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Synthesis , Characterization and Thermal analysis study of new organometallic monomers and polymers based on tellurium

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Abstract:

This paper describes in details methods of preparation of some new organometallic monomers and polymers based on Tellurium and the thermal study of these compounds. The monomers synthesized are : Bis (4-aminophenyl) ditelluride and Bis (4-aminophenyl)telluride. The dimethylolic derivatives of the new former monomers were prepared by condensation with formaldehyde in a-one-pot reaction system at definite temperature and pH. The dimethylolic organometallic monomers were cured thermally to give their corresponding setting polymers. The new monomers and polymers were characterized using infrared spectroscopy and differential scanning calorimetric (DSC) techniques. Characteristics of the newest class polymers, namely electrical conductivity and thermal stability will be explored in further reports.

Introduction:

Elemental tellurium normally could be converted to telluride's this may be achieved by several methods(1,2). Literatures in this field are widely published. A method for the preparation of stable solution of potassium and sodium tellurocyanate(3) has been standardized. It is well known that the exchange of halogen by tellurocyanato group is a simplest and general rout for the preparation of aryl telluride(4-6). In other hand, organotellurium compounds containing Para amino groups are little known(7,8), and only few examples of this class of compounds has been reported in the literature(9).

A series of organotellurium compounds with an amino group ortho to tellurium atom were synthesized by a new route involving reaction of the 2-amino aryl mercury chloride with $TeBr_4$ in glacial acetic acid(9,10).

In this paper, the preparation of some new and known tellurated anilines and their derivatives are described. Telluration of the starting organic compounds was performed via the reaction of KTeCN with Para bromoaniline. The ditellurides were readily prepared by a similar way described for the preparation of the diorganoditelluride(11,12). Furthermore diorganotelluride containing amino group are prepared and used as monomers for the preparation of some new polymers by solution polymerization technique. The goal of this effort is to add new bases in the research field of this newest class of polymers especially rare information are found in the literature concerning organotellurium polymers.

Experimental

a) Instruments

Melting points were determined using Gallen Kamp. Infrared (KBr) spectra were recorded in the range 4000-200 cm^{-1} on a pye-unicam SP3-300s spectrophotometer. The thermal analysis was carried out using thermal analyzer (Seiko Instrument Inc.). The DSC thermograms were recorded over a temperature range (ambient- 450°C) at 20 °C/min and N_2 was used as a purge gas.

b) preparation methods

- ***4-aminobenzenotellurocyanate(I) :***

  This compound was prepared following adopted procedure(3,13). A solution of potassium tellurocyanate was readily prepared by stirring together 8 mmol. each of powdered tellurium and dry powdered KCN in dry DMSO at 100°C for 1h. under nitrogen. The resulting pale yellow solution was cooled to room temperature and diluted with dry DMSO. A solution of 4-bromoaniline 8mmol. in dry DMSO was added drop wise to the mixture and the reaction mixture was stirred at room temperature for 3h. and filtered. The filtrate was poured into distilled water and left overnight.

  A yellow precipitate was collected and washed several time with cold water then with ethanol. Recrystallization from ethanol gave yellow crystals(m.p.191°C).

- ***bis (4-aminophenyl)ditelluride (II) :***

  Compound (I) (0.7 mmol.) was dissolved in ethanol (30 ml) and excess of sodium hydroxide was added to the solution. The mixture was stirred and refluxed until the spot of (I) was completely disappeared on TLC(about 3h.). An aqueous saturated solution of NH_4Cl was added and the mixture was extracted with dichloromethane (4 * 50 ml.). The organic layer was dried over Na_2SO_4, then the solvent was removed by a rotary evaporator . Purification of the product by petroleum ether(60-80 °C) gave orange crystals of m.p 80-81 °C.

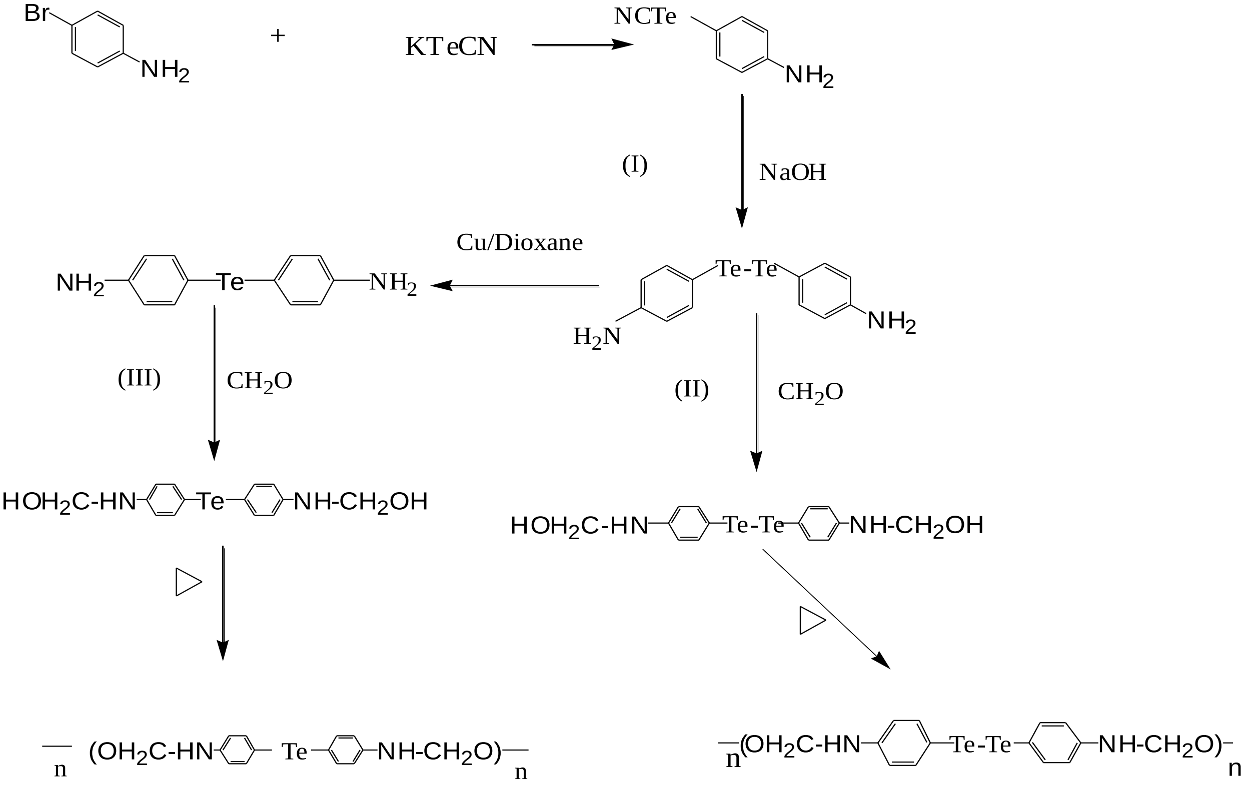
- ***bis (4-aminophenyl)telluride(III) :***

  To a solution of bis(4-aminophenyl) ditelluride (2mmol.) dissolved in dioxane (20 ml.), activated copper powder (6 mmol.) was added. The mixture was refluxed for 10h., then filtered hot, and the solution was evaporated in vacuum. The residue was recrystallized from petroleum ether (60-80 °C) giving brown crystals of (III) m.p. (107-108 °C).

- ***bis (4-methlolaminophenyl) telluride(IV) :***
- ***bis (4-methylolaminophenyl) ditelluride (V) :***

  They were prepared according to literature methods(14,15); Compound (II)(0.1mol.) was dissolved in formaline (37% w/v)(0.2mol.) under nitrogen atmosphere and amount of NaOH was added slowly to the solution to keep the pH in (9-10). After stirring for 3h. at 70°C until the spot of (II) disappeared on TLC . At the end of the reaction time, the mixture was cooled. Neutralized with cold dilute phosphoric acid(5%). The organic layer was separated and purified by washing with distilled water then dissolved in tetrahydrofurane, filtered to remove traces of salt. The organic layer was then isolated and yellow oil was obtained in 90% yield.

The setting characteristics of polymers IV and V were studied by heating a sample of polymer at a heating rate of 20 °C/min. typical thermograms are shown in figures (8-10).



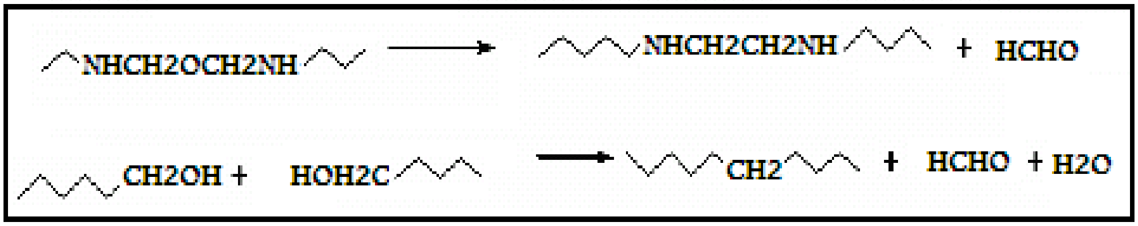
Schematic representation of the synthesis modes of the new organotelluride monomers and polymers.

Results and Discussion:

The new organotellurium diamines II and III and their corresponding dimethylols IV and V were prepared according to adopted procedures carried out in our laboratory. The schematic representation of the reaction modes and chemical structures of the starting materials and products are clarified in scheme (1). The new monomers were characterized by IR spectroscopy. Typical representative spectra for the new compounds prepared in this work are shown in figures (1-7). The vibration bands which were observed in the new prepared compounds are listed in table (1). The stretching vibration bands of NH at 3300 and 3425 cm^{-1} of the new diameter and the stretching vibration band of –OH at 3400 cm^{-1} and the vibration band of the other functional groups indicates the right compositions of the new compounds. On the other hand, the condensation reactions of organometallic monomers have generally been conducted at high temperature and resulting product have often not well characterized$^{(8)}$. The optimum condition of the condensation reaction of the new organotellurium diamine with formaldehyde monomers were estimated and they seemed to proceeds via a mechanism similar to that which proceeds between urea and formaldehyde(16). The dimethylolic resulted derivatives were characterized using DSC technique.

Typical also DSC thermograms of the prepared dimethylols derivatives IV and V are shown in Fig. (8-10).

The scanning covered the temperature ranging from 20-400 °C. The DSC thermograms showed that two types of curing reactions takes place. The two types are exothermic at about 212.5°C and 352°C for IV and at about 179.7°C and352°C for V respectively. The first type of curing reaction may be related to dehydroformylation :



The second exothermic reaction can be related to chain scission degradation reaction of the polymers. The two exothermic reaction are familiar in the technology of the curing and degradation of polyethers(16). On the other hand the ditelluride polymer seemed to be dehydroformylated with lower curing energy 12.8 J/g compared to 26.6 J/g for the telluride polymer and this may be attributed to the lower activation energy of the ditelluride derivative which posses higher molecular weight.

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تخليق وتشخيص ودراسة الخواص الحرارية لمونوميرات وبوليمرات عضوية فلزية مسندة إلى التلوريوم.

عمار كاظم مكي البعاج

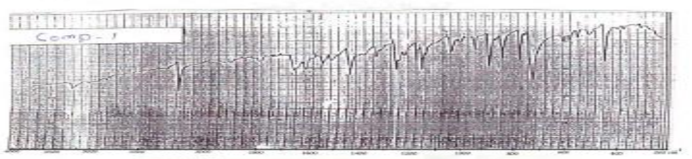
قسم الهندسة الكيميائية ، كلية الهندسة ، جامعة البصرة ، البصرة ، العراق.

المستخلص

يتضمن البحث تحضير بعض مونمرات التلوريوم العضوية الجديدة والمتضمنة بس (4-امينوفنيل)ثنائي التلوريوم و تلوريد بس (4-امينو فنيل) عن طريق تكثيفها مع الفورمالديهايد عند ظروف تجريبية من درجة الحرارة والدالة الحامضية. تم تقسية المشتقات المثيلولية للحصول على البوليمرات المقابلة. تم تشخيص المونمرات والبوليمرات المحضرة باستخدام مطيافية الأشعة تحت الحمراء وتقنية المسح ألمسعري التفاضلي.

Table (1) Selected IR data for some the new organotellurium monomers and polymers

Comp. No.	υ_{as}(NH) υ_s(NH)	Aromatic υ(CH)	Aliphatic υ(CH)	υ(NH) deformation υ(NH)Wagg.	υ_{as}(C=C) $\upsilon_{a(C=C)}$	$\upsilon_{=CH}$ out of plain	υ (C=C) Out of plain ring bending	Aromatic $\upsilon_{(C-N)}$	υ_{as} (C-Te) υ_s (C-Te)	υ_{as}(OH)	$\upsilon_{as(CN)}$
I	3300m	3090w	-	1560s	1615s	800s	680m	1200s	525w 490m	-	2200m
II	3350m 3310	3070w	-	1600s 710w	1500s 1495m	805s	690m	1210s	520w 480m	-	-
III	3425m 3320m	3040w	-	1610s 715w	1505s 1490s	810s	690m	1200s	530w 495m	-	-
IV	3280w	3020w	2950m 2860w	1690s 715w	1485m	860w	610m	1210w	510w 485w	3400 br.	-
V	3310m	3010w	2980m 2870w	1695s 695w	1500m	830w	600m	1200m	535w 500w	3390 br.	-
VI	3300m	3060w	2980m 2910w	1600s 710w	1540m	810m	600m	1200m	530w 595w	-	-
VII	3320m	3050 w	2985m 2900w	1620s 695m	1550m	815m	600m	1205m	530w 590w	-	-



Fig(1): IR spectrum for compound 1

Fig (2): IR spectrum for compund 2

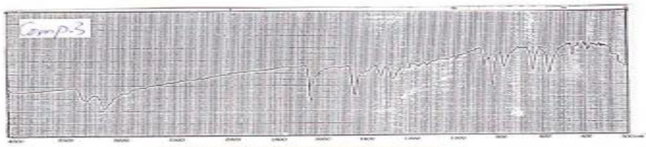


Fig (3) : IR spectrum for compund 3

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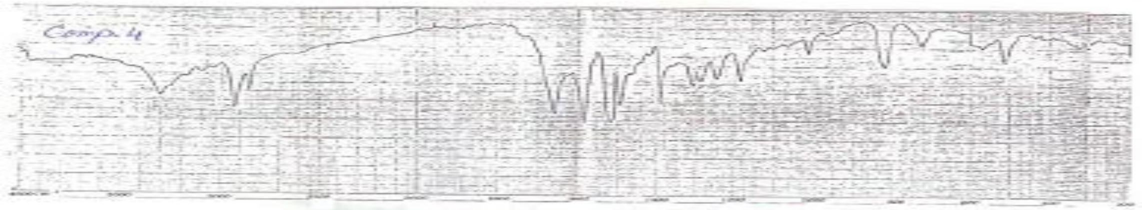

Fig (4) : IR spectrum for compund 4

Fig (5) :IR spectrum for compund 5

Fig (6) :IR spectrum for compund 6

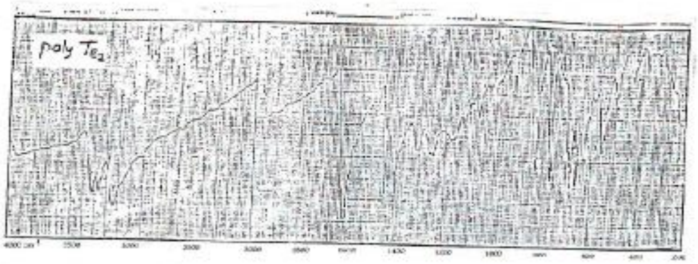

Fig (7) :IR spectrum for compund 7

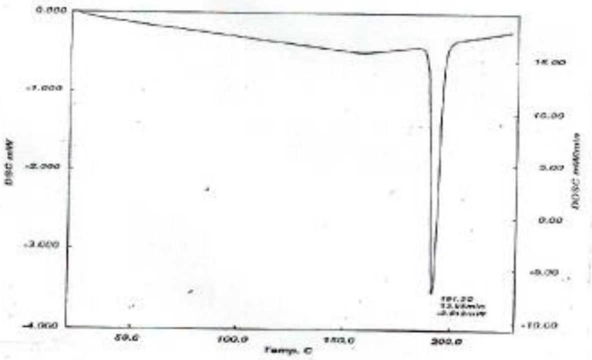

Fig (8) :DSC thermogram for compund 1