

## Synthesis and electrochemical properties of a polynorbornene derivative containing a carbazole moiety

Ji-Hoon Lee<sup>1</sup>, Jong-Wook Park<sup>1</sup>, J. M. Ko<sup>2</sup>, Young-Hwan Chang<sup>1</sup>, and Sam-Kwon Choi<sup>1,\*</sup>

<sup>1</sup>Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1 Kusong-Dong, Yusong-Gu, Taejon, 305-701 Korea

<sup>2</sup>R&D Center, HanKook Tire Mfg. Co., Yusong-Gu, Taejon, 305-701 Korea

### Summary

A new polymer, poly(5-[[6-N-carbazoylhexyl]oxy]methyl]-2-norbornene) [Poly(NCHN)], was synthesized by ring-opening metathesis polymerization (ROMP) with various transition metal catalyst systems. The structure of the poly(NCHN) was analyzed by NMR, IR, and UV-vis spectroscopy. The electrochemical properties of the poly(NCHN) were characterized by cyclic voltammetric technique. From the cyclic voltammetric results it was concluded that the carbazole units in side chain of the polymer were oxidized and coupled irreversibly to form dicarbazyls. The redox kinetics was mainly controlled by both electron transfer and  $\text{ClO}_4^-$  diffusion processes preserving the electro-neutrality of the polymer.

### Introduction

Since the first application of poly(N-vinylcarbazole) in xerography(1), great interest has focused on photoconductivity and electrochemical property of carbazole-containing polymers (2-5). Of particular importance are electrodes coated with polymers because of the ease of preparation and the wide range of applications such as electrocatalysis, solar energy conversion, and electrochromic bilayer film devices. Although many carbazole-containing polymers are known, there are a few example of electrochemical characteristics of such materials. Hsieh et al. reported electrochemical properties of poly(N-acycylethylenimines) with pendant carbazole derivatives(6). Also, Ambrose et al. have reported anodic oxidation pathways of carbazole and its N-substituted derivatives(7-8). To our knowledge, there is no details on the synthesis method for a carbazole-containing polymer by ring-opening metathesis polymerization (ROMP). Here, we will describe a new polymer synthesis by ROMP and its electrochemical redox properties will be discussed.

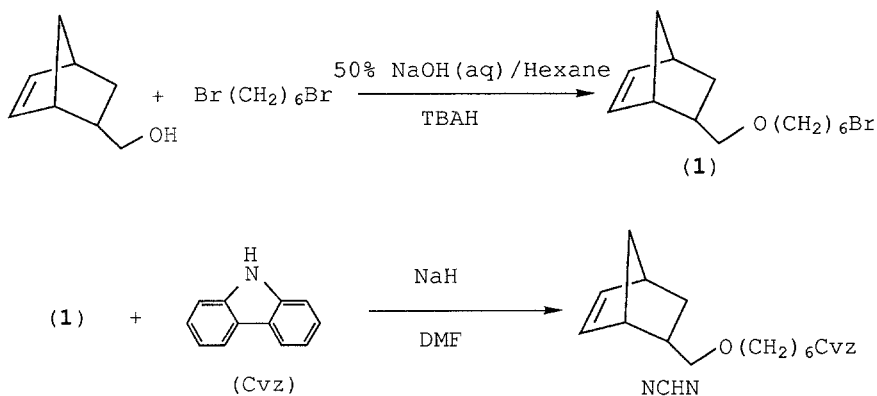
### Experimentals

#### *Materials and Instruments.*

Carbazole, 1,6-dibromohexane, 5-norbornene-2-methanol (mixture of endo and exo), and sodium hydride were purchased from Aldrich and used without further purification. Solvents were purified by normal procedures and handled under moisture free atmosphere. The polymerization solvents were distilled from calcium hydride.

\*Corresponding author

Scheme I



The polymerization glasswares and syringes were dried at 150°C for at least 24 h before use. <sup>1</sup>H-NMR spectra were recorded with Bruker AC-200 spectrometer and chemical shifts were reported in ppm units with tetramethylsilane as internal standard. <sup>13</sup>C-NMR spectra were recorded with Bruker AC-200 spectrometer. FT-Infrared spectra were measured as KBr pellet or NaCl cell on a Bomem Michelson MB-100 spectrometer and frequencies are given in reciprocal centimeters. Molecular weights and polydispersities of polymers were obtained by GPC analysis with polystyrene standards calibration. Thermogravimetric analysis (TGA) was performed with a Du Pont 2000 TGA in nitrogen atmosphere at a heating rate of 20°C/min up to 700°C. Thermal transition was measured with a Du Pont 2000 differential scanning calorimeter (DSC) under nitrogen atmosphere at a heating rate of 10°C/min.

#### Measurement of electrochemical properties.

To examine electrochemical properties, the polymer was coated with solution-coating method onto platinum foil as a working electrode with the area of 1 cm<sup>2</sup>. After coating, the films adhered to the electrode were dried in a vacuum oven for 10 min. The thickness of the polymer film was 5 μm. The electrochemical measurements were performed in 0.1 M tetrabutylammonium perchlorate (TBAP, freshly distilled, Aldrich) containing acetonitrile solution. Ag wire and platinum foil were used as a reference and a counter electrode, respectively. Cyclic voltammetric waves were produced by using a Hokuto Denko HA-301 potentiostat/galvanostat equipped with a HA-301 functional generator and an X-Y recorder.

#### Preparation of monomer. 5-[[6-(N-carbazoylhexyl)oxy]methyl]-2-norbornene (NCHN).

5-[[6-bromohexyl]oxy]methyl-2-norbornene (**1**) was synthesized using a phase-transfer catalyst. A mixture of an n-hexane solution (150 mL) of 5-norbornene-2-methanol (8.46 mL, 0.07 mol, mixture of endo and exo), 1,6-dibromohexane (51.24 g, 0.21 mol), tetrabutylammonium hydrogen sulfate (1.19g, 3.5 mmol)

and 50% NaOH aqueous solution was allowed to react with stirring at room temperature for 12h. The mixture was boiled for a short time (about 1h). The resulting solution was extracted two times with diethyl ether (70 mL, each). Then it was washed two times with hydrochloric acid aqueous solution (20%, 100mL, each). Product was separated by evaporating the solvent after drying the solvent with anhydrous magnesium sulfate. The crude product was purified by vacuum distillation ( b.p. 120°C under 1mmHg, Yield 65 %).

NCHN was synthesized by the reaction of carbazole and (**1**) [Scheme I]. To the mixture of carbazole (29.1 g, 0.174 mol) and sodium hydride (60%, 8.35g, 0.209 mol) in DMF (200 mL) was added dropwise (**1**) (10 g, 0.35 mol) followed by refluxing for 12h. The solution was poured into water (200 mL) and extracted with ethyl acetate three times (80 mL, each). Removing the solvent with evaporator, residue was purified by using silica gel column chromatography (eluent; ethyl acetate:hexane=1:6). Yield 70 %.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 0.8-1.8 [m, 12H, (-CH<sub>2</sub>-)<sub>4</sub> and 2(-CH<sub>2</sub>-)]; 2.3-3.1 [m, 3H, the nonolefinic norbornene protons]; 3.2-3.4 (m, 4H, -CH<sub>2</sub>OCH<sub>2</sub>-); 4.3 (t, -CH<sub>2</sub>N-); 5.88-6.01 [m, 2H olefinic methines of exo and endo mixture]; 7.1-8.1 [m, 8H, aromatic protons]

<sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 140.3, 136.5, 136.2, 135.1, 125.5, 122.7, 120.3, 118.7, 108.6, 70.8, 67.9, 42.7. IR (KBr pellet, cm<sup>-1</sup>); 1596 (ν<sub>C=C</sub> vinylic), 1606, 1484 (ν<sub>C=C</sub> aromatic stretching), 1334 (ν<sub>C-N</sub>), 749, 721 (ν<sub>C-N</sub> carbazole ring out of plane). Elemental anal. calc for C<sub>26</sub>H<sub>31</sub>ON: C, 83.60; H, 8.36; N, 3.76. Found: C, 83.53; H, 8.34, N, 3.68.

#### *Polymerization procedure.*

The ring-opening metathesis polymerization (ROMP) of NCHN, was carried out by metathesis catalysts, Mo-, W-, and Ru-based catalysts, under nitrogen atmosphere, the results of which are shown in Table 1. A typical procedure was as follows; To a solution of 0.3 g of NCHN in 1 mL of chlorobenzene-ethanol mixture (0.5 mL, each) was added 0.32 mL of 0.05 M RuCl<sub>3</sub>·xH<sub>2</sub>O in a mixture of chlorobenzene and ethanol (1/1 chlorobenzene/ethanol). The reaction was carried out at 80 °C for 24h. The polymer was precipitated in methanol. The precipitated polymer was again dissolved in THF and reprecipitated in methanol, filtered, and dried in a vacuum oven at 40 °C overnight.

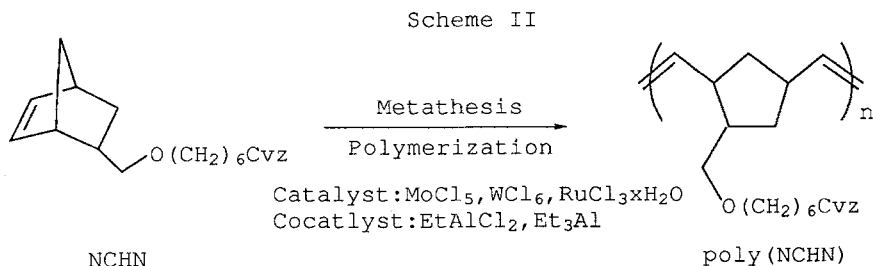
## RESULTS AND DISCUSSION

#### *Polymerization.*

The metathesis reaction of NCHN gave a ring-opened unsaturated polymer, poly(NCHN), containing a carbazole moiety by the following sequence scheme II.

Table 1 gives the results on the polymerization of monomer by various catalyst systems. As shown in Table 1, ruthenium-based and molybdenum-based catalyst systems were generally more effective than the tungsten-based catalyst systems. (12, 13) In particular, the resulting polymer prepared using ruthenium-based catalyst was soluble in common organic solvents such as chloroform, THF, pyridine, and so on. However, most of the polymers prepared using molybdenum-based catalysts were swelled.

The results of the polymerization of monomer by RuCl<sub>3</sub>·xH<sub>2</sub>O catalyst systems using various solvents are summarized in Table



2. The polymerization proceeded well in most organic solvents. Chlorobenzene and benzene were found to be more adequate solvents than other solvents such as THF and  $\text{CCl}_4$  at fixed temperature. The number average molecular weight ( $\bar{M}_n$ ) values and the polydispersity of the polymers obtained found to be in the range of  $2.4\text{--}7.2 \times 10^4$  and  $2.0\text{--}3.2$ , respectively. The resulting polymers exhibited decomposition at  $340^\circ\text{C}$  and showed a glass-transition temperature at  $26^\circ\text{C}$  by thermal analysis.

Table 1  
Polymerization of NCHN by various transition metal catalysts.<sup>a</sup>

Exp No	Catalyst. (mole ratio)	M/C <sup>b</sup>	[M] <sub>0</sub> <sup>c</sup>	Temp (°C)	Polymer <sup>d</sup> Yield(%)	$\bar{M}_n/10^4$	$\bar{M}_w/\bar{M}_n^f$
1	$\text{MoCl}_5\text{-EtAlCl}_2$ (1:4)	25	0.15	70	90 <sup>e</sup>	-	-
2	$\text{MoCl}_5\text{-EtAlCl}_2$ (1:4)	50	0.25	70	95 <sup>e</sup>	-	-
3	$\text{WCl}_6\text{-Et}_2\text{AlCl}$ (1:4)	100	0.5	80	-	-	-
4	$\text{WCl}_6\text{-Et}_3\text{Al}$ (1:4)	100	1.0	80	trace	-	-
5	$\text{RuCl}_3 \cdot x\text{H}_2\text{O}$	50	1.5	80	90	5.1	2.8
6	$\text{RuCl}_3 \cdot x\text{H}_2\text{O}$	50	1.0	80	95	7.2	3.2
7	$\text{RuCl}_3 \cdot x\text{H}_2\text{O}$	50	0.25	80	40	2.4	2.0

- Polymerization was carried out in chlorobenzene for 24 h.
- Monomer to Catalyst mole ratio.
- Initial monomer concentration.
- Methanol-insoluble polymer.
- These were swelled in THF, 1,4-dioxane, and so on.
- Values were obtained by GPC analysis with polystyrene standards calibration.

#### Polymer structure.

The  $^1\text{H-NMR}$  spectra of both the monomer (a) and the polymer (b) prepared using ruthenium-based catalyst are shown in Figure 1. As the polymerization proceeded, the vinylic proton peaks at 5.88 and 6.01 ppm disappeared. The  $^1\text{H-NMR}$  spectrum of the polymer shows new vinylic protons as broad signal in the range of 5.02~5.28 ppm. This broad signal corresponds to the vinylic protons of the predominant trans double bond of the ring-opened polymer. In general, ruthenium catalysts provide predominantly trans double bonds in metathesis polymerization of other norbornenes (9).

Table 2.  
Solvent effect in the polymerization of NCHN using ruthenium-based catalyst.

solvent	[M] <sup>a</sup>	M/c <sup>b</sup>	Temp (°C)	Time (h)	Yield (%) <sup>c</sup>
chlorobenzene	0.5	50	80	24	90
benzene	0.5	50	70	72	90
1,4-dioxane	0.5	50	70	72	60
CCl <sub>4</sub>	0.5	50	70	72	40
THF	0.5	50	70	72	trace

a. Initial monomer concentration.

b. Monomer to catalyst mole ratio.

c. Methanol-insoluble polymer.

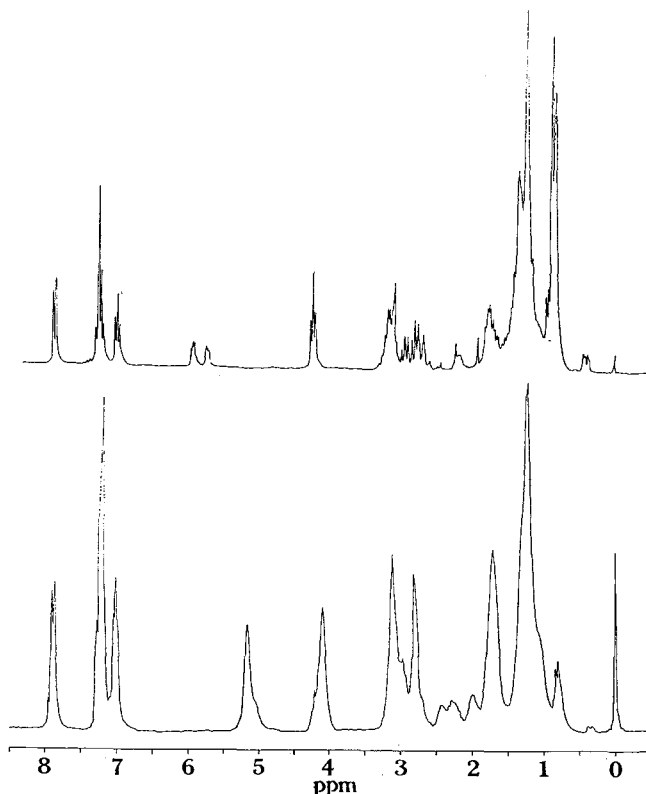


Figure 1. <sup>1</sup>H-NMR spectra of monomer(a) and polymer(b) in CDCl<sub>3</sub>.

The infrared spectra for the monomer and the polymer are shown in Figure 2. There is a large broad at near 970cm<sup>-1</sup> in the polymer. The broad band is due to the trans arrangement about a double bond in which the =C-H bond can do out of bending vibration(10). Above IR information also supports that

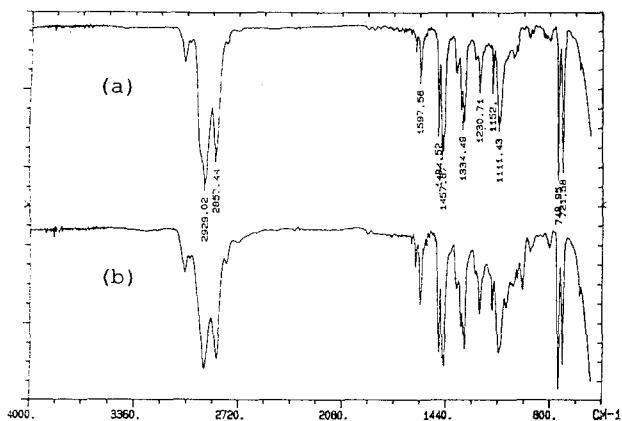


Figure 2. IR spectra of monomer(a) and polymer(b)

the ring-opened polynorbornene main chain has predominant trans double bond.

*Electrochemical properties of poly(NCHN).*

Figure 3 shows the cyclic voltammetric waves of the poly(NCHN) film in 0.1 M TBAP/acetonitrile solution. In the first scan, the oxidation occurs at 1.4V, where the carbazole units are oxidized and coupled irreversibly to form the dicabazyls. Oxidation peaks at 0.98V and 1.32V are attributed to the dicabazyls coupled after the first scan. The reproducibility means that the number of electroactive sites is nearly the same during the forward and reverse scan. It may be due to the stabilization of the cation radical by extended delocalization. These electrochemical properties are similar to those of N-alkyl carbazole derivatives(6).

Figure 4 shows the variation of the redox peak current density ( $I_p$ ) as the various scan rates ( $\nu$ ). The redox current

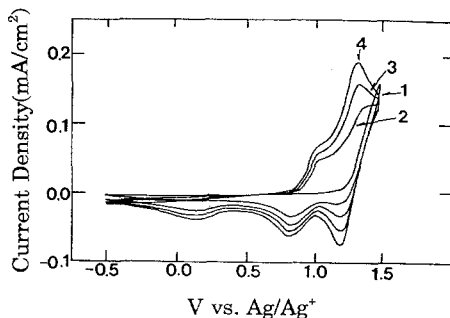


Figure 3. Growth CVs for the surfaced-coated poly(NCHN) in 0.1M TBAP/ $\text{CH}_3\text{CN}$ . Numbers indicate cycling number.

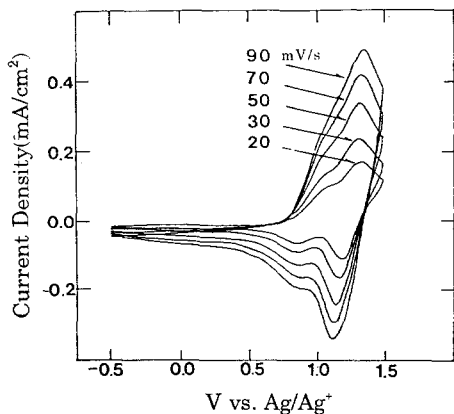


Figure 4. Scan rate dependencies of CVs of surfaced-coated poly(NCHN) in 0.1M TBAP/CH<sub>3</sub>CN.

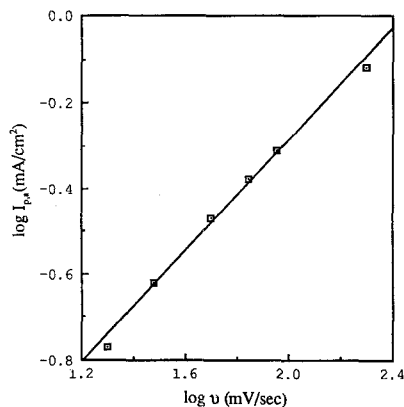


Figure 5. Plot of  $\log I_{p,a}$  vs.  $\log \nu$  for poly(NCHN).

value increased as the scan rate increased. The relationship between  $I_p$  and  $\nu$  can be expressed as a power-law type equation (see eq.[1]) (11).

$$I_p = k\nu^x \quad [1]$$

where,  $I_p$ ; redox peak current density,  
 $k$ ; the proportionality constant,  
 $\nu$ ; the scan rate,  
 $x$ ; the exponent of the scan rate.

Assuming that electrode kinetics satisfies eq.[1], the type of redox process can be determined by the value of  $x$ . The electrochemical redox reaction on the electrode is controlled by either the electron transfer process, where  $x=1$ , or the reactant diffusion process, where  $x=0.5$ .(14) The value of  $x$  can be calculated by using eq.[2], obtained by rearranging eq.[1].

$$\log I_p = \log k + x \log \nu \quad [2]$$

Relations between the oxidation current density ( $\log I_{p,a}$ ) and the scan rate ( $\log \nu$ ) are shown in Figure 5. It was almost a linear relationship, and the slope  $x$  was about 0.7. It was concluded that the redox kinetics was mainly controlled by both electron transfer and  $\text{ClO}_4^-$  diffusion processes preserving the electro-neutrality of the polymer.

Further studies in the photoconductivity of poly(NCHN) including copolymer systems containing a TNF moiety are in progress.

References

1. R.M.Schaffert, IBM, J.Rev.Develop 15, 75 (1975)
2. H.Naarmann, D.Strohriegel, in "Handbook of Polymer synthesis," ed. by H.R.Kricheldorf, Marcel Dekker, Inc, New York, 1404 (1992)
3. M.Stolka and D.M.Pai, "Advances in Polymer Science," ed. by H.-J.Cantow et al. Springer-Verlag Berlin Heidelberg, New York, 29 1 (1978)
4. J.W.Park, J.H.Lee, H.N.Cho, and S.K.Choi, Macromolecules 26 1191 (1993)
5. G.Helary, C.Chevrot, G.Sauvet, and A.Siove, Polym.Bulletin 26 131 (1991)
6. B.R.Hsieh, M.H.Litt, Macromolecules 19 521 (1986)
7. J.F.Ambrose and R.F.Nelson, J.Electrochem.Soc 115 1159 (1968)
8. J.F.Ambrose, L.L.Carpenter, and R.F.Nelson, J.Electrochem.Soc 122 876 (1975)
9. H.F.Ardill, J.J.Rooney, in "Ring-Opening Polymerization" ed by J.E.McGrath, ACS Symposium series 286 275 (1985)
10. S.H.Kim, H.J.Lee, S.H.Jin, H.N.Cho, and S.K.Choi, Macromolecules 26 846 (1993)
11. J.M.Ko, H.W.Rhee, and S.M.Park, J.Electrochem.Soc 137(3) 905 (1990)
12. H.N.Cho, K.Y.Choi, and S.K.Choi, J.Polym.Sci., Polym.Chem. 23 1469 (1985)
13. G.C.Bazan, R.R.Schrock, H.N.Cho, and V.C.Gibson, Macromolecules 24 4495 (1991)
14. A.J.Bard, L.R.Faulker, "Electrochemical Methods" Chapter 3, 6, and 10, Wiley, New York (1980)