

Synthesis and Optical Properties of Poly[6'-(N-carbazolyl)hexyl-2-ethynylpyridinium bromide]

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The polymerization of 2-ethynylpyridine by alkyl bromide carrying carbazole moiety, 6-(N-carbazolyl)hexyl bromide, relatively proceed well to give the corresponding poly[6'-(N-carbazolyl)hexyl-2-ethynylpyridinium bromide] in high yields under DMF reflux conditions without any initiator or catalyst. This polymerization was influenced upon the initial monomer concentration. The polymer yields and inherent viscosities of the resulting polymers were in the range of 34-85% and 0.11-0.21 dL/g, respectively. Instrumental analyses using NMR, IR, and UV-visible spectroscopies and elemental analysis indicated that the resulting polymer has a conjugated polymer backbone system carrying pyridine and n-hexyl carbazole moiety. The polymers were mostly brown powders and completely soluble in DMF, DMSO, nitrobenzene, and formic acid. The photoluminescence spectrum of the dilute polymer solution with the excitation at 383 nm exhibited two sharp peaks at 495 and 540 nm.

Introduction

Conjugated polymers have potentials as organic semiconductors,¹⁻⁴ as membranes for gas separation and for liquid-mixture separation,⁵⁻⁹ as a side-chain liquid crystal,¹⁰⁻¹⁴ as materials for chemical sensors,¹⁵⁻¹⁷ and for nonlinear optical materials.¹⁸⁻²²

The cyclopolymerization of dipropargyl monomers carrying ionic nature is a facile synthetic method for as self-doped conjugated ionic polymers.²³ Various dipropargyl quaternary ammonium salts were polymerized to yield the unusual conjugated polymers.²⁴⁻²⁷ The potential counter ions are ionically bound to the polymer. Dihexyldipropargylammonium salts (counter ion: Br, *p*-CH₃C₆H₄SO₃⁻) were firstly polymerized to give the corresponding conjugated polymers in high yields.²⁴ Similar water-soluble conjugated polymer was obtained from the polymeric reaction of poly(N-hexyldipropargylamine) and methyl trifluoromethanesulfonate. The precursor polymer, poly(dipropargylhexylamine) was obtained in good yield *via* a cyclopolymerization of the corresponding monomer using Schrock catalyst, Mo(CH-t-Bu)(NAr)[OCMe(CF₃)₂]₂.²⁵ Treatment of this polymer with methyl trifluoromethanesulfonate in methylene chloride affords the poly(dipropargyl-N-hexyl-N-methylammonium triflate) in 92% yield. The dihexyldipropargylammonium tetraphenylborate was also easily polymerized to give the corresponding polymer having a quite different solubility behaviors compared to that of poly(dihexyldipropargylammonium bromide).²⁶

The cyclopolymerizations of multipropargylammonium bromides such as tripropargylammonium bromide and tetrapropargylammonium bromide yielding a highly conjugated and cross-linked polymers were also performed.^{28,29} The

cyclopolymerization of 2-ethynyl-N-propargylpyridinium bromide having two different triple bond functionalities (acetylene and propargyl) yielded an interesting conjugated cyclopolymer having cumulated pyridine moiety.³⁰

The synthesis of simple mono- and di-substituted ionic polyethynylpyridines had been carried out through the activation of the acetylene bond in ethynylpyridines.³¹⁻³⁴ We have also studied the synthesis of polyacetylene derivatives carrying pyridine moiety such as poly(2-ethynylpyridine),³⁵ poly(N-propargylpyridinium bromide),³⁶ and poly(2-ethynyl-N-propargylpyridinium bromide).³⁰ And also, water-soluble conjugated ionic polymer, poly(2-ethynylpyridinium bromide) having a pendant propargyl moiety by the simple polymerization reaction of 2-ethynylpyridine and propargyl bromide in refluxing methanol.³⁷

Now we report the synthesis of ionic conjugated polymer having carbazole moiety by the simple polymerization of 2-ethynylpyridine and 6-(N-carbazolyl)hexyl bromide under DMF reflux conditions. And the characterization of the resulting poly[6'-(N-carbazolyl)hexyl-2-ethynylpyridinium bromide] [poly(CHEPB)] will also be discussed.

Experimental Section

Materials. 2-Vinylpyridine (Aldrich Chemicals, 97%) and carbazole (Aldrich Chemicals, 96%) was used as received. 1,6-Dibromohexane (Aldrich Chemicals, 96%) was dried with calcium hydride and distilled. Sodium amide (NaNH₂, Aldrich Chemicals, tech., 90%) was also used as received. The solvents were analytical grade materials. They were dried with an appropriate drying agent and fractionally distilled.

Preparation of 2-ethynylpyridine. 2-Ethynylpyridine was prepared by the bromination of 2-vinylpyridine and the

consecutive dehydrobromination reaction according to the literature method.³⁵

Preparation of 6-(N-carbazolyl)hexyl bromide. To a solution of carbazole (30 g, 0.18 mol), 1,6-dibromohexane (87 g, 0.36 mol) and benzyltriethylammonium chloride (1.00 g, 4.39 mmol) in benzene (200 mL) was added a water solution of 50% sodium hydroxide (100 mL) in one portion. The mixture was stirred under reflux for 4 hr. The reaction mixture was cooled to room temperature to yield solid product. The product was collected by filtration and recrystallized twice from THF/water to afford pure white crystal of 6-(N-carbazolyl)hexyl bromide in 85% yield; ¹H NMR (CDCl₃, δ, ppm): 1.43 (4H), 1.75 (4H), 3.34 (2H), 4.30 (2H), 7.23 (2H), 7.44 (4H), 8.10 (2H). ¹³C NMR (CDCl₃, δ, ppm): 26.37, 27.84, 28.73, 32.48, 33.69, 42.74, 108.52, 118.72, 120.24, 120.35, 122.76, 125.53, 140.31. IR (KBr pellet, wavenumbers, cm⁻¹): 3045, 2925, 2854, 1898, 1593, 1484, 1452, 1325, 754, 725, 637.

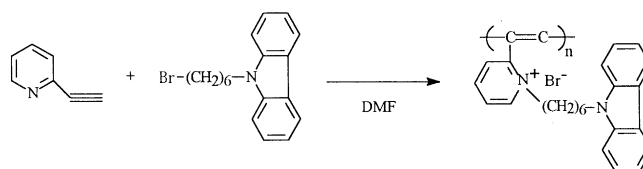
Synthesis of Poly(CHEPB). In a 250 mL three-neck flask equipped with reflux condenser, thermometer, and rubber septum, DMF (150 mL), 2-ethynylpyridine (1.00 g, 9.70 mmol), and 6-(N-carbazolyl)hexyl bromide (3.20 g, 9.70 mmol) were introduced in the given order. And the reaction mixture was refluxed in DMF. In order to check the polymer yields and polymer viscosities according to the time during the polymerization, each 10 mL reaction solution was taken from the polymerization mixture at the scheduled polymerization time (1, 3, 6, 12, 24 hrs). As the reaction proceeds, the color of reaction mixture was consecutively changed into dark-black. After a given polymerization time, the resulting polymer solution was precipitated into a large amount of ethyl ether. The precipitated polymer was filtered and dried under vacuum at 40 °C for 24 hr. The polymer yields were calculated by gravimetry.

Instruments. ¹H NMR spectra were recorded on a Bruker AM-200 spectrometer in DMSO-d₆. ¹³C NMR spectra of polymer were recorded on Bruker AMX-500 spectrometer. IR spectra were obtained with a Bomem MB-100 spectrometer using a KBr pellet. Elemental analyses were performed with Perkin-Elmer 240C Elemental Analyzer. UV-visible spectra were taken on a JASCO V-530 spectrophotometer in DMF solvent. The inherent viscosities (η_{inh}) were determined at a concentration of 0.5 g/dL in DMF solvent at 30 °C. Thermogravimetry (TG) was performed under a nitrogen atmosphere at a heating rate of 10 °C/min. upto 800 °C with a DuPont 1090 Analyzer. DSC thermograms were taken on a DuPont 910 differential scanning calorimeter under nitrogen atmosphere at a scanning rate of 10 °C/min. The photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz.

Results and Discussion

The poly(CHEPB) was prepared by the direct polymerization reaction of 2-ethynylpyridine and 6-(N-carbazolyl)hexyl bromide under DMF reflux condition without any initiator

and catalysts.



The polymerization of ethynylpyridines by using a simple alkyl halides such as ethyl iodide,³¹ 1-octyl bromide,³⁸ and lauryl bromide,³¹ had been known to proceed even at the mild reaction condition of low temperature (50 °C). The activated acetylene triple bond of N-alkyl-2-ethynylpyridinium halide was found to be susceptible to the polymerization under mild conditions. However, in this polymerization, the polymerization did not proceed at the reaction conditions of 90 °C. Thus the polymerization reaction were tested at the elevated temperature of DMF reflux condition.

Table 1 shows the results for the direct polymerization of 2-ethynylpyridine by 6-(N-carbazolyl)hexyl bromide. This indicates that the polymerization was activated by the elevation of reaction temperature. This polymerization was influenced strongly upon the initial monomer concentration ([M]₀). As the initial monomer concentration is increased, the polymer yield and inherent viscosity were also increased. The polymerization behaviors at DMSO were similar with those at DMF. Thus the polymer yield and viscosity were similar.

The polymer yield according to the polymerization time were calculated from the precipitation of the solution taken from the polymerization reactor (Figure 1). This reveals that the polymerization of 2-ethynylpyridine by 6-(N-carbazolyl)hexyl bromide proceeded gradually upto 24 hr and the polymer yield reaches 75%, and then plateau. The absorbance of polymer solution according to the polymerization time were also consecutively evaluated. Figure 2 shows the UV-visible spectra of the initial mixture of 2-ethynylpyridine and 6-(N-carbazolyl)hexyl bromide and the reaction mixtures taken from the reactor during the polymerization at the given times. The UV-visible spectrum (λ) of initial mixture did not show any absorption peak above 400 nm, which is originated from the conjugation of polymer chain. As the polymerization time increased, the absorption peaks at the visible regions increased gradually. Even after 1 hr, an

Table 1. Polymerization of 2-Ethynylpyridine Activated by 6-(N-Carbazolyl)hexyl bromide^a

Experiment no	[M] ₀ ^b	Solvent	Polymer Yield ^c (%)	η_{inh} ^d
1	0.128	DMF	85	0.21
2	0.064	DMF	75	0.15
3	0.039	DMF	34	0.11
4	0.128	DMSO	80	0.19
5	0.128	nitrobenzene	62	0.16

^a Polymerization was carried out under DMF reflux condition. ^b Initial concentration of 2-ethynylpyridine. ^c Ethyl ether-insoluble polymer yield. ^d Inherent viscosities were determined at a concentration of 0.5 g/dL in DMF solvent at 30 °C.

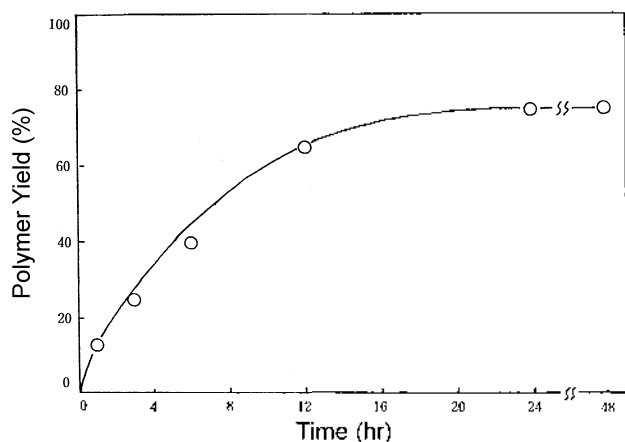


Figure 1. The polymer yield according to the polymerization time in the polymerization of 2-ethynylpyridine activated by 6-(*N*-carbazolyl)hexyl bromide under DMF reflux condition.

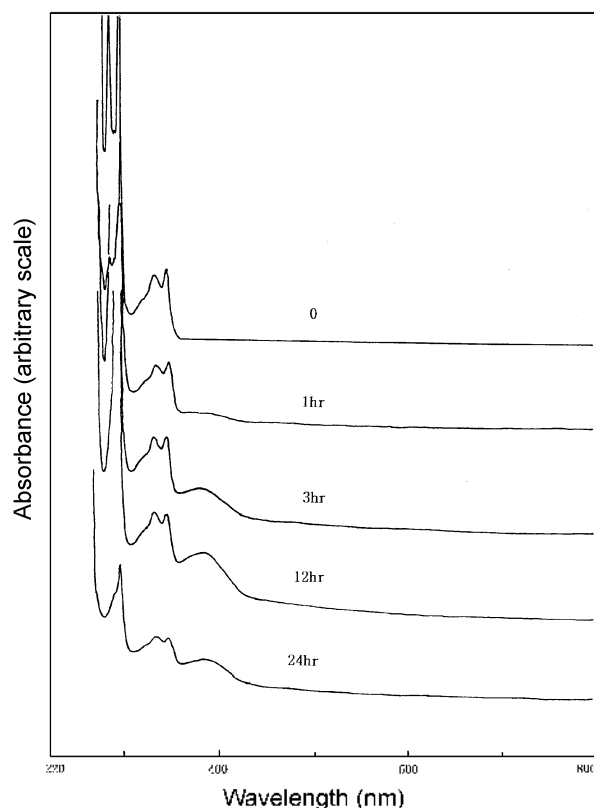


Figure 2. UV-visible spectra of the initial mixture of 2-ethynylpyridine and 6-(*N*-carbazolyl)hexyl bromide and the reaction mixtures taken from the reactor during the polymerization according to the polymerization time.

absorption peak in the visible region were slightly observed. After 12 hrs, the new broad peak at 381 nm were observed. The UV-visible spectrum after 24 hrs show the peak at 383 nm and the long-wavelength absorption peak upto 750 nm.

The polymer structure of poly(CHEPB) was characterized by elemental analysis, NMR (^1H - and ^{13}C -), infrared, and UV-visible spectroscopies. The elemental analysis data of reprecipitated poly(CHEPB) agreed with the theoretical value: Calcd for $(\text{C}_{25}\text{H}_{12}\text{BNBr})_n$: C, 71.60%; H, 6.01%; N,

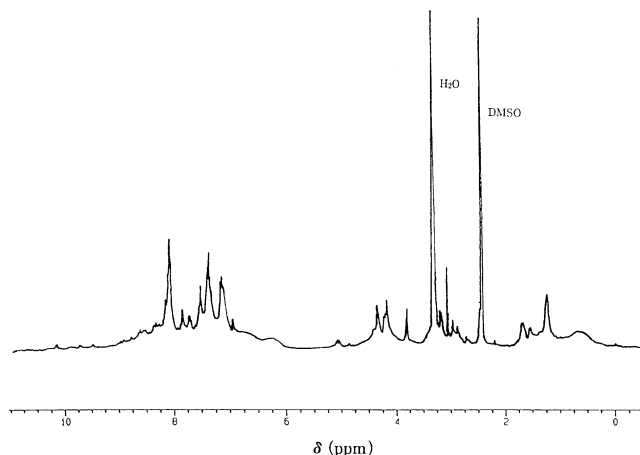


Figure 3. ^1H NMR spectrum of poly(CHEPB) in DMSO-d_6 .

3.34%; Br, 19.05% Found: C, 71.20%; H, 6.03%; N, 3.50%; Br, 19.27%. Figure 3 shows the ^1H NMR spectrum of poly(CHEPB) prepared by direct polymerization of 2-ethynylpyridine and 6-(*N*-carbazolyl)hexyl bromide under DMF reflux conditions. The aromatic proton peaks of pyridine and carbazole moiety are observed in the range of 6.0-9.0 ppm. Especially the three more strong peaks at 7.19, 7.44, and 7.95 ppm were originated from the carbazole moiety in polymer. The methylene proton peaks adjacent to the nitrogen atom of pyridine and carbazole moiety were observed at about 4.35 ppm and 4.22 ppm, respectively. Other four methylene protons of *n*-hexylcarbazole were also observed in the range of 0.5-2.0 ppm.

Figure 4 shows the 125.76 MHz ^{13}C NMR spectrum of poly(CHEPB) in DMSO-d_6 . The aromatic carbon peaks at 109.32, 119.20, 121.08, 122.00, 125.13, and 139.93 ppm is originated from the carbazole moiety. The conjugated C-C double bond peaks of polymer main chain were also observed broadly at about 150 ppm.

Figure 5 shows the IR spectra of 2-ethynylpyridine, 6-(*N*-carbazolyl)hexyl bromide, and poly(CHEPB) in KBr pellets. In the IR spectrum of poly(CHEPB), it did not show the acetylenic $\text{C}\equiv\text{C}$ bond stretching frequency (2110 cm^{-1}) and the acetylenic C-H stretching frequency at 3293 cm^{-1} .

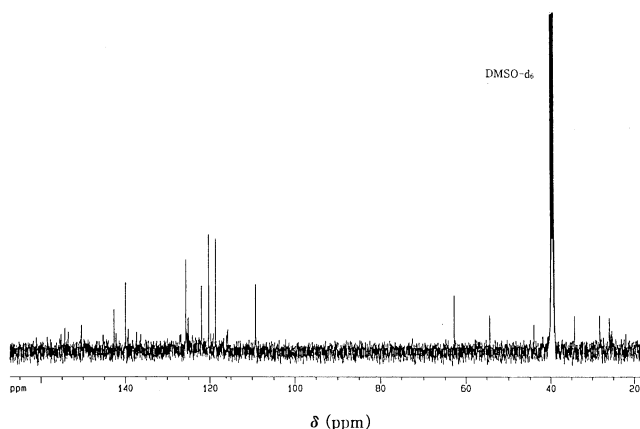


Figure 4. ^{13}C NMR spectrum of poly(CHEPB) in DMSO-d_6 .

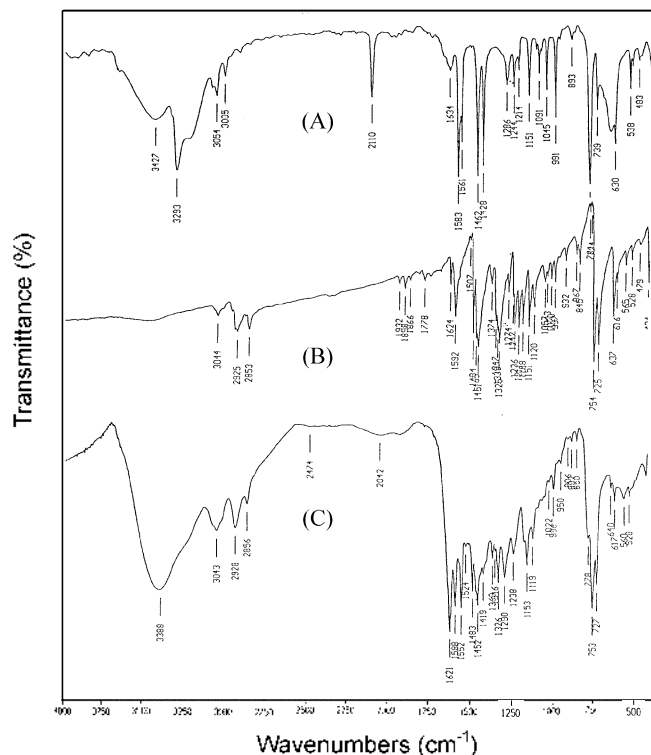


Figure 5. IR spectra of 2-ethynylpyridine (A), 6-(N-carbazolyl)hexyl bromide (B), and poly(CHEPB) (C) in a KBr pellet.

Instead, the C–C stretching frequency of conjugated polymer backbone at 1621 cm^{-1} became more intense than those of 2-ethynylpyridine and 6-(N-carbazolyl)hexyl bromide.

These spectral data indicates that the resulting poly(CHEPB) have a conjugated polymer backbone carrying a pyridine and n-hexyl carbazole moiety.

The resulting poly(CHEPB)s were generally brown powders. The solubility test was performed for powdery samples in excess solvent. The poly(CHEPB) was completely soluble in DMF, DMSO, nitrobenzene, and formic acid, and partially soluble in water, acetone, and methanol, but insoluble in benzene, THF, ethyl ether, and n-hexane. The inherent viscosities of the resulting poly(CHEPB)s were in the range of 0.11–0.21 dL/g, depending on the polymerization conditions.

The TGA thermogram (Figure 6) of poly(CHEPB) was also tested under nitrogen atmosphere. This polymer shows a rapid decomposition phenomenon after $210\text{ }^{\circ}\text{C}$. The other similar polymers such as poly(2-ethynylpyridinium bromide) having propargyl moiety and poly(2-ethynylpyridinium bromide) having simple alkyl chain also showed an gradual weight loss phenomenon even at the low temperature (below $100\text{ }^{\circ}\text{C}$).³⁷ The poly(CHEPB) retains 99% of its original weight at $200\text{ }^{\circ}\text{C}$, 90% at $265\text{ }^{\circ}\text{C}$, 60% at $300\text{ }^{\circ}\text{C}$, 40% at $375\text{ }^{\circ}\text{C}$, and 22% at $800\text{ }^{\circ}\text{C}$. Figure 7 shows the DSC thermogram of poly(CHEPB). This polymer did not show the characteristic T_g peak as like other similar conjugated polymers.^{39–41} The exothermic peak starting at about $220\text{ }^{\circ}\text{C}$ is due to the thermal decomposition of the polymer system.

The absorption spectra of the dilute solution and thin film

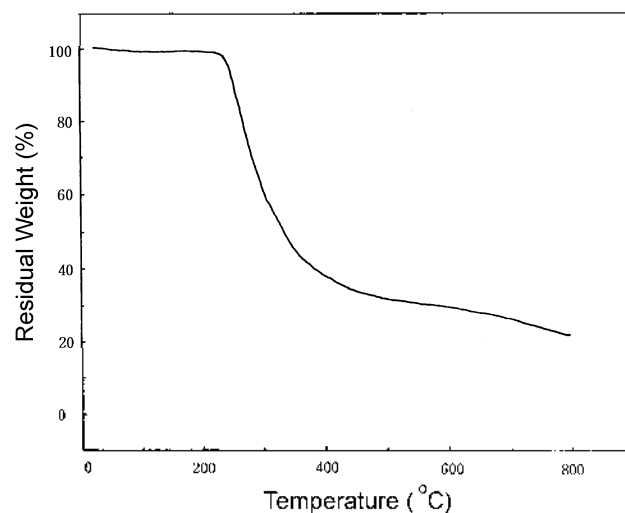


Figure 6. TGA thermogram of poly(CHEPB).

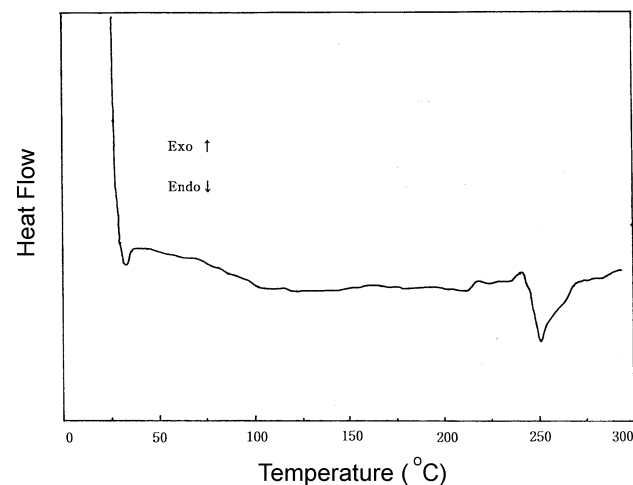


Figure 7. DSC thermogram of poly(CHEPB).

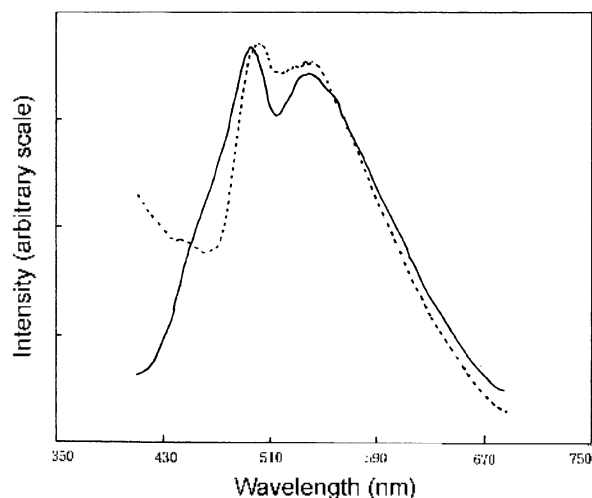


Figure 8. PL spectra of the thin solid film (—) and the dilute solution (----) of the poly(CHEPB) with the excitation wavelength at 383 nm .

of polymer had a relatively sharp peak at 383 nm , with an onset of absorption at 750 nm . Both spectra were almost

identical except that the peak was broader in case of solid film. The band gap of the polymer (taken from the onset of the absorption spectrum) was 2.13 eV.

The PL spectra of the polymer dilute solution and the solid state (thin film) coated on a carboglass are shown in Figure 8. The PL spectrum of the polymer thin film with the excitation wavelength at 383 nm has two sharp peaks at 495 and 540 nm. And also, the PL spectrum of the polymer dilute solution exhibited two similar peaks at 503 and 542 nm.

Conclusions

New conjugated ionic polymer, poly(CHEPB) having pyridine and carbazole moiety, which can show some peculiar properties, was effectively synthesized by the direct polymerization of 2-EP and 6-(N-carbazolyl)hexyl bromide without any initiator or catalyst system. The polymerization relatively proceed well at high temperature of DMF reflux condition. The polymer yield and inherent viscosities were in the range of 34-85% and 0.11-0.21 dL/g, respectively. The structure of the resulting polymer was identified to have a conjugated polymer backbone system having pyridyl and (N-carbazolyl)hexyl moiety by various instrumental method. The polymers were mostly brown powders and completely soluble in such polar solvents as DMF, DMSO, nitrobenzene, and formic acid.

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