속보

전도성 복합재료 개발을 위한 텔레킬릭 고분자: 메타크릴레이트-끝 씌어진 폴리피롤 합성

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Synthesis of Methacrylate-Endcapped Conductive Polypyrrole as a Telechelic Polymer

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초록: 일반적인 전도성고분자-폴리피롤(polypyrrole, PPy)의 경우, 화학구조상 화학결합을 할 수 있는 작용기가 없어 그 응용성에 많은 제한이 따른다. 이에 피롤-단량체에 새로운 고분자 중합이 가능한 비닐(vinyl) 작용기를 한쪽 끝에 화학적으로 도입하여, 필요에 따라 선택적으로 고분자 중합을 할 수 있는 이중 작용기 피롤-단량체 유도체, 메타크릴레이트-끝 씌어진 피롤을 합성하였다. 새롭게 합성된 이 단량체를 전기화학적인 방법으로 고분자 중합을 선택적으로 실시하여, 비닐 작용기를 포함하는 새로운 전도성고분자, 메타크릴레이트-끝 씌어진 폴리피롤을 성공적으로 합성하였다. 이는 전도성 복합재료 개발을 위한 텔레킬릭 고분자로써 다른 비닐작용기를 포함하는 범용 플라스틱 단량체와 전기화학 이외의 방법으로 다양한 그래프트 공중합체(graft copolymer) 합성이 가능하다.

Abstract: This paper reports on the electrochemical synthesis of electrically conductive *N*-methacrylated polypyrrole as a unique telechelic polymer with highly reactive vinyl functionality, which can be further polymerized to prepare graft copolymers with low molecular weight typical monomers such as other (meth)acrylates, styrenes, (meth)acrylamides, and (meth)acrylonitriles using ionic, radical, and other specialized polymerization techniques. It is based on a new dual reactive monomer containing each methacrylate and pyrrole functionalities at each opposite end of the structure, 3-((3-(1*H*-pyrrol-1-yl)propanoyl)oxy)-2-hydroxypropyl methacrylate, whose synthesis is presented in this work.

Keywords: conductive polymer, polypyrrole, telechelic polymer, dual functional monomer, macromonomer.

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Introduction

Electrically conductive polymers have been demonstrated as promising materials for numerous applications such as sensors,[1] tissue engineering,[2] light-emitting diodes,[3] batteries,[4] electrochromic devices,[5] electromagnetic shielding,[6] and corrosion inhibition.[7] In particular, PPy is one of the most popular conductive polymers because of its high electroactivity, low density, high electrical conductivity, and environmental stability.[8-10]

Due to the lack of reactive functional groups in pyrrole monomer itself, however, much intensive efforts have been devoted to chemically introduce pendent functionalities into PPy backbone skeleton.[11] Although the most common strategy is to use functionalities of dopants physically entrapped into PPy during the electropolymerization,[12-14] it may result in impairing the electrical and mechanical properties due to disruption of PPy by the trapped dopants.[15] Lee *et al.* presented carboxylic acid-functionalized PPy derivatives by electrically polymerizing monomeric 3-(1*H*-pyrrol-1-yl)propanoic acid and 1*H*-pyrrole-2-carboxylic acid precursors, respectively, and demonstrated them as a bioactive platform for cell adhesion by facilitating the covalent conjugation with a cell-adhesive Arg-Gly-Asp (RGD) motif on the polymer surfaces to direct cellular behavior.[16-18] Mecerreyes *et al.* reported 2-(1*H*-pyrrol-1-yl) ethanol and 2-(1*H*-pyrrol-1-yl)ethyl 2-bromo-2-methylpropanoate as pyrrole-functionalized polymerization initiators for reparing pyrrole-endcapped poly(ε-caprolactone) by ring-opening polymerization of ε-caprolactone and pyrrole-endcapped polymethacrylates by atom-transfer radical polymerization of methyl, *tert*-butyl, (dimethylamino)ethyl, and methoxyethoxyethyl methacrylates and poly(ethylene oxide) monomethacrylate.[19] The desired pyrrole precursor for further polymerization was introduced at the one end of the polymers by using the pyrrole-functionalized initiators. Alkan *et al.* also prepared pyrrole-endcapped polytetrahydrofuran by terminating the cationic polymerization of tetrahydrofuran with the potassium salt of pyrrole.[20]
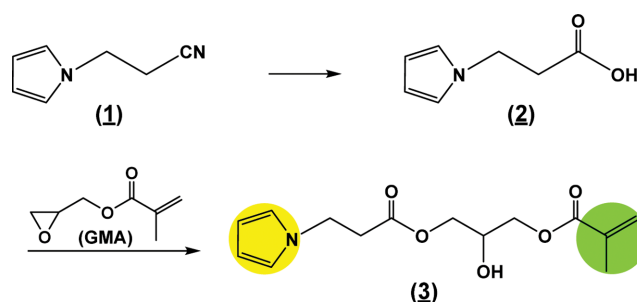
In a study related to this interest, it could be desirable to synthesize polymer architectures that are capable of imparting crosslinking or branching sites. Acrylates and methacrylates are common monomers in polymer plastics, easily forming the homopolymers or copolymers with a variety of monomers such as other (meth)acrylates, styrenes, and (meth)acrylamides, due to the presence of very reactive vinyl functionality.[21,22] For this reason, a dual reactive monomer composed of each polymerizable methacrylate and pyrrole precursors at the both ends would be a promising monomer candidate to architect three-dimensional (3D) conductive quasi-composites by grafting (block) copolymers. Here, synthesis of a new functional pyrrole monomer with a polymerizable methacrylate moiety, 3-((3-(1*H*-pyrrol-1-yl)propanoyl)oxy)-2-hydroxypropyl methacrylate (Py-*N*-MA) (**3**), is presented, and this dual reactive Py-*N*-MA (**3**) is electropolymerized into methacrylate-endcapped PPy (PPy-*N*-MA) (**4**) as a telechelic polymer capable of further polymerization with different vinyl monomers.

Experimental

All reagent grades of 1-pyrrolepropionitrile (Aldrich), potassium hydroxide (KOH, Fischer), hydrochloric acid (HCl, Fischer), diethyl ether (Aldrich), *n*-heptane (Aldrich), triethylamine (TEA, Fischer), glycidyl methacrylate (GMA, Aldrich), sodium bicarbonate (NaHCO$_3$, Fischer), anhydrous magnesium sulfate (MgSO$_4$, Fischer), and tetrabutyl ammonium perchlorate (TBAP, Fluka) were used without further purification; however, *N*,*N*-dimethylformamide (DMF, Alfa Aesar) was dried over phosphorus pentoxide and vacuum-distilled immediately prior to use, and dichloromethane (CH$_2$Cl$_2$, Fischer) was dried over calcium hydride (CaH$_2$, Aldrich) and distilled. Fluoride-doped tin oxide (SnO$_2$:F, FTO) coated glass slides (Hyogo) with typical sheet resistance of 15 Ω/sq were ultrasonically cleaned in ethanol and double deionized (DDI) water for 2 min each, then dried under vacuum.

Schematic chemical reactions for the synthesis of *N*-methacrylated pyrrole, Py-*N*-MA (**3**), as a dual functional monomer are presented in Scheme 1.

3-(1*H*-pyrrol-1-yl)propanoic acid (PyCOOH) (**2**) was hydrolyzed from 1-pyrrolepropionitrile (**1**) as described elsewhere.[16] Briefly, 100 mmol of (**1**) was added to 60 mL of 6.7 M KOH. This mixture was refluxed under argon atmosphere until NH$_3$(g) no longer evolved. The reddish solution was acidified to pH 5 using 8 M HCl, and the product was then extracted with diethyl ether. The diethyl ether was evaporated, and the

Scheme 1. Synthetic scheme for dual functional Py-*N*-MA (**3**), which was synthesized by the coupling reaction of GMA with PyCOOH (**2**) via an epoxide ring-opening mechanism.

resulting crude product was twice recrystallized from boiling *n*-heptane to the white crystalline product (**2**) (yield 65%). The ^{1}H NMR and ^{13}C NMR spectra (not shown) confirmed the structure and were in agreement with the literature.[17]

For the synthesis of Py-*N*-MA (**3**), 75 mmol of TEA was added to 50 mmol of PyCOOH (**2**) in 50 mL DMF at 0 °C and the mixture was stirred for 1 h under argon atmosphere. A solution of 40 mmol of glycidyl methacrylate (GMA) in 10 mL DMF was added dropwise into the mixture. The reaction mixture was warmed to room temperature, stirred overnight, and the volatile components were removed under reduced pressure. The resulting crude product was dissolved in CH$_2$Cl$_2$, and washed with saturated NaHCO$_3$ solution, followed by water three times. The organic layer was dried over anhydrous MgSO$_4$, filtered and the excess solvent was evaporated to yield the dual functional *N*-methacrylated pyrrole monomer (Py-*N*-MA) (**3**) (yield 79%).

Perchlorate-doped poly[3-((3-(1*H*-pyrrol-1-yl)propanoyl)oxy)-2-hydroxypropyl methacrylate] (PPy-*N*-MA) (**4**) films were electrochemically polymerized using a potentiostat/galvanostat (Model 273, Princeton Applied Research) in a three-electrode cell: a stainless steel wire mesh (SUS304 EXMET, 325 mesh) served as the counter electrode, an Ag/AgCl (in saturated KCl) electrode served as the reference electrode, and a FTO glass slide (2.5×7.5 cm) served as the working electrode. A 1.0 mM solution of the monomeric Py-*N*-MA (**3**) was prepared in CH$_2$Cl$_2$ with 0.2 M of TBAP, and the solution was purged with N$_2$ for 10 min to prevent oxidation of the monomer prior to polymerization. The polymerization onto a FTO glass slide was carried out in three cycles, from 0.0 to +1.5 V at a scan rate of 2 mV/s.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity 300 (300 MHz) spectrometer, and mass spectra (MS) were obtained in fast atom/ion bombardment ionization (FAB)

mode on a Thermo Scientific TSQ triple quadrupole mass spectrometer. Morphology was examined using scanning electron microscopy (SEM) (S-4000, Hitachi).

Results and Discussion

The synthesis of dual functional *N*-methacrylated pyrrole monomer, Py-*N*-MA (**3**), in 79% yield by a base-catalyzed esterification of PyCOOH (**2**) with GMA in Scheme 1 was straightforward and its spectral data was consistent with this structure. Its ^{1}H NMR spectrum is compared with that of PyCOOH (**2**) by assigning characteristic peaks arose from GMA moiety in Figure 1. The signals at 6.13 ppm and 5.63 ppm in the Py-*N*-MA (**3**) spectrum were assigned to vinyl carbon-linked hydrogens, H_A and H_B, respectively. The peaks at 1.94 ppm corresponded to methyl carbon-linked hydrogen at the vinyl carbons (CH_3) and the broad signal at 3.02 ppm was attributed to hydroxyl group (OH) of the glyceryl ester moiety. The appearance of these signals indicates the formation of Py-*N*-MA (**3**), which is the major reaction product resultant of the epoxide ring-opening pathway at the least sterically hindered end.[23] For reference, the PyCOOH (**2**) spectrum) presented signals at 2.81 (t, 2H, CH_2COO), 4.21 (t, 2H, CH_2CH_2), 6.09 (dd, 2H, $CH_{\beta\text{-pyrrole}}$), 6.68 (dd, 2H, $CH_{\alpha\text{-pyrrole}}$), and 10.78 ppm (br, 1H, COO*H*: not shown). Multiplet signals in the spectral region of 4.5 - 2.5 ppm were attributed to the glyceryl and propanoyl spacers from GMA and PyCOOH (**2**), respectively.[17,23]

In FAB-MS analysis, the most intense ion peak at 282 *m/z* in Figure 2 was found to be the protonated molecular ion, [MH]$^+$, with the formula mass of 281.13 amu calculated for Py-*N*-MA (**3**) ($C_{14}H_{19}NO_5$) and the second most peak at 196 *m/z* corresponded to the structural fragment [M-85]$^+$, which was produced by cleavage next to the methacrylate moiety of Py-*N*-MA (**3**) as seen in inset of Figure 2. Based on the molecular formula, detection of the parent ion and the corresponding daughter ion at 196 *m/z* supports the successful incorporation of methacrylate moiety from GMA at the *N*-end of the PyCOOH (**2**).

The electrochemical behavior of Py-*N*-MA (**3**) was investigated in CH_2Cl_2 solution of 0.2 M TBAP using potential cycling between 0.0 V and +1.50 V (versus Ag/AgCl) at 2 mV/s scan rate with a FTO glass slide (2.5×7.5 cm) electrode. Electrochemical oxidation of Py-*N*-MA (**3**) monomer was performed under anodic polymerization, which excluded the possibility of cathodic electrografting and radical polymerizing of methacylate moieties.[24] The resulting polymer, PPy-*N*-MA
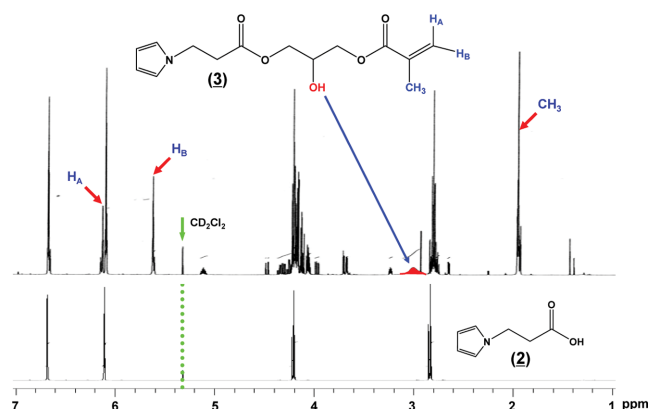

Figure 1. ^{1}H NMR spectrum of monomeric Py-*N*-MA (**3**), where characteristic peaks arose from GMA moiety are assigned with comparing that of PyCOOH (**2**).
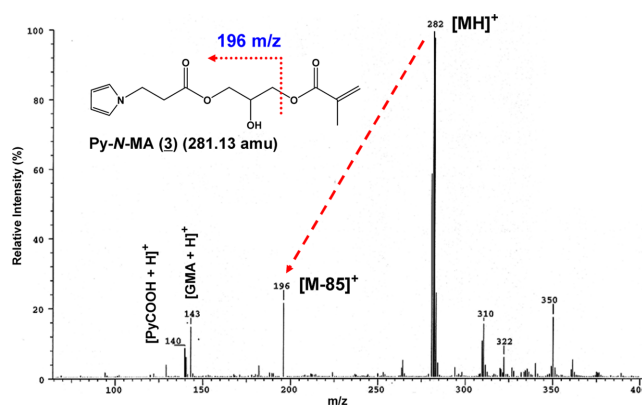

Figure 2. FAB mass spectrum of monomeric Py-*N*-MA (**3**), where the most intense peak at 282 m/z was detected as the protonated molecular ion species, [MH]$^+$.

(**4**), was deposited onto the surface of the FTO electrode in Figure 3. Figure 3(B) demonstrated three cycles obtained in the same solution of 1.0 mM Py-*N*-MA (**3**). The formation and growth of the PPy-*N*-MA (**4**) film as a telechelic macromonomer can be easily seen as the number of potential cycles increases. The intensity of the peaks from the redox of the (**4**) film increased and the anodic peak potentials shifted to positive direction as the film grew. A broad oxidation peak was observed at the peak potential of +1.25 V and reverse cathodic peak was seen at a peak potential of +1.00 V. The color of the resulting polymer (**4**) film on the FTO glass slide electrode was dark brown. The morphology of the polymer (**4**) was investigated using SEM in Figure 3(C), where the cauliflower-like feature was identical to that of typical PPy thin films electrodeposited on electrodes.[16] From a chemical point of view, it is demonstrated that incorporating carbon-carbon π-bond from
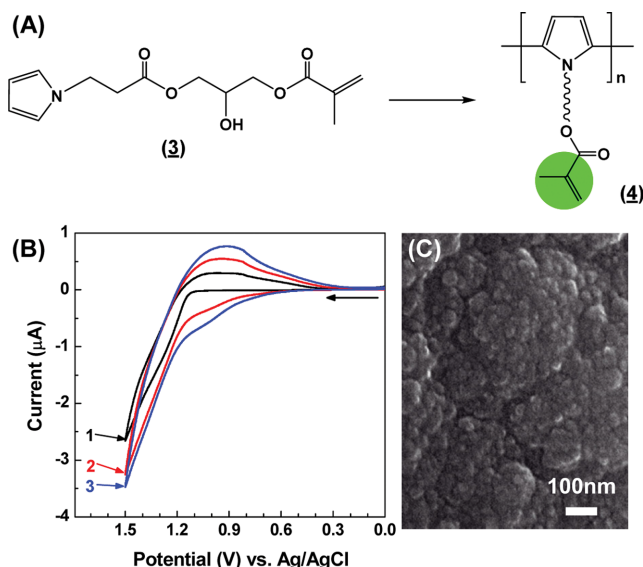
Figure 3. (A) Synthetic scheme of an electrically conductive telechelic macromonomer, PPy-*N*-MA (**4**), from Py-*N*-MA (**3**). (B) Cyclic voltammograms (CVs) of the PPy-*N*-MA (**4**) electropolymerization recorded for 1.0 mM monomeric Py-*N*-MA (**3**) on a FTO glass slide electrode in a 0.2 M TBAP/CH$_2$Cl$_2$ solution during three consecutive potential cycles between 0.0 V and +1.5 V at a scan rate of 2 mV/s. (C) Scanning electron microscopy (SEM) image demonstrating the typical feature of PPy-*N*-MA (**4**) film.

the GMA onto the structure of pyrrole is a suitable strategy for producing a telechelic polypyrrole because its vinyl functionality could enable it to undergo a gelling process through a grafting or crosslinking polymerization reaction.

The relatively high potential of the redox peaks of PPy-*N*-MA (**4**) compared to conventional polypyrrole (PPy) may suggest that oligomers with short conjugation length would be formed. Homopolymers of dual functional pyrrole derivatives would sacrifice intrinsic PPy bulk properties due to steric hindrance of the pendent side chains. In the previous reports, terthiophene derivatives (*i.e.*, 3'-substituted trimers of heterocyclic thiophene) exhibited lower oxidation potential, compared to thiophene derivatives (*i.e.*, 3-substituted monomer of thiophene).[25-27] This led to high electrical conductivity and mechanical integrity of polymers from the terthiophene over the thiophene derivatives, attributed to alternate side chains that reduce steric interactions and structural irregularities.[28] Therefore, preferential bulk properties of PPy-*N*-MA (**4**) could be optimized by adding pristine pyrrole to the Py-*N*-MA (**3**) solution before the film was oxidized in the electrochemical reduction/re-oxidation (dedoping/doping) processes, finally leading to the copolymer, poly(pyrrole-*co*-(**3**)).[17]

Conclusions

A new methacrylate-endcapped pyrrole monomer (Py-*N*-MA) (**3**) has been synthesized and utilized for the preparation of a telechelic methacrylate-functional polypyrrole (PPy-*N*-MA) (**4**) by electropolymerization. It could be a promising macromonomer to be further polymerized or chemically modified with other reactive vinyl functionalities in order to achieve desired conductive PPy composites. The graft copolymers of poly(meth)acrylates with PPy-*N*-MA (**4**) are currently underway to fabricate three-dimensional (3D) conductive quasi-composites, and/or to improve the conventional PPy processability.

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