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Synthesis and Property of Tellurium-containing Polymers Obtained by Simple Condensation Reaction of Tetrachlorotellurium and 1,3-Dimethoxybenzene

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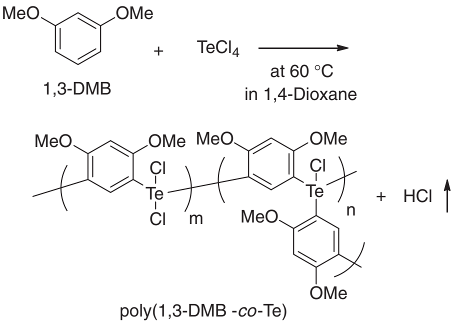
Polycondensation reaction of 1,3-dimethoxybenzene and $TeCl_4$ was performed at a feed ratio of 1,3-DMB/$TeCl_4$ = 1/10 without catalyst in 1,4-dioxane at 60 °C for 48 h, affording poly(1,3-DMB-*co*-Te) with $M_n = 45100$ and $M_w/M_n = 1.89$ in 75% yield, with release of HCl. ^{1}H NMR, IR, and X-ray fluorescence spectroscopy indicated that poly(1,3-DMB-*co*-Te) had a partially branched skeleton. This polymer had good solubility, good film-forming ability, high thermal stability, and a high refractive index (1.769 at 0.6328 μm).

Tellurium is one of the chalcogens, which form the 16th group in the periodic table; the other members are oxygen, sulfur, selenium, and polonium. Except for oxygen, the chalcogens have rather similar characteristics, i.e., they have similar Allred–Rochow electronegativity, ionization energy, and electron affinity. There are many reports of the synthesis of sulfur-[1] and selenium[2]-containing polymers, some of which have interesting properties, such as high refractive index and electrical conductivity. However, tellurium-containing polymers have received relatively little attention. Sugimoto and Yoshida synthesized a poly(thiocarbonyl telluride) by the reaction of dilithium telluride with thiophosgene, and examined its electrical conductivity.[3] The synthesis of polytellurophenes[4] was also reported, and their electrical conductivity was compared to those of polythiophene[5] and polyselenophene.[4g,6] However, the electrical conductivities of tellurium-containing polymers were not superior to those of sulfur- and selenium-containing polymers. On the other hand, Ueda reported that selenium-containing polymer showed a higher refractive-index value than sulfur-containing polymer.[7] However, there is no report concerning the refractive index of tellurium-containing polymers. This prompted us to investigate the synthesis and refractive-index characteristics of tellurium-containing polymers. We focused on a synthetic route to a tellurium-polymer containing an aromatic moiety in the main chain, anticipating that it might have high molecular refraction and greater stability.

Bergman[8] et al. reported the synthesis of diphenyl telluride, which has good thermal stability and a melting temperature of about 280 °C, by simple condensation reaction of tetrachlorotellurium ($TeCl_4$) and anisole in bulk, without any catalyst. Thus, the condensation reaction of benzene with a pendant electron-donating group and $TeCl_4$ can proceed smoothly without catalyst. Here, we report a novel condensation reaction of 1,3-dimethoxybenzene (1,3-DMB) as a A_2 type monomer and tetrachlorotellurium ($TeCl_4$) as a B_2 type monomer to afford poly(phenylene telluride), as shown in Scheme 1. Table 1 summarizes the reaction conditions and results.

Although condensation polymerization should theoretically be carried out at a monomer feed ratio of 1:1, we first accidentally examined the reaction at a feed ratio of 1,3-DMB/$TeCl_4$ = 1/10 in 1,4-dioxane as a solvent at 60 °C for 24 h.[9] Fortunately, the polymer was obtained in 66% yield with $M_n = 38100$ and $M_w/M_n = 1.47$ as estimated by SEC, though multiple peaks were apparent (Entry 5 in Table 1). The structure of the obtained polymer was confirmed by ^{1}H NMR and IR spectroscopy. ^{1}H NMR showed two broad peaks at about 3.50 and 6.45 ppm, which are assignable to methoxy and aromatic moieties, respectively.[10] IR spectra showed characteristic peaks at 1206 and 1503 cm^{-1}, which are assignable to stretching vibrations of $-OCH_3$ and –CH=CH– in the aromatic moiety, respectively.[11] These results indicate that condensation proceeded with release of hydrogen chloride to give poly(1,3-DMB-*co*-$TeCl_4$). The reaction was then examined at other feed ratios of 1,3-DMB/$TeCl_4$ = 1/1, 1/5, 1/20, and 20/1 at 60 °C for 24 h. In the case of 1,3-DMB/$TeCl_4$ = 1/1, high-molecular-weight polymer was not formed, but an oligomer with $M_n = 1600$ ($M_w/M_n = 1.02$) was obtained in 3% yield (Entry 3 in Table 1). When the reaction was performed with 1,3-DMB/$TeCl_4$ = 1/5, the molecular weight of the obtained oligomer was increased to 2100 ($M_w/M_n = 1.61$) (Entry 4 in Table 1). At 1,3-DMB/$TeCl_4$ = 1/20, oligomer with $M_n = 4900$ ($M_w/M_n = 1.31$) was obtained in 35% yield (Entry 6 in Table 1). However, no polymer or oligomer was obtained in the case of excess 1,3-DMB (1,3-DMB/$TeCl_4$ = 20/1) (Entry 7 in Table 1). Thus, it turned out that 1,3-DMB/$TeCl_4$ = 1/10 was the most appropriate feed ratio in this polycondensation reaction.

Next, we examined the effects of reaction temperature and reaction time on this polycondensation at the feed ratio of 1,3-DMB/$TeCl_4$ = 1/10. The values of molecular weight and yield of poly(1,3-DMB-*co*-$TeCl_4$) increased with increasing temperature up to at 60 °C, and then decreased at 80 and 100 °C (Entries 1, 2, 5, 11, and 12 in Table 1). The reaction time was changed in the range between 24 and 96 h, and it was found that



Scheme 1. Synthesis of tellurium-containing polymers by the reaction of 1,3-DMB and $TeCl_4$.

Table 1. Condensation reaction of $TeCl_4$ and 1,3-DMB[a]

Entry	Feed ratio 1,3-DMB/$TeCl_4$	React Temp /°C	React Time /h	Yield[b] /%	M_n (M_w/M_n)[c]	n[d]	$T_d^{5\%}$[e]
1	1/10	25	24	4	4500 (1.56)	1.692	181.4
2	1/10	40	24	7	10800 (1.53)	1.701	180.4
3	1/1	60	24	3	1600 (1.02)	1.665	220.9
4	1/5	60	24	8	2100 (1.61)	1.733	198.9
5	1/10	60	24	66	38100 (1.47)	1.723	173.8
6	1/20	60	24	35	4900 (1.31)	1.702	201.3
7	20/1	60	24	—	—	—	—
8	1/10	60	48	75	45100 (1.89)	1.769	183.78
9	1/10	60	72	65	43600 (1.53)	1.691	175.7
10	1/10	60	96	60	6500 (1.38)	1.750	147.0
11	1/10	80	24	34	27100 (2.62)	1.769	214.7
12	1/10	100	24	47	7800 (2.35)	1.698	237.2

[a]Conditions: $TeCl_4$ (5 mmol) in 1,4-dioxane (5 mL) in an argon atmosphere. [b]Ethyl ether-insoluble part. [c]Estimated by SEC based on polystyrene standards in DMF. [d]Determined by ellipsometry. [e]$T_d^{5\%}$ = 5%-loss temperature determined by TGA.

Table 2. Ratio of tellurium, chlorine, and aromatic moiety in the products as determined by X-ray fluorescence analysis

Entry	Feed ratio 1,3-DMB/$TeCl_4$	Content ratio Te:Cl:$C_8H_8O_2$
1	1/10	1.0:0.7:2.5
2	1/1	1.0:0.6:2.5
3	Theory[a]	1.0:2.0:1.0

[a]In the case of poly(1,3-DMB-*co*-Te) has linear skeleton.

48 h was an appropriate time (Entries 5 and 8–10 in Table 1). Finally, the polycondensation reaction of 1,3-DMB and $TeCl_4$ proceeded at the feed ratio of 1,3-DMB/$TeCl_4$ = 1/10 in dioxane at 60 °C for 48 h to give poly(1,3-DMB-*co*-$TeCl_4$) with high molecular weight, $M_n = 45100$ ($M_w/M_n = 1.89$), in 75% yield (Entry 8 in Table 1). These results might suggest that polycondensation reaction of 1,3-DMB and $TeCl_4$ proceeds through an unusual mechanism via an intermediate which might be constructed by 1,3-DMB, $TeCl_4$, and 1,4-dioxane.

Although all the synthesized poly(1,3-DMB-*co*-$TeCl_4$)s showed the same ^{1}H NMR and IR spectra, we wondered whether the polymers and oligomers obtained at different feed ratios of 1,3-DMB and $TeCl_4$ actually have similar structures. Therefore, the unit ratios of tellurium (Te), chlorine (Cl), and aromatic moiety ($C_8H_8O_2$) of two poly(1,3-DMB-*co*-$TeCl_4$)s obtained at feed ratios of 1,3-DMB/$TeCl_4$ = 1/10 and 1/1 (Entries 3 and 5 in Table 1) were determined by X-ray fluorescence spectroscopy. These results are summarized in Table 2. If the linear polymer is synthesized in this polycondensation, the unit ratio of Te, Cl, and $C_8H_8O_2$ would be 1:2:1 (Entry 3 in Table 2). The X-ray fluorescence analysis showed that the ratios of Te:Cl:$C_8H_8O_2$ were almost the same, irrespective of the feed ratio, i.e., Te:Cl:$C_8H_8O_2$ = 1:0.7:2.5 and 1:0.6:2.5 (Entries 1 and 2 in Table 2). These results indicate that the synthesized poly(1,3-DMB-*co*-$TeCl_4$) has a partially branched structure, as shown in Scheme 1, because the value of Cl was smaller and that of $C_8H_8O_2$ was larger than those expected for the linear structure.

Next, the solubility, film-forming ability, thermal stability, and refractive index of the polymer were examined. Poly(1,3-DMB-*co*-$TeCl_4$) was soluble in common organic solvents, such as dimethyl sulfoxide, dimethylformamide, tetrahydrofuran (THF), and chloroform, and showed good film-forming ability, affording a thin film with 0.1 µm thickness on a silicone wafer by spin-coating. The thermal decomposition temperature of poly(1,3-DMB-*co*-$TeCl_4$) was determined by thermogravimetric analysis (TGA) and the 5%-loss temperature ($T_d^{5\%}$) values were in the range 147 and 237 °C (Table 1). These values are sufficient for application to optoelectronics using poly(1,3-DMB-*co*-$TeCl_4$). The refractive-index (n) values of the resulting films (ca. 0.1-µm thick) were measured by ellipsometry at 0.6328 µm. These results are summarized in Table 1. The n values were in the range between 1.665 and 1.769 (Table 1). Although solubility, film-forming ability, and thermal stability were independent of molecular weights, the value of n increased with increasing molecular weight, presumably due to the increase of the density. Because the value of n in the polymer is consitent with those of molar refraction and density as shown in the Lorentz–Lorenz equation.[12] Furthermore, no transmittance of the resulting poly(1,3-DMB-*co*-$TeCl_4$) fim was observed in the range between 250 and 600 nm deteremined by UV–vis spectroscopy. Although poly(1,3-DMB-*co*-$TeCl_4$) was stable in water, its hydrolysis proceeded in acid or base aqueous solutions.

In summary, we have achieved the first synthesis of poly(phenylene telluride) by taking advantage of a novel condensation reaction of 1,3-DMB and $TeCl_4$. This reaction proceeded at a feed ratio of 1,3-DMB/$TeCl_4$ = 1/10 without catalyst in 1,4-dioxane at 60 °C for 48 h, affording poly(1,3-DMB-*co*-Te) with $M_n = 45100$ and $M_w/M_n = 1.89$ in 75% yield. The ^{1}H NMR, IR, and X-ray fluorescence spectroscopy indicated that poly(1,3-DMB-*co*-Te) has a branched skeleton in part. Poly(1,3-DMB-*co*-Te) showed good solubility, good film-forming ability, and high thermal stability. The refractive index value of its thin film (0.1 µm) was 1.769, as measured by ellipsometry at 0.6328 µm. Poly(1,3-DMB-*co*-Te) seems to be a promising candidate for application in the field of optoelectronics in the future.

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10 ^{1}H NMR spectra (500 MHz, DMSO-d_6, TMS) of poly(1,3-DMB-*co*-Te) ($M_n = 38100$, $M_w/M_n = 1.47$, Entry 5 in Table 1). δ (ppm): 3.5 (broad m, –OCH_3), 6.45 (broad s, aromatic H).

11 IR spectra of poly(1,3-DMB-*co*-Te) ($M_n = 38100$, $M_w/M_n = 1.47$, Entry 5 in Table 1). IR (KBr, cm^{-1}): 2937 (ν C–H aromatic), 2836 (ν C–H aliphatic), 1503 (ν C=C aromatic), and 1206 (ν –OCH_3 ether).

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