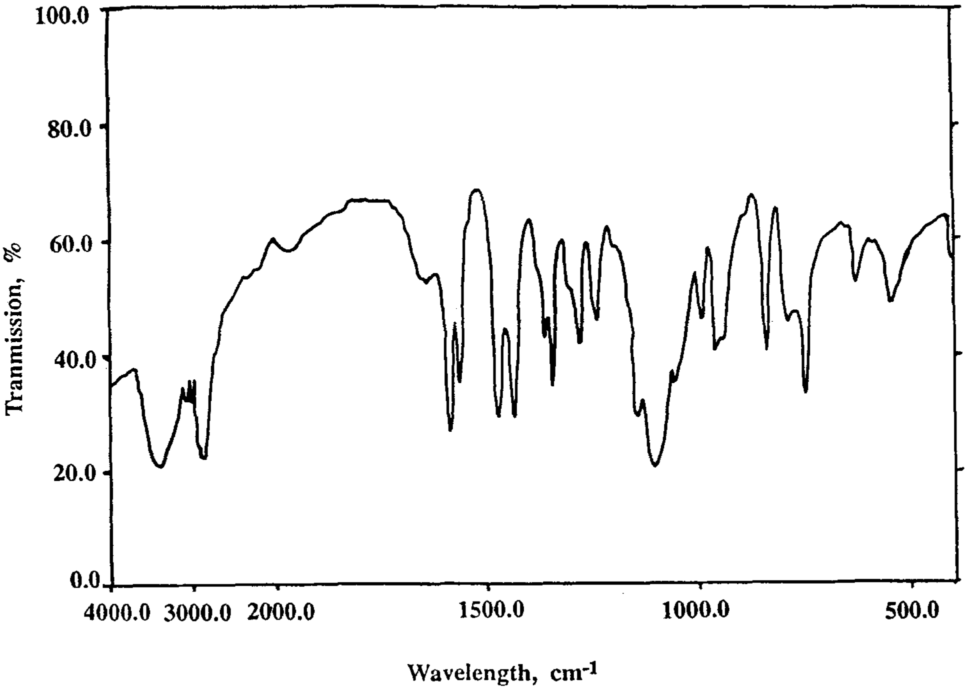

FIG. 5. IR spectrum of P2-VP-*graft*-PEO by using a KBr pellet (M_{nc} = 2.2 × 10^4, 38.0 wt% PEO).

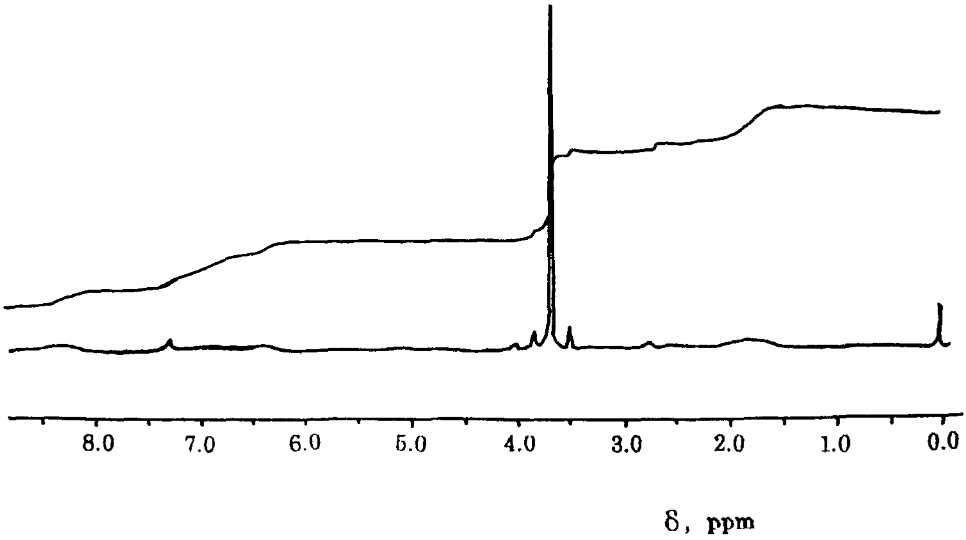

FIG. 6. ^{1}H-NMR (80 MHz) spectrum of P2-VP-*graft*-PEO in $CDCl_3$ (M_{nc} = 2.2 × 10^4, 38.0 wt% PEO).

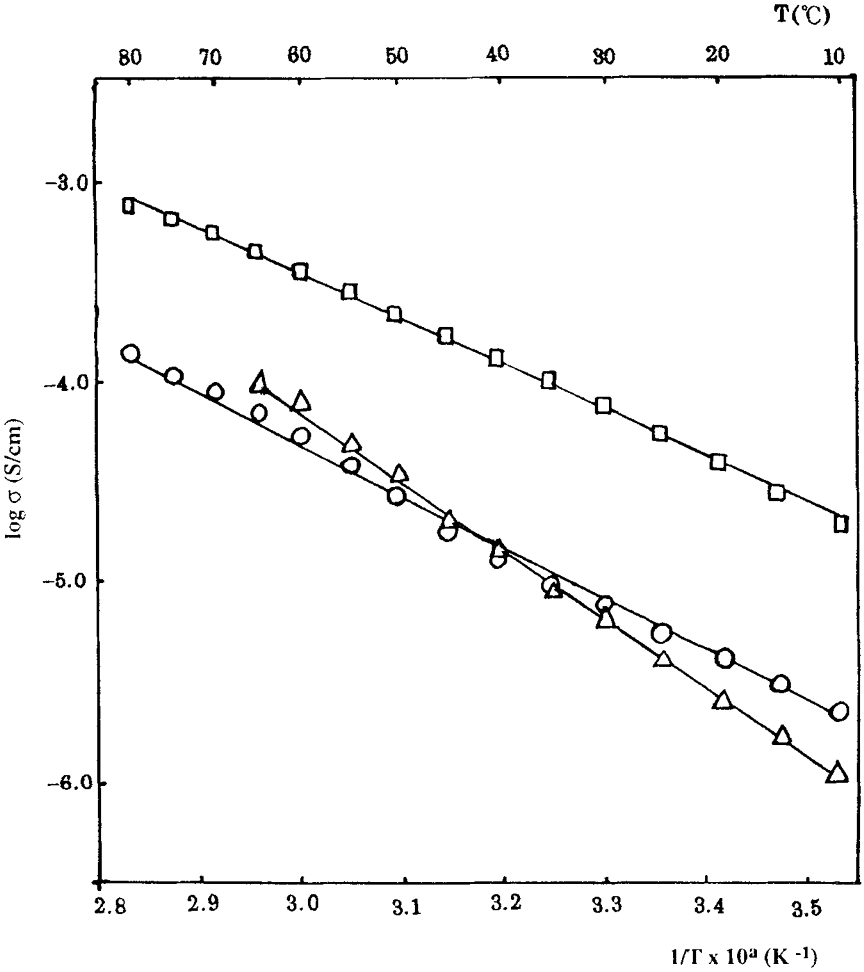

FIG. 7. Arrhenius conductivities (σ) plot for the graft copolymer (M_{nc} = 2.5 × 10^4 and 47.1 wt% PEO) complexes. (△) Molar ratio EO/Li = 10; (○) molar ratio 2-VP/TCNQ = 2; (□) molar ratio EO/Li = 10 and 2-VP/TCNQ = 2.

TABLE 2. Conductivities σ of the Graft Copolymer[a]

	2-VP/TCNQ, molar ratio	EO/Li$^+$, molar ratio	Temperature, °C	σ, S/cm × 10^{-6}
$LiClO_4$	0	10	25	4.10
$LiClO_4$	0	10	60	80.0
TCNQ	2	0	25	5.50
TCNQ	2	0	60	54.4
$LiClO_4$, TCNQ	2	10	25	54.0
$LiClO_4$, TCNQ	2	10	60	360

[a] The graft copolymer was the same as the one in Fig. 7.

CONCLUSION

Poly(2-vinylpyridine)-*graft*-PEO with uniform side grafts can be obtained by the copolymerization of 2-vinylpyridine with PEO macromer using AIBN as the initiator. The grafting efficiency can reach about 56%. The purified graft copolymers were characterized by IR and ^{1}H-NMR to be composed of 2-VP and EO units. The number-average molecular weight of grafts and copolymers can be varied from 3000 to 9000 and from 13,000 to 65,000, respectively. The graft copolymers showed electronic conductivity after being complexed with TCNQ, ionic conductivity after being complexed with $LiClO_4$, and mixed conductivity with a synergistic effect after being complexed with both TCNQ and $LiClO_4$.

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