Poly(thiophene-2,5-diyl)s with a Crown Ethereal Subunit. Preparation, Optical Properties, and n-Doped State Stabilized against Air

Takakazu Yamamoto,*,† Masakatsu Omote,† Yuichi Miyazaki,† Akio Kashiwazaki,† Bang-Lin Lee,† Takaki Kanbara,† Kohtaro Osakada,† Tetsushi Inoue,† and Kenji Kubota‡

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan, and Faculty of Engineering, Gunma University, Tenjincho, Kiryu 376, Japan

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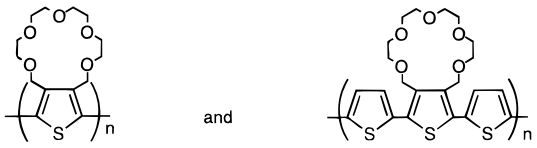
ABSTRACT: Five kinds of polythiophenes bearing a crown ethereal subunit directly bonded to the thiophene ring have been prepared by the following organometallic polycondensation: (i) nX−Ar−X + nNi^{0}L$_m$ → {Ar}$_n$; (ii) aX−Ar−X + bX−Ar′−X + (a + b)Ni^{0}L$_m$ → {Ar}$_a${Ar′}$_b$, and (iii) nX−Ar−X + nMe$_3$Sn−Ar′−SnMe$_3$ → {Ar−Ar′}$_n$ (Pd-catalyzed); Ar = thiophene-2,5-diyl with the crown ethereal subunit. Polythiophenes with alkoxy substituents (OCH_3 and $O(CH_2)_2OCH_3$) are also prepared by the organometallic polycondensation. The crown ethereal polymers exhibit photoluminescence in a range of 467−603 nm in both $CHCl_3$ solutions and films. Their electroluminescence spectra essentially agree with the photoluminescence spectra. The crown ethereal polythiophenes have a high affinity toward Na^+. After chemical oxidation (or p-doping) and reduction (or n-doping), the polymers show an electrical conductivity of 5.4 × 10^{-7} to 1.8 S cm^{-1}. The Na-doped and electrically conducting state of crown ethereal polythiophenes shows some stability under air, which is attributed to the strong affinity of the polymer to Na^+. Cyclic voltammetry of the crown and linear ethereal polythiophenes reveals a large difference (about 2 V) between n-doping and n-undoping potentials.

Introduction

Preparation and properties of π-conjugated poly(arylene)s are a subject of recent interest.[1] Many pieces of research have been carried out, especially on polythiophenes,[2,3] and polythiophene[2a] and poly(3-alkylthiophene)[3a] were first prepared by organometallic polycondensation by us. Recently, introduction of crown ethereal substituents to polythiophene has been reported,[4,5] and Swager and his co-workers have demonstrated the usefulness of the polymers in sensing (or recognizing) molecules in solutions.[4]

Here we report chemical, optical, and electrical properties of new polythiophenes with the crown ethereal subunits directly bonded to the thiophene unit.

Examples are



Due to the strong affinity of the crown ethereal subunit for Na^+, Na-reduced (or n-doped) polymers have a certain stability against oxygen in air. We have also compared their chemical and physical properties with those of corresponding low-molecular-weight crown ethers and related polymers with linear ethereal groups.

Results and Discussion

Preparation. Organometallic polycondensations using a zerovalent nickel complex Ni^{0}L$_m$[6] (eqs 1 and 2) and the Stille reaction[7] (eqs 3 and 4) give polythiophenes with the crown ethereal subunit in high yields. Table 1 summarizes results of the preparation of the crown ether type polythiophenes and related polymers. The composition of the random type copolymers, *ran*-Copoly-11 and -12, essentially agrees with the feeding ratios of the two monomers. Use of DMF in eq 3 gives the copolymers in high yield; however, use of THF[7] has not given successful results.

The following related low-molecular-weight compound $CrTh_3$ and polymers with linear ethereal groups[8] have also been prepared by the organometallic process.

Solubility, M_w, and IR. PCrTh, *reg*-Copoly-11, and *reg*-Copoly-12 are highly soluble in organic solvents including THF, MeOH, and $CHCl_3$ due to the presence of the solubilizing crown ethereal subunit. *ran*-Copoly-11 and *ran*-Copoly-12 are fractionated into two parts by solubility in organic solvents. IR spectroscopy reveals that the $CHCl_3$-soluble fraction (62−65 wt %) of *ran*-Copoly-11 and *ran*-Copoly-12 contains the crown ethereal thiophene unit in a higher proportion than the $CHCl_3$-insoluble fraction.

Polythiophenes with the linear ethereal substituents (eq 6) show rather low solubility. For example, PMeOTh has a low solubility in organic solvents, although PMeOTh prepared by chemical and electrochemical oxidation (eq 7) of 3-methoxythiophene has a high solubility.[8] The high solubility of PMeOTh prepared by the oxidative polymerization may be due to its relatively low molecular weight[8a] and/or partially branched structure by contamination with β-bonding. An NMP (*N*-

† Research Laboratory of Resources Utilization, Tokyo Institute of Technology.
‡ Faculty of Engineering, Gunma University.
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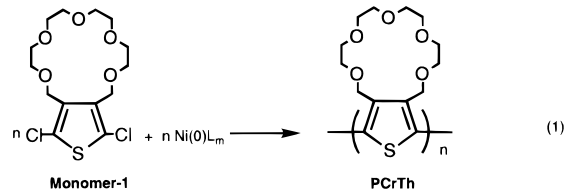
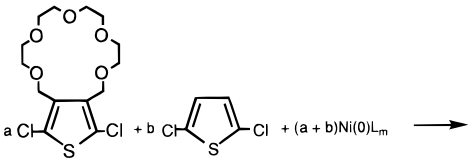


(1)

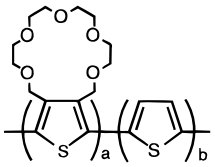
Monomer-1 **PCrTh**

$Ni(0)L_m$: a mixture of bis(1,5-cyclooctadiene)nickel(0) ($Ni(cod)_2$) and 2,2'-bipyridiyl (bpy).



Monomer-2

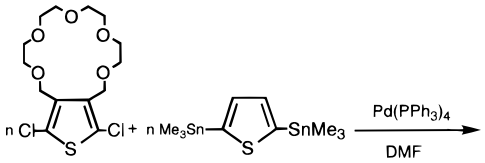
1 : 1
or 1 : 2



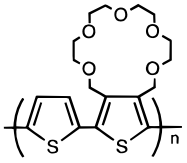
(2)

rand-Copoly-11 (a : b = 1 : 1)

rand-Copoly-12 (a : b = 1 : 2)

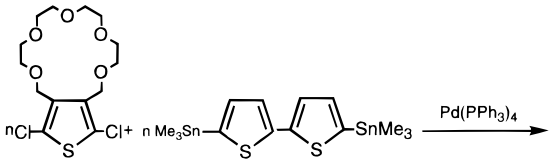


Monomer-3

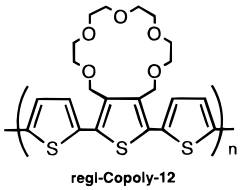


(3)

regI-Copoly-11



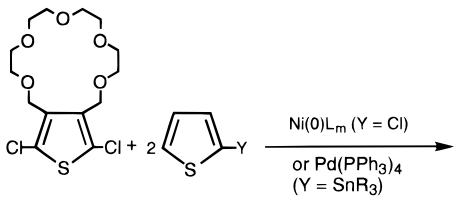
Monomer-4

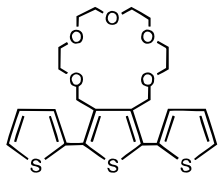


(4)

regI-Copoly-12

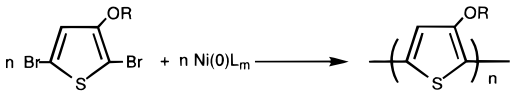
methyl-2-pyrrolidone)-soluble part (M_n = 1800, *vide infra*) of PMeOTh prepared according to eq 6 exhibits a $\pi-\pi^*$ absorption band (λ_{max} = 576 nm) at a longer wavelength than those (480 nm[8a,c] to 540 nm[8b]) of PMeOTh prepared by the oxidation methods, presumably due to the regulated α-bonding in the present polymer. PMeOEtOTh has a somewhat higher solubility in solvents and also exhibits λ_{max} (578 nm) at a longer wavelength than that (552 nm) of PMeOEtOTh prepared by chemical oxidation of the corresponding monomer with $FeCl_3$.





(5)

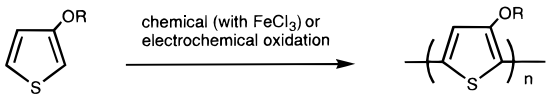
$CrTh_3$



(6)

R = OCH_3 **(Monomer-5)** R = OCH_3 **(PMeOTh)**
R = $O(CH_2)_2OCH_3$ **(Monomer-6)** R = $O(CH_2)_2OCH_3$ **(PMeOEtOTh)**

PCrTh, *ran*-Copoly-11 (soluble part), *ran*-Copoly-12 (soluble part), and *reg*-Copoly-11 have molecular weights of $M_w = 4.6 \times 10^4$, 2.2×10^4, 1.3×10^4, and 8.6×10^3, respectively, as determined by a light-scattering method[9,10] in $CHCl_3$, which is one of the best solvents for poly(3-alkylthiophene)s.[10c] PCrTh shows a small (but non-zero) degree of depolarization[9,10a] (ρ_v = 0.05) in $CHCl_3$, whereas the copolymers with thiophenes give larger ρ_v values (ca. 0.10), indicating that the copolymers take a stiffer structure in the solution. PCrTh exhibits an [η] value of 0.24 dL g^{-1} in $CHCl_3$ at 30 °C. The NMP-soluble part of PMeOTh shows M_n and M_w values of 1800 and 3000, respectively, as determined by GPC (polystyrene standard).



(7)

PCrTh, *reg*-Copoly-11, and *reg*-Copoly-12 show T_g at about 1, 8, and 14 °C, respectively. *reg*-Copoly-11 and *reg*-Copoly-12 exhibit endothermic peaks at 96.9 and 116.9 °C, respectively, which are assigned to their melting points. TGA analysis indicates that rapid thermal decomposition of PCrTh, *reg*-Copoly-11, and *reg*-Copoly-12 starts at about 300 °C under N_2 and the polymers give residual weights of about 20%, 40%, and 50%, respectively, at 800 °C.

IR spectra of the polymers are reasonable for their structures shown in eqs 1−4 and 6. The ν(C−halogen) peaks of the monomers are not observed in the IR spectra. IR spectra of PMeOTh and PMeOEtOTh are similar to those of the corresponding polymers prepared by the chemical oxidative polymerization (eq 7).

NMR. The ^{1}H-NMR spectrum of PCrTh exhibits CH_2 signals at almost the same position as that of Monomer-1. ^{1}H-NMR spectra of *reg*-Copoly-11 and *reg*-Copoly-12 (Figure 1) are reasonable for the structure of the polymers. A somewhat complex pattern of the aromatic-H signals at about δ 7.2 ppm suggests the presence of conformers concerning the bond connecting the monomeric units (e.g., *s*-cis and *s*-trans conformers). The peak area ratios agree with the structures of the polymers.

^{1}H-NMR spectra of other polymers and $CrTh_3$ (eq 5) as well as ^{13}C-NMR spectra of the compounds shown in

Table 1. Preparation of Crown Ether Type Polythiophenes and Related Compounds[a]

			λ_{max}, nm		photoluminescence, nm		
run	polymer	yield, %	in $CHCl_3$[b] or in NMP	film	in $CHCl_3$	film	electroluminescence,[c] nm
1	PCrTh	86	333 (5.1×10^3)	333	467	469	470
2	*ran*-Copoly-11	79	374[d]	364[d]	528[d]	559[d]	550
3	*ran*-Copoly-12	96	363[d]	361[d]	531[d]	528[d]	
4	*reg*-Copoly-11	74	408 (6.5×10^3)	437	551	594	
5	*reg*-Copoly-12	74	424 (1.9×10^4)	452	555	603	
6	$CrTh_3$	76	329 (1.9×10^4)		435		
7	PMeOTh	76	576[e]				
8	PMeOEtOTh	85	578[e]				

[a] The polymerization and synthesis of $CrTh_3$ were generally carried out in DMF (cf. Experimental Section and Supporting Information). [b] For runs 1−6. The molar absorption coefficient ϵ (in M^{-1} cm^{-1}) is given in the parentheses. Molarity is based on the repeating unit, e.g., $C_4H_2S-C_{14}H_{20}O_5S-C_4H_2S$ for *reg*-Copoly-12. [c] With ITO glass |polymer|Al (or Mg(Ag)) diodes. [d] For the $CHCl_3$−soluble part. [e] In NMP (*N*-methyl-2-pyrrolidone) for runs 7 and 8. An NMP-soluble part for run 7.

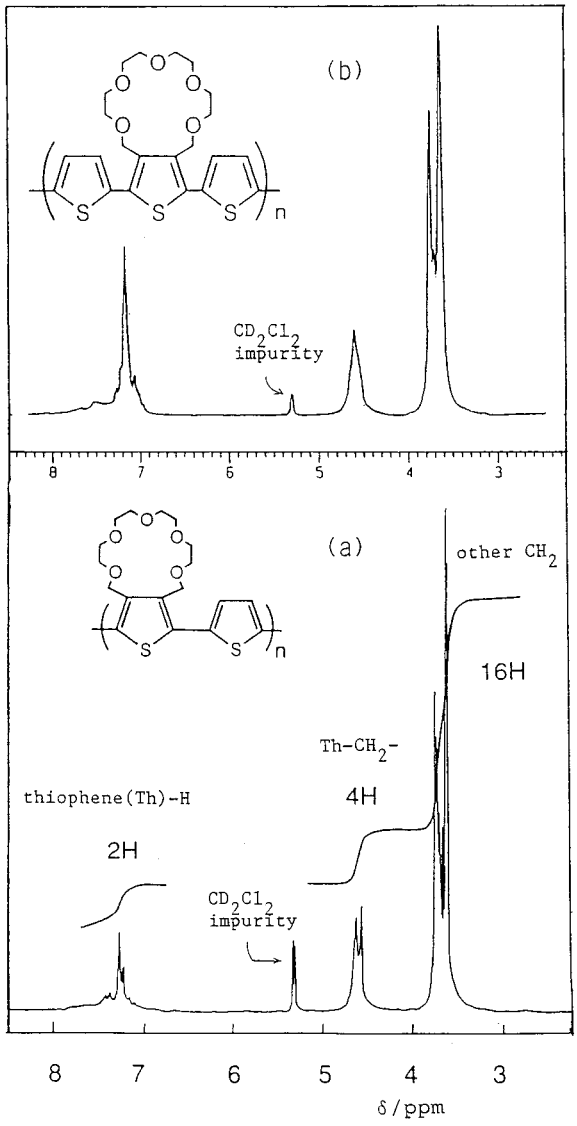


Figure 1. ^{1}H-NMR spectra of (a) *reg*-Copoly-1 and (b) *reg*-Copoly-2 in CD_2Cl_2.

eqs 1−6 are also reasonable. The absorption pattern of aromatic ^{1}H-NMR signals of $CrTh_3$ varies with the kind of solvent, suggesting that $CrTh_3$ also has several conformers in view of the structure of the crown ether ring.

The ^{1}H-NMR spectrum (cf. Supporting Information) of the soluble part of PMeOTh in $CDCl_3$ shows two signals of the methoxy protons (δ 3.8 and 4.0 ppm) and four signals of the aromatic protons (δ 6.83, 6.87, 6.92, and 7.02 ppm). Two methoxy proton signals at δ 3.8 and 4.0 ppm are assigned to head-to-head (HH) and head-to-tail (HT) conjunctions, respectively, from analogy with the ^{1}H-NMR chemical shifts of poly(3-alkylthiophene-2,5-diyl)s.[3] Four aromatic proton signals are assigned to four possible triads in PMeOTh.

Optical Properties. UV−Visible Data in Solution. The UV−visible spectrum of the trimeric compound, $CrTh_3$, exhibits an absorption peak at 329 nm (run 6 in Table 1), which is shifted to a longer wavelength from that of thiophene (λ_{max} = 232 nm). However, the degree of the bathochromic shift (ΔE = 12 700 cm^{-1}) is somewhat smaller than that observed with α-terthiophene (α-Th_3) (λ_{max} = 354 nm, ΔE = 14 900 cm^{-1}).[10c,11]

PCrTh gives the $\pi-\pi^*$ absorption band at λ_{max} = 333 nm (run 1; ΔE = 13 100 cm^{-1}), suggesting that the polymer also has an effective π-conjugation length corresponding to about three thiophene units. By introducing a nonsubstituted thiophene (Th) unit, which serves as a spacing π-conjugated group, the $\pi-\pi^*$ absorption band of the copolymers is shifted to longer wavelengths (runs 2−5 in Table 1). The $\pi-\pi^*$ absorption band of the soluble part of the random-type copolymers (runs 2 and 3) appears near a $\pi-\pi^*$ absorption band of α-quarterthiophene (α-Th_4) (λ_{max} = 385 nm).[11] In cases of the regular-type copolymers, the steric repulsion by the crown ethereal subunit is avoided more effectively, and *reg*-Copoly-12 gives rise to a UV−visible absorption peak (λ_{max} = 424 nm, run 5) near those of α-Th_5 (λ_{max} = 418 nm),[11] poly(3-hexylthiophene-2,5-diyl) (λ_{max} = ca. 430 nm depending on its regioregularity[3,12,13]), and poly(alkylthiazole)s (λ_{max} = 420 nm)[13b,14] constituted of similar five-membered rings.

UV−Visible Data in Film. Films of PCrTh, *ran*-Copoly-11, and *ran*-Copoly-12 give rise to the $\pi-\pi^*$ absorption band at almost the same position as the solutions of the polymers. However, the $\pi-\pi^*$ absorption band of films of *reg*-Copoly-11 and *reg*-Copoly 12 is shifted to a longer wavelength (runs 4 and 5 in Table 1), suggesting that these regular copolymers take a stacked structure similar to that of regioregular poly(3-alkylthiophene)s (P3RThs) and poly(alkylthiazole)s in the solid[3,13,15] and the regularly repeating structure is crucial for the polymers to take such a stacked structure. The degree of the bathochromic shift (about 1500 cm^{-1} for both *reg*-Copoly-11 and *reg*-Copoly-12) is, however, smaller than that (ca. 4000−6000 cm^{-1})[3,13] observed with poly(3-alkylthiophene)s and poly(alkylthiazole)s. Fell, Samuelsen, and co-workers[3m] reported crystallinity of films of octylphenyl-substituted polythiophene and its relation to the conjugation length of the polymer.

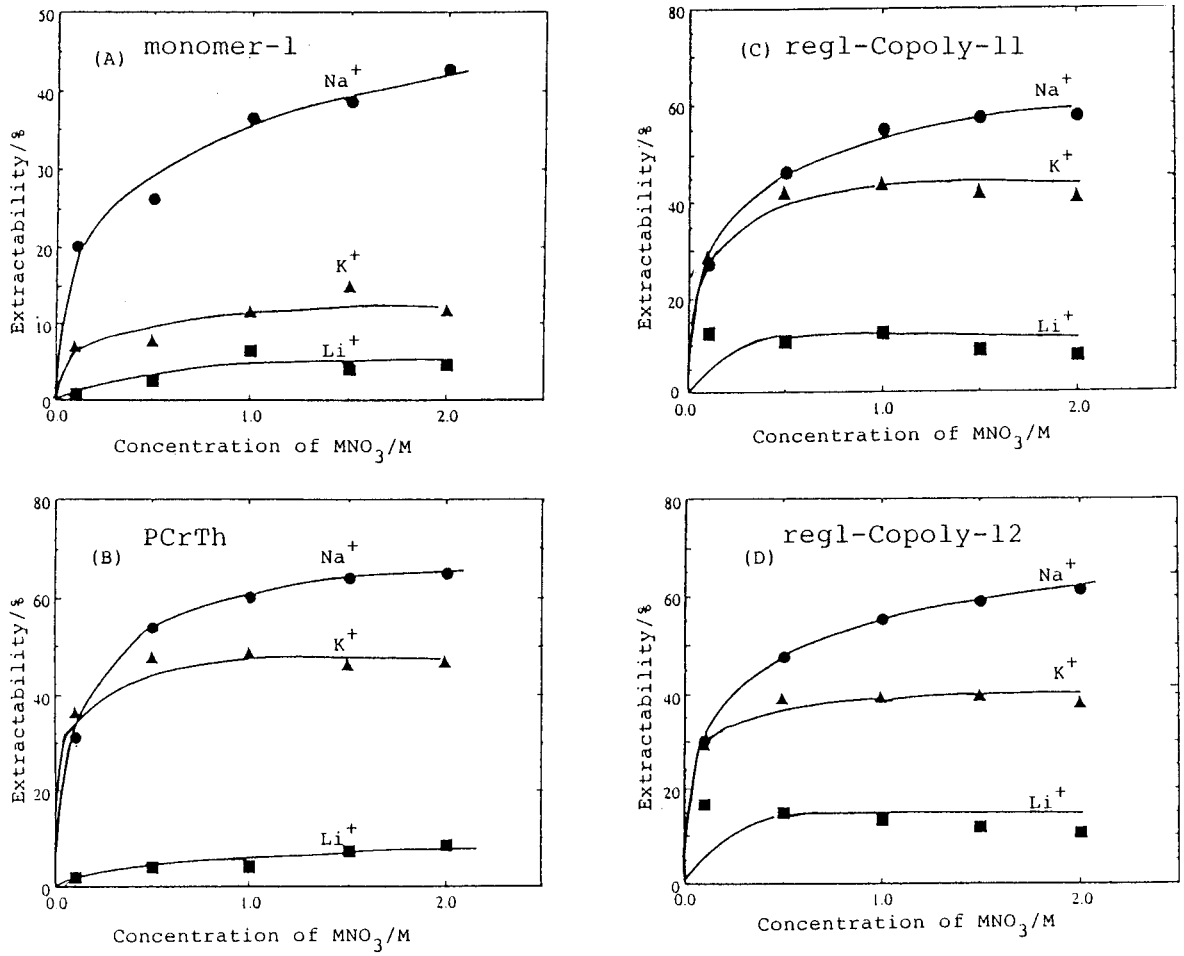


Figure 2. Extractability of Na^+, K^+, and Li^+ by (A) Monomer-1, (B) PCrTh, (C) *reg*-Copoly-11, and (D) *reg*-Copoly-12. Extractability was determined by Pedersen's method.[17] Extraction conditions: CH_2Cl_2 (10 mL)/H_2O (10 mL) two phase system; [extractant] = [picric acid] = 7×10^{-5} M; [crown ether] = 7×10^{-4} M; $T = 22 \pm 1$ °C; shaking time = 12 h.

Luminescence. All of the polymers and $CrTh_3$ having the crown ethereal subunit are photoluminescent (Table 1) and give a photoluminescence peak (λ_{ph}) at an onset position of the $\pi-\pi^*$ absorption band, as usually observed with photoluminescent aromatic compounds and polymers.[1,3,6] As for PCrTh and *ran*-Copoly-11, their electroluminescent behavior has also been investigated by constructing (+) ITO/polymer/metal (−) (ITO = indium−tin−oxide glass; metal = Al or Mg(Ag); the shown (+) and (−) direction is the direction of a forward bias) light-emitting diodes. The electroluminescence spectra of PCrTh and *ran*-Copoly-11 agree with the photoluminescence spectra of the respective polymers, as shown in Table 1 (runs 1 and 2) and the Supporting Information. Similar agreement between the photoluminescence spectrum and electroluminescence spectrum has been reported for many π-conjugated polymers.[16]

According to the shift of the $\pi-\pi^*$ absorption band to the longer wavelength by insertion of the spacing Th unit, the onset of the $\pi-\pi^*$ absorption band as well as the electroluminescence peak of the copolymer is shifted to a longer wavelength compared with that of PCrTh.

Chemical and Redox Behavior. Affinity against Alkaline Metal Ions. Crown ethers usually have a strong affinity toward alkaline metals,[17] and the relative affinity of Monomer-1 against Li^+, Na^+, and K^+ has been estimated[18] by using an extraction method (extraction of M^+ in an aqueous solution by a CH_2Cl_2 solution of the crown ether) developed by Pedersen.[17] We have followed the results for Monomer-1 reported by Sone and his co-workers[18] and obtained essentially the same results (Figure 2A), which indicate that Monomer-1 has the highest affinity toward Na^+ among the alkaline metal cations.

PCrTh, *reg*-Copoly-11, and *reg*-Copoly-12 also have the highest affinity toward Na^+, as depicted in Figure 2B−D. The relatively large affinity of the crown ethereal polymers against K^+, compared with that of Monomer-1, suggests some cooperative effects of the polymeric crown ether to capture K^+ (e.g., by forming a crown ether−K^+−crown ether type 2:1 adduct in the polymer matrix). Data from ICP emission spectrometry of the CH_2Cl_2 extract agree with the data shown in Figure 2. Drying up the CH_2Cl_2 solution of PCrTh after extraction of Na^+ from the aqueous solution of $NaNO_3$ gives the polymer adduct with $NaNO_3$, and its IR spectrum shows a new absorption band of the NO_3 group at 1380 cm^{-1}. However, no obvious change is observed in UV−visible, photoluminescence, and ^1H-NMR spectra of the polymer.

Redox Behavior and Conducting Properties. Although the polymers shown above give only low electrical conductivity, they are converted into semiconducting materials by oxidation (p-doping) and reduction (n-doping). Data of electrical conductivity of chemically oxidized (with I_2) and reduced (with Na) polymers are summarized in Table 2.

p-Doping. By the iodine-doping, a new broad absorption band assigned to the ring vibration of the p-doped thiophene ring appears at about 1400 cm^{-1} in the IR spectrum, similarly to cases of iodine-doped polythiophenes.[1−3] In addition to the change in the ring

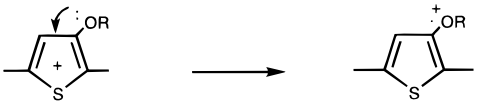
Table 2. Electrical Conductivity of Chemically Doped Polymers[a]

		conductivity, S cm^{-1}		
no.	polymer	nondoped	iodine doped	sodium doped
1	PCrTh	$<10^{-10}$	1.1×10^{-6}	6.7×10^{-6}
2	*ran*-Copoly-11	$<10^{-10}$	8.7×10^{-7}	1.2×10^{-4}
3	*ran*-Copoly-12	$<10^{-10}$	1.0×10^{-4}	1.0×10^{-4}
4	*reg*-Copoly-11	$<10^{-10}$	1.4×10^{-6}	4.6×10^{-7}
5	*reg*-Copoly-12	$<10^{-10}$	8.1×10^{-6}	5.4×10^{-7}
6	PMeOTh	2.8×10^{-4}	1.8×10^{0}	3.2×10^{-2}
7	PMeOEtOTh	2.7×10^{-5}	2.1×10^{-1}	2.5×10^{-2}

[a] For the doping process, see Experimental Section.

vibration, the iodine-doping generally brings about severe weakening of the aliphatic ν(C−H) absorption band. Similar weakening of the aliphatic ν(C−H) absorption band has been reported with iodine-doped poly(3-alkylthiophene)s (P3RThs),[19] and these results indicate that the iodine-doping causes changes in not only the electronic state of the thiophene ring but also that of the alkyl and alkoxy side chains.

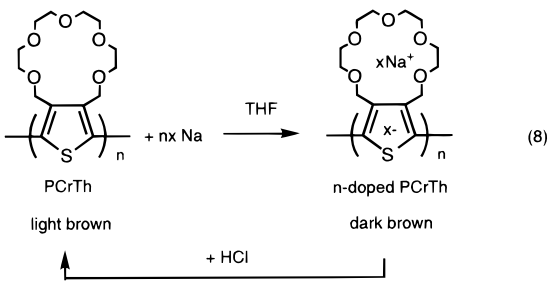
As for the linear ethereal polythiophenes, an electron migration[8d]



(7)

which will lead to a more severe electronic change in the side chain than in the main chain, may take place. Actually, comparison of ^{1}H-NMR spectra (Figure 3) of p-doped and undoped P3MeOTh prepared by the electrochemical oxidation indicates that the p-doping gives a more severe effect on the alkoxy hydrogens than the thiophene ring hydrogen.

n-Doping. Chemical n-Doping. Reactions of the crown ethereal polythiophenes with metallic Na give Na-doped (or n-doped) polymers. On the Na-doping of PCrTh, the IR absorption band at 1100 cm^{-1} assigned to ν(C-O-C) is somewhat weakened and a new strong absorption band appears at about 1450 cm^{-1}. Treatment of the Na-doped PCrTh with dilute HCl(aq) recovers original PCrTh, as manifested by IR spectroscopy, indicating that no cleavage of the chemical bond of PCrTh takes place in the Na-doping. By the Na-doping, PCrTh is converted into a semiconducting material (Table 2), and these results are explained by the formation of the following Na-adduct of PCrTh with delocalized negative carrier in the π-conjugated main chain.



(8)

Similar IR changes (weakening of the ν(C−O−C) absorption band at about 1100 cm^{-1} and appearance of a new strong absorption band at about 1450 cm^{-1}) are also observed with other Na-doped polythiophenes with the crown ethereal or linear ethereal subunit. The new strong absorption band at 1450 cm^{-1} may be assigned to a ν(C−O−C) absorption band of the ethereal group with a strong interaction with Na^+.

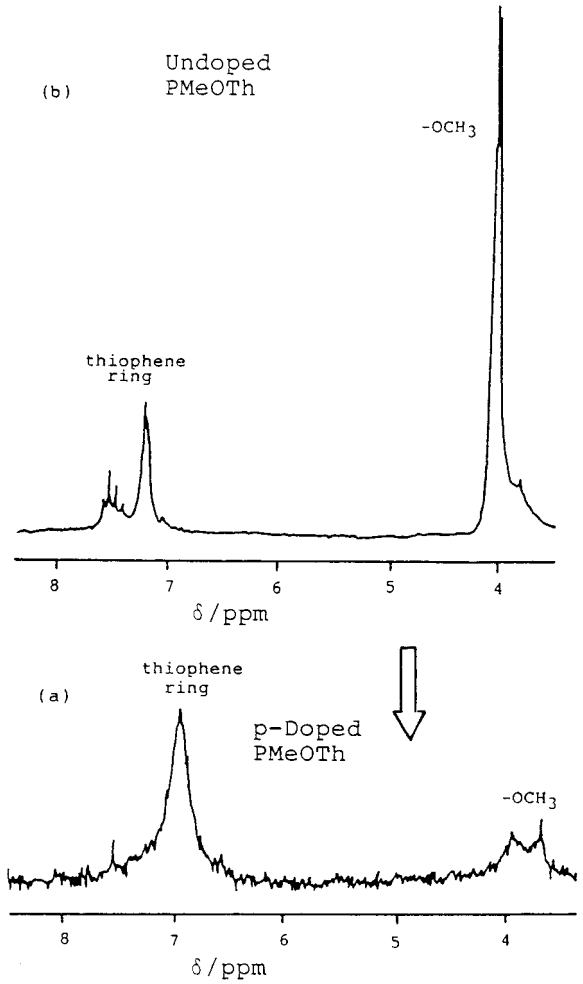


Figure 3. (a) ^{1}H-NMR spectrum of PMeOTh prepared electrochemically[8] in an acetonitrile solution of 3-methoxythiophene (0.3 M) at 20 °C and 2 mA cm^{-2}. Electrolyte = [N(n-C_4H_9)$_4$]-[PF_6] (0.05 M). An as-prepared p-doped sample is used. (b) ^{1}H-NMR spectrum of the electrochemically prepared PMeOTh after p-undoping with N_2H_4. NMR solvent = DMSO-d_6 for both (a) and (b). The p-doping (a) causes a severe decrease in the area of the OCH_3 signal, in contrast to a minor effect (only broadening) on the thiophene H signal.

Stability of n-Doped State against Air. Due to the strong interaction of the crown ethereal subunit of PCrTh with Na^+ (Figure 2), the Na-doped PCrTh exhibits some stability against dry air.[5] Although exposure of Na-doped PTh and P3RTh (R = usual alkyl group like hexyl) to dry air leads to rapid changes with an obvious color change and decrease in the electrical conductivity, similar exposure of the Na-doped PCrTh to dry air does not cause such changes. Even after 1 month exposure to dry air, a relatively small change in the dc electrical conductivity (to 64% of the original electrical conductivity of the Na-doped PCrTh) is observed. Quenching of the negative carrier in the main chain (eq 8) by O_2 may require removal of Na^+ from the crown ethereal subunit to form sodium oxide (or peroxide or superoxide), e.g., n-doped PCrTh (eq 8) + O_2 → PCrTh + NaO_2 (9), and the high affinity of the crown ethereal subunit to Na^+ may retard such n-undoping.

Electrochemical n-Doping. Figure 4 exhibits the cyclic voltammogram of a CH_3CN solution of PCrTh. As shown in this figure, PCrTh gives a reduction (or n-doping) peak at about −2.2 V vs Ag/Ag^+), and the

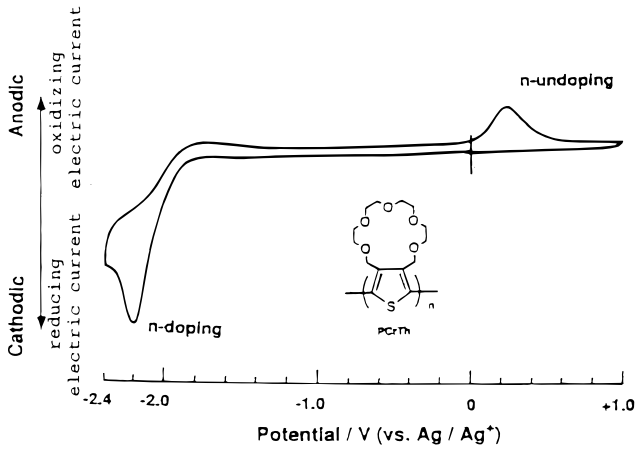
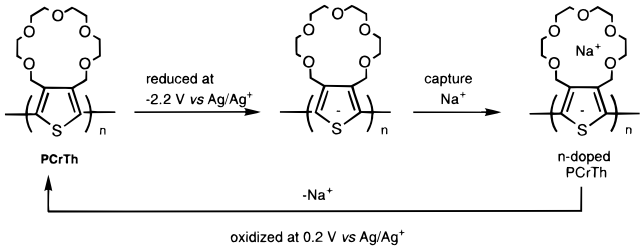


Figure 4. Cyclic voltammogram of PCrTh, in an acetonitrile solution of 0.1 M $NaClO_4$ and at 50 mV s^{-1}.

n-doping potential corresponds to the reported n-doping potential (about −2.2 V vs Ag/Ag^+) of a film of PTh.[20] In the case of PTh, the n-doping peak is coupled with an oxidation (or n-undoping) peak near (at about −2.0 V vs Ag/Ag^+)[20] it. However, PCrTh does not give such a peak near the n-doping peak. Instead of that, PCrTh affords an oxidation peak at about 0.2 V vs Ag/Ag^+ assignable to an n-undoping peak of the n-doped PCrTh. The large difference (about 2.5 V) between the reduction and oxidation potentials is attributed to the strong interaction of PCrTh with Na^+. Namely, PCrTh reduced at −2.2 V vs Ag/Ag^+ will gather Na^+ in the



solution, and the gathered Na^+ will be captured by the crown ethereal subunit. The n-doped state thus formed is considered to be stabilized, and its oxidation (or n-undoping) is considered to require a much higher potential than the n-doping potential.

Cyclic voltammograms obtained under various conditions support this view and assignment of the CV peaks. For example, scanning in a narrower range of −1.8 V to +1.0 V vs Ag/Ag^+ leads to disappearance of both the n-doping and n-undoping peaks discussed above. In contrast to the n-doping and n-undoping couple, the solution of PCrTh gave no obvious p-doping−undoping couple in the cyclic voltammogram up to 1.0 V vs Ag/Ag^+.[21] The CV curve shown in Figure 4 is reproducible.

Comparison with PTh with a Linear OR Group. In cases of the linear ethereal polythiophenes, investigation of their redox behavior with the film is possible, and Figure 5 shows the cyclic voltammograms of films of PMeOTh and PMeOEtOTh. As shown in Figure 5, the film of PMeOTh and PMeOEtOTh also gives an n-doping peak at -2.1 ± 0.1 V vs Ag/Ag^+ (peak α) and an n-undoping peak (peak β) at about -0.4 ± 0.1 V. The large difference (about 1.7 V) between the n-doping and n-undoping potentials is also attributed to the strong interaction of the cationic dopant with the ethereal oxygen.

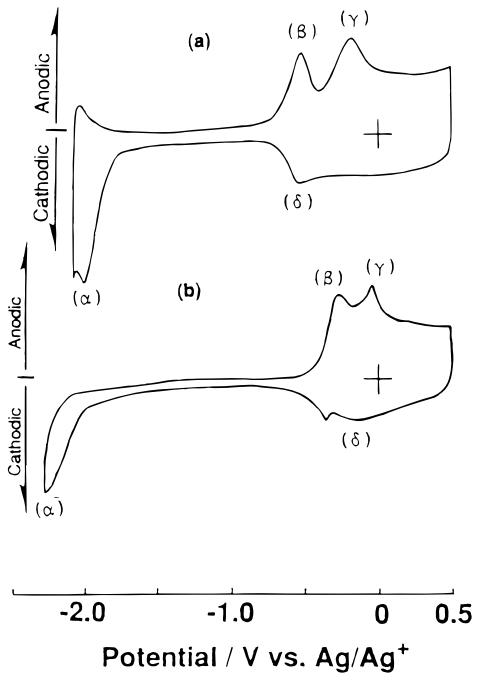


Figure 5. Cyclic voltammograms of (a) a film of PMeOTh and (b) PMeOEtOTh, in an acetonitrile solution of 0.1 M $[N(n\text{-}C_4H_9)_4]ClO_4$ and at 10 mV s^{-1}.

As for the films of PMeOTh and PMeOEtOTh, the cyclic voltammogram exhibits another redox couple with oxidation (p-doping) and reduction (p-undoping) peaks at -0.1 ± 0.1 V (peak γ) and -0.3 ± 0.2 V (peak δ) vs Ag/Ag^+, respectively. The p-doping and p-undoping potentials of PMeOTh agree with those reported for electrochemically prepared PMeOTh.[8]

Conclusion

Polythiophenes with crown ethereal subunits or linear ethereal subunits can be prepared by the organometallic polycondensation. By introducing the spacing π-conjugated thiophene-2,5-diyl unit, copolymers with a longer effective π-conjugation length have been obtained. The copolymers with regular structures show a bathochromic shift in films.

The crown ethereal polythiophenes have a high affinity toward Na^+. Na^+-doped (or n-doped) PCrTh has some stability against dry air, and this stability is accounted for by the strong interaction of the crown ethereal subunit with Na^+. Electrochemical data of the polymers support this view.

Experimental Section

Materials and General Procedures. Monomer-1,[18] Monomer-3,[22] bis(1,5-cyclooctadiene)nickel(0) $(Ni(cod)_2)$,[23] and $Pd(PPh_3)_4$[24] were prepared according to the literature. Monomer-2 was purchased from Tokyo Chemical Industries Co. Ltd. and purified by distillation. Synthesis and polymerization were carried out by using standard Schlenk techniques.

Synthesis of Monomer-4. A hexane solution of butyllithium (45 mmol) was added to a THF (100 mL) solution of 2,2′-bithiophene (3.74 g, 22.5 mmol) at −50 °C. After the mixture was stirred for 30 min at the temperature, a THF (20 mL) solution of $SnMe_3Cl$ (10 g, 50 mmol) was added at −50 °C. After stirring for 4 h at −50 °C, the reaction mixture was poured into water. The organic layer was separated and dried over $MgSO_4$. After removal of the solvent by evaporation, the residue was recrystallized twice from diethyl ether to obtain 6.16 g (55.5%) of Monomer-4. Anal. Calcd: C, 34.2; H, 4.5. Found: C, 34.4; H, 4.5. ^{1}H-NMR (CD_2Cl_2): δ (ppm) 0.37 (s,

18H, $SnMe_3$), 7.09 and 7.27 (d, 2H for each, 3 Hz). ^{13}C-NMR (CD_2Cl_2): δ (ppm) −8.20 ($SnMe_3$), 125.11, 136.30, 137.69, and 143.23.

Synthesis of $CrTh_3$. A DMF (10 mL) solution containing Monomer-1 (590 mg, 1.6 mmol) and 2-chlorothiophene (370 mg, 3.0 mmol) was added dropwise to a DMF (10 mL) solution containing $Ni(cod)_2$ (1.56 g, 5.7 mmol), 1,5-cyclooctadiene (1 mL), and bpy (860 mg, 5.7 mmol). After stirring for 48 h at 60 °C, the reaction mixture was added to dilute hydrochloric acid. The product was extracted with $CHCl_3$ and treated with an Al_2O_3 column (eluent = ethyl acetate) and SiO_2 column (eluent = ethyl acetate). Removal of ethyl acetate under vacuum gave a yellow viscous liquid of $CrTh_3$ (yield = 17%). Anal. Calcd: C, 56.6; H, 5.6. Found: C, 57.0; H, 5.6. ^{1}H-NMR (CD_2Cl_2): δ (ppm) 3.64 (s, 8H), 3.73 (s, 8H), 4.61 (s, 4H), 7.12 (dd, 2H, 5.1 and 3.7 Hz), 7.27 (dd, 2H, 3.7 and 1.2 Hz), 7.4 (dd, 2H, 5.1 and 1.2 Hz). ^{1}H-NMR (acetone-d_6): δ (ppm) 3.62 (s, 8H), 3.73 (s, 8H), 4.60 (s, 4H), 7.22 (dd (seemingly triplet), 2H, 4.9 and 3.4 Hz), 7.36 (d, 2H, 3.4 Hz), 7.71 (d, 2H, 4.9 Hz). Decoupling analysis of the aromatic H signals supports the coupling pattern. ^{13}C{^{1}H}-NMR (CD_2Cl_2): δ (ppm) 65.3, four signals in a range of 70.2−71.3, 127.0, 127.5, 128.1, 136.4, 135.2, 135.1.

A coupling reaction between Monomer-1 and 2-(trialkylstannyl)thiophene[25] (eq 5) also gave CrTh with a higher yield; however, the product contained triphenylphosphine and its oxide (cf. Supporting Information), which were difficult to remove.

Preparation of PCrTh. A DMF (5 mL) solution of Monomer-1 (560 mg, 1.5 mmol) was added dropwise to a DMF (10 mL) solution containing $Ni(cod)_2$ (550 mg, 2 mmol), 1,5-cyclooctadiene (150 μL), and bpy (310 mg, 2.0 mmol). After stirring for 48 h at 60 °C, the reaction mixture was added into an excess amount of methanol. After removal of the solvent, the residue was dissolved in chloroform, and the chloroform solution was washed with dilute hydrochloric acid (twice), an aqueous solution of disodium ethylenediaminetetraacetic acid (twice), an aqueous solution of disodium ethylenediaminetetraacetic acid (Na_2EDTA) in ammonia alkaline conditions (twice), dilute aqueous ammonia (once), water (once), dilute hydrochloric acid (twice), and water (once) in this order. Chloroform was removed, and PCrTh thus obtained was dried under vacuum (yield = 86%). Anal. Calcd: C, 56.0; H, 6.8. Found: C, 55.7; H, 6.8. ^{1}H-NMR ($CDCl_3$): δ (ppm) 3.67 (8 H), 3.74 (8 H), 4.62 (4H). ^{13}C{^{1}H}-NMR (DMSO-d_6): δ (ppm) 65.5, 70.3−71.1, 132.5, 138.9.

ran-Copoly-11 and *ran*-Copoly-12 were prepared analogously (Supporting Information).

Preparation of *reg*-Copoly-11 and *reg*-Copoly-12. A DMF (20 mL) solution of $Pd(PPh_3)_4$ (87 mg, 0.075 mmol) was added dropwise to a DMF (30 mL) solution containing Monomer-1 (557 mg, 1.5 mmol) and Monomer-3 (614 mg, 1.5 mmol) under stirring. After stirring for 48 h at 80 °C, the reaction mixture was poured into 800 mL of dilute hydrochloric acid. The copolymer was extracted with chloroform, and the chloroform solution was washed with hydrochloric acid (twice) and water (once). The chloroform solution was condensed by evaporation and poured into hexane to obtain a yellow powder of *reg*-Copoly-11 (420 mg, 74%). Anal. Calcd: C, 56.5; H, 5.5. Found: C, 55.8; H, 5.5. ^{1}H-NMR (CD_2Cl_2): δ (ppm) 3.64 (8H), 3.76 (8H), 4.66 (4H), 7.22−7.29 (2H) (Figure 1). ^{13}C{^{1}H}-NMR (CD_2Cl_2): δ (ppm) 65.4, 70.3, 70.9, 71,2, 71.3, 128.2, 136.9.

reg-Copoly-12 was prepared analogously. Anal. Calcd: C, 56.9; H, 5.2. Found: C, 55.6; H, 5.1. ^{1}H-NMR (CD_2Cl_2): δ (ppm) 3.62 (8H), 3.74 (8 H), 4.59 (4 H), 6.96−7.69 (4H) (Figure 1). ^{13}C{^{1}H}-NMR (CD_2Cl_2): δ (ppm) 65.2, 70.0−72.0, 124.8, 128.2, 134.9, 135.0, 136.5, 138.2.

Preparation of PMeOTh and PMeOEtOTh. A DMF (3 mL) solution of 3-methoxy-2,5-dibromothiophene (460 mg, 1.7 mmol) was added dropwise to a DMF (10 mL) solution containing $Ni(cod)_2$ (550 mg, 2.0 mmol), 1,5-cyclooctadiene (150 μl), and bpy (310 mg, 2 mmol). After stirring at 60 °C for 48 h, the reaction mixture was poured into l L of methanol. The black precipitate was separated by filtration and washed with dilute aqueous ammonia (twice), an aqueous solution of Na_2-EDTA (twice), an aqueous solution of Na_2EDTA containing ammonia (once), dilute aqueous ammonia (once), and water (once) in this order. PMeOTh thus obtained was collected by filtration and dried under vacuum. Yield = 71%. Anal. Calcd: C, 53.6; H, 3.6. Found: C, 53.3; H, 3.4.

PMeOEtOTh was prepared analogously from 3-(2-methoxyethoxy)-2,5-dibromothiophene (540 mg, 1.7 mmol), $Ni(cod)_2$ (550 mg, 2.0 mmol), 1,5-cyclooctadiene (150 μL), and bpy (310 mg, 2 mmol) in DMF at 60 °C. Yield = 85%. Anal. Calcd: C, 53.9; H, 5.1. Found: C, 54.6; H, 5.2.

Electrochemical preparation of PMeOTh was carried out according to the literature,[8] and IR spectra of PMeOThs prepared by using $Ni(cod)_2$ and electrochemically are almost identical.

Measurements. IR spectra were recorded on a JASCO IR-810 spectrometer. NMR spectra were taken using JEOL JNM GX-500, JNM-400, and JNM-90 spectrometers. Elemental analysis was carried out by Mrs. M. Tanaka of our institute with a Yanagimoto CHN Autocorder Type MT-2. GPC curves, TGA curves, and UV−visible spectra were measured with a Shimidzu liquid chromatography system, a Shimadzu thermoanalyzer DT-30, and a Hitachi Model 200-20 or a Shimadzu UV-3100 PC spectrometer, respectively. Light-scattering analysis was carried out as previously reported[10] or by using a DLS-700 dynamic light-scattering spectrophotometer (made by Otsuka Electronics Co. Ltd.).

Cyclic voltammetry was carried out with a Hokuto Denko HA-501 galvanostat/potentiostat and a Hokuto Denko KB-104 function generator. The electrical conductivity was measured with a Takeda Riken TR-8651 electrometer and Mitsubishi-yuka Loresta IP electrometer. Photoluminescence and electroluminescence spectra were obtained as previously reported.[16c]

X-ray crystallographic analysis was carried out using a Rigaku AFC-5R.

Chemical Doping and Undoping. Polymer was exposed to a vapor of iodine in a vacuum line, and the excess iodine was removed under vacuum. The procedure for the Na-doping depended on the kind of polymer. For the highly soluble crown ethereal polymers, a THF solution of the polymer in a Schlenk type tube was stirred with a block of Na for 1 day. The turbid solution thus obtained was separated and dried under vacuum to obtain the Na-doped polymer. In cases of other polymers, the Na-doping was carried out by using sodium naphthalenide according to the usual manner.[3,6]

The Na-doped polymer was undoped by treating it with water and dilute hydrochloric acid with stirring. In the case of PCrTh, the undoped polymer was dissolved in $CHCl_3$, and the $CHCl_3$ solution was washed with dilute hydrochloric acid and water. The $CHCl_3$ solution was dried under vacuum.

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Supporting Information Available: Synthetic and analytical data of polymers and related compounds other than those described in the Experimental Section, solubility of polymers, selected NMR and photoluminescence spectra of $CrTh_3$ and polymers, and X-ray crystallographic data of Monomer-3 and Monomer-4 (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the American Chemical Society, and can be downloaded from the Internet. See any current masthead page for ordering information and Internet access instructions.

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