Room temperature polymerization and spectroscopic analysis of germanium phthalocyanine polymers

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This paper describes a one-step, room temperature synthesis utilizing ultrasonic energy of a coaxially stacked poly(phthalocyanato) germanium oxide ($[Ge(Pc)O]_n$) from $Ge(Pc)Cl_2$. The synthesis is conducted in the presence of a sodium chalcogenide. Based on photoacoustic *FT*i.r. and u.v.–vis. spectroscopic analysis, the mechanism of the $[Ge(Pc)O]_n$ formation is proposed. The use of isotopic H_2O/D_2O exchange is also utilized in an effort to reveal the role of traces of water present during the polymerization reaction.

(Keywords: synthesis; spectroscopic analysis; germanium phthalocyanine polymers)

Introduction

Synthesis of metallomacrocycles in a cofacial assembly was pioneered[1,2] on phthalocyanogermanium and phthalocyanomanganese oxide complexes. Soon after, it was shown[3] that a related stacked siloxane, $[Si(Pc)O]_n$, could be formed by the dehydration of the dihydroxysiloxane, $SiPc(OH)_2$. It was demonstrated[4,5] that cofacially arranged phthalocyanines can be prepared in a traditional two-step synthesis of the oxygen-bridged phthalocyanines, but extreme conditions of high vacuum (0.13 Pa) and high temperatures (440°C) over extensive periods of time (12 h) were required. Recently, a novel one-step synthesis utilizing ultrasonic energy and a sodium chalcogenide has been described[6,7], which circumvents the traditional two-step synthesis by directly polymerizing $[Si(Pc)O]_n$ from the $Si(Pc)Cl_2$ monomer. Utilizing this one-step approach, simple modification of the starting monomers provides means to replace the central metal atom in the phthalocyanine macrocycle. Although in this case the role of ultrasound was not clearly understood, it is apparent that sonication of the reaction mixture increases solubility and reaction rates, which leads to higher yields[8–11]. Most studies on effects of physical processes on chemical reactions have been conducted on homogeneous[12,13] systems; however, heterogeneous[14–17] sonochemistry has concentrated on synthetic goals and high reaction yields, which are usually associated with the increased reactive surface area, continuous cleaning of the surface of the solid reagent, and/or improved mass transport[18]. In this study, we will explore the possibility of using ultrasonic irradiation in the synthesis of poly(phthalocyanato) germanium oxides and spectroscopic analysis of the products.

Experimental

Synthesis of $Ge(Pc)Cl_2$. Germanium phthalocyanine dichloride was prepared by a modification of the method of Kenney and Joyner[2]. Under nitrogen, 30 ml (0.263 mol, Johnson/Matthey) of germanium tetrachloride, 50 g (0.344 mol, Aldrich) of 1,3-diiminoisoindoline and 300 ml of freshly distilled, dry quinoline (Aldrich) was charged into a 1000 ml three-necked round-bottomed flask equipped with a nitrogen inlet and thermal temperature probe fitted upon a Claisen adaptor, a mechanical stirrer, and a dry-ice condenser fitted upon a West-type condenser. The resulting solution was refluxed for 1 h and slowly cooled to room temperature. The crude product was centrifuged in portions and Buchner filtered with chloroform, acetone, deionized distilled water and acetone, respectively. The resulting purple, crystalline powder was dried for 4 h at 150°C.

Analysis. Calculated for $C_{32}H_{16}N_8GeCl_2$: C, 58.54; H, 2.46; N, 17.08; Cl 10.66%. Found: C, 59.55; H, 2.54; N, 17.18; Cl, 10.58%.

Ultrasonic synthesis of $[Ge(Pc)O]_n$. Inside an argon glovebox, 0.070 g (4.0×10^{-4} mol, Cerac Inc.) of sodium telluride and 25 g (3.0×10^{-4} mol) of germanium phthalocyanine dichloride were added to an oven-dried 50 ml three-necked round-bottomed flask. The flask was transferred to a hood and approximately 15 ml of tetrahydrofuran (Aldrich) was syringed into the flask. The flask was purged with nitrogen and was submerged in an ultrasonic laboratory cleaner (Bransonic Model 2200) filled with water. The mixture was sonicated at low temperature over periods from 5 min to 8 h. The resulting poly(phthalocyanato) germanium oxide product was centrifuged and Buchner filtered with acetone, distilled deionized water and acetone, respectively. The resulting powder product was oven dried at 150°C for 4 h.

Analysis. Calculated for $C_{32}H_{16}N_8GeO$: C, 63.69; H, 2.69; N, 18.58; Cl, 0.00%. Found: C, 61.03; H, 2.65; N, 17.90; Cl, 0.64%.

Synthesis of $Ge(Pc)(OH)_2$. Germanium phthalocyanine dihydroxide was prepared following a modified procedure reported by Davison and Wynne[19]. A three-necked 1000 ml round-bottomed flask was equipped

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with a stopper, thermometer and water-cooled reflux condenser and was placed in a heating mantel equipped with a mechanical stirrer. Open to the atmosphere, 10 g (0.0152 mol) of freshly prepared $GePcCl_2$, 300 g (2M) of NaOH and 60 g (61.35 ml) pyridine were charged to the flask. The mixture was refluxed for 3 h and continuously stirred. The solution was cooled to room temperature, centrifuged, washed with water and acetone and vacuum dried at room temperature overnight.

Thermal synthesis of $[GePcO]_n$. Poly(phthalocyanato) germanium oxide was prepared via the thermal synthetic procedure by Joyner and Kenney[20]. A 0.500 g (8×10^{-4} mol) sample of germanium phthalocyanine dihydroxide was weighed in an aluminium boat and was placed into a quartz pyrolysis tube and heated to 440°C in a Lindberg heavy-duty tube furnace under a continuous vacuum (0.13 Pa) for 8 h.

Spectroscopic measurements. Photoacoustic Fourier transform infra-red (PA *FT*i.r.) spectra were collected on a Diglab FTS-10 spectrometer equipped with a photoacoustic cell (Digilab). The spectrometer was continuously purged with purified air (Balston Filter Products) to eliminate carbon dioxide and water. Prior to spectra collection, the PA *FT*i.r. cell sample compartment was purged with helium. Single-beam spectra of the phthalocyanine samples were recorded at a solution of 4 cm^{-1} and ratioed against a carbon black reference. All spectra were transferred to an IBM compatible computer and analysed using Spectra Calc Software (Galactic Ind.).

Elemental analysis. Elemental analysis of C, H, N and Cl was performed by Desert Analytics Organic Microanalysis of Tucson, AZ, USA.

Optical spectroscopy. Solution spectra of the metal phthalocyanines were recorded on a multiple cell Hewlett-Packard 8451A diode array u.v.–vis. spectrophotometer equipped with a deuterium lamp. Tetrahydrofuran (THF, Aldrich) was utilized as a solvent and reference. The samples, approximately 1.0×10^{-4} M, were sonicated in THF prior to spectral collection to aid in sample dispersion and solubility.

Results and discussion

The focus of this study is to expand the usefulness of the one-step, low temperature ultrasonic synthesis of poly(phthalocyanato) silicon oxide[21] and to synthesize and characterize poly(phthalocyanato) germanium oxide. The i.r. active bands of the monomers, $Ge(Pc)Cl_2$ and $Ge(Pc)(OH)_2$, and polymers obtained by sonication and thermal synthesis, $[Ge(Pc)O]_n$, along with the tentative band assignments, are listed in *Table 1*[22–24].

In an effort to establish the effect of the metal atoms, PA *FT*i.r. spectra of $Ge(Pc)Cl_2$ and $Si(Pc)Cl_2$ are shown in *Figure 1*. Upon metal substitution, traces A ($Ge(Pc)Cl_2$) and B ($Si(Pc)Cl_2$), illustrate a shift of the C=N intraligand stretching vibration from 1533 to 1512 cm^{-1} and the C–C stretching mode from 1431 to 1425 cm^{-1}. In addition, a shift of the C–H in-plane deformation modes from 1063 to 1057 cm^{-1}, as well as the C–H out-of-plane deformation modes from 914 to 905 cm^{-1}, are detected. The above data indicate that the observed shifts are attributed to the metal substitution from silicon to the larger germanium. To understand further the origon of the in-plane Pc ring vibrational shifts, let us consider how molecular symmetry, electronegativity, and the size of the central atom may influence the bonding characteristics of the ligand.

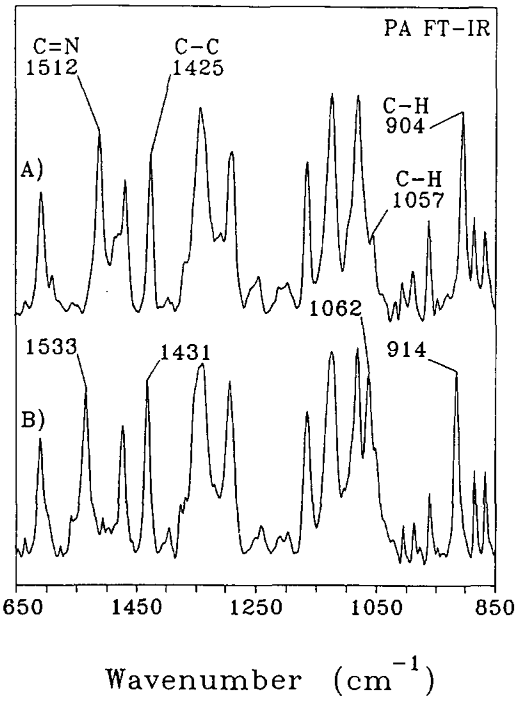

Figure 1 PA *FT*i.r. spectra: A, $GePcCl_2$; B, $SiPcCl_2$

Stable metal phthalocyanine complexes result from the formation of four equivalent N → M σ bonds that are filling vacant s, p_x, p_y, and $d_{x^2-y^2}$ orbitals of the cation with σ electrons of the central nitrogen atoms. The resulting σ bonds are so strong that, for most solid metal phthalocyanine complexes, practically no replacement of the metal ions by protons takes place at H_2SO_4 concentrations ranging from 2 to 7 M (ref. 25). For coordination of a quadruply charged ion, such as Si^{4+}, Ge^{4+} and Sn^{4+}, the formation of a covalent complex involves the aforementioned orbitals plus the p_z and d_{z^2} orbitals that participate in the attachment of the extra ligands along the *z*-axis perpendicular to the plane of the phthalocyanine molecule.

In many cases where the metal ion has filled d orbitals of π symmetry (d_{xy}, d_{xz}, d_{yz}), it forms backward dative π bonds with the phthalocyanine ligands[26]. The metal serves as a donor of π electrons, and the ligand serves as their acceptor. These bonds have opposite directions to the σ bonds, that is M → N, and are referred to as the backward bonds. In contrast, the d_π electrons of the metal fill the antibonding π orbitals of phthalocyanine. The filling of the π^* orbitals increases their energy, preventing the *n* electrons of the peripheral N atoms from entering into a π conjugation, as well as enhancing their σ character and capacity for acid protonation. Such a redistribution of electrons is referred to as the dative π effect. Apart from the backward dative π bond M → N, a forward dative π bond N → M may occur, coinciding in direction with the dative σ bond which may appear in complexes whose central atom has vacant d_π orbitals ($SiPcCl_2$)[25].

When the central metal atom becomes less electronegative, such as substitution of Si with Ge, electrons tend to shift from the metal atom towards the ligand ring. If the σ shell shifts, the charge on the N atoms will

Table 1 Photoacoustic *FT*i.r. spectral data[a] of $GePcCl_2$, $GePc(OH)_2$ and both thermally and sonically polymerized $[GePcO]_n$

Band no.	Band assignment	$GePcCl_2$	$GePc(OH)_2$	$[GePcO]_n$	
				Sonic	Thermal
	Ge–Cl A Str	312 s	–	–	–
1	C–C Def$_{ro}$	437 w	–	435 w	435 w
2	C–C Def$_{ro}$	513 s	–	507 w	509 w
3	C–C Def$_{ro}$	572 s	573 s	573 m	572 w
4	C–C Def$_{ro}$	644 m	–	642 w	642 w
	Ge–OH A Str	–	648 vs	650 w	–
5	C–H Def$_o$	727, 723 s	725 vs	727 vs	729 vs
6	C–H Def$_o$	756 vs	758 vs	756 s	756 s
7	N–H Def$_o$	–	–	–	–
8	C–H Def$_o$	768 s	770 s	–	764 w
9	C–H Def$_o$	779 s	777 s	775 sh	777 s
10	C–H Def$_o$	806 m	802 w	804 w	806 w
11	C–H Def$_o$	868 m	874 m	871 m	–
	Ge–O–Ge Str	–	–	885–850 bd	890–840 bd
12	C–H Def$_o$	885 m	–	883 m	883 sh
13	C–H Def$_o$	905 vs	903 vs	901 s	902 s
14	C–H Def$_o$	947 w	953 m	951 w	947 w
15	–	–	–	–	–
16	N–H Def	–	–	–	–
17	C–H Def$_i$	–	1069 s	1072 s	1070 m
18	C–N Str	1082 vs	1082 s	1090 vs	1088 s
19	C–H Def$_i$	–	1096 s	–	–
20	C–H Def$_i$	1124 vs	1121, 1134 s	1124 vs	1124 vs
21	C–H Def$_i$	1165 s	1169 s	1167 s	1168 m
22	C–H Def$_i$	–	1186 s	–	–
23	C–C Str	1288 s	1288 s	1288 s	1288 m
24	N–H Def	–	–	–	–
25	N–H Def	–	–	–	–
26	C–N Str	–	1337 s	1337 vs	1333 vs
	C–N Str	1344 vs	1346 s	1346 vs	1344 s
27	C–C Str	1425 s	1423 s	1423 s	1423 s
28	C=N/C=C Str	1470 s	1468 m	1468	1467 w
29	C=N/C=C Str	1487 m	1476 w	1477 m	1477 w
30	C=N Str	1512 s	1502 s	1502 s	1499 m
31	C=C Str	1589 w	1583 w	1589 w	1589 w
32	C=C Str	1609 s	1612 m	1612 m	1612 m
	C–H Str	3013 w	3013 w	3011 w	3013 w
	C–H Str	3057 m	3043 m	3045 m	3048 m
	C–H Str	3074 w	3078 w	3078 w	3080 w
	O–H Str	–	3497 bd	3464 bd	–

[a] vs = very strong, s = strong, m = medium, w = weak, bd = broad, sh = shoulder; Def$_o$ = out-of-plane deformation (e.g. wagging and twisting); Def$_i$ = in-plane deformation (e.g. rocking and scissoring); Def$_{ro}$ = out-of-plane ring deformation. Far i.r. bands are in accordance with refs 19, 20. Band numbering scheme is in accordance with ref. 21

change, raising the energy of the e_g and a_{2u} orbitals by inductive effect. Furthermore, the π electron density located in the metal p_π orbital can move back to the ring causing a rise in energy of the a_{2u} orbital through a diminishing of the conjugative effect[26].

The increase in atomic radii of the central metal has been observed to cause the phthalocyanine ring to alter slightly to accommodate the increased metal radii. For example, adding an electron to the vacant, strongly σ antibonding $d_{x^2-y^2}$ orbital, while going from Ni^{2+} to Cu^{2+}, increases the in-plane M–N(Pc) bond lengths by 11 pm (ref. 27). Similarly, adding an electron to the vacant and strongly axial σ antibonding orbital d_{z^2} while going from Fe^{2+} to Co^{2+} increases the axial bond length M–N by 30 pm (ref. 27).

In view of the above considerations let us discuss the C=N frequency shift observed in *Figure 1*. Following the literature considerations[27], it is possible that the phthalocyanine ring can change the geometry to accommodate the increased M–N bond length by lengthening of the C–N bond of the bridging atoms of the indoline rings. The near-neighbouring C=N bonds, which are fairly good electron donating sources, could move some of the electron density towards the N bridging atoms to accommodate the weakening of the N bridging bonds. If this is the case, the end result would be a smaller force constant for the C=N bond which would correspond to the C=N stretching band shifting to a lower wavenumber. This corresponding shift is reflected in *Figure 1*, traces A and B, as the C=N intraligand band shift from 1533 to 1512 cm^{-1} is observed.

If the electron density shift is indeed the case, the neighbouring bond vibrational energies, in particular the stretching normal modes, would be expected to be altered. As illustrated in traces A and B of *Figure 1*, the C–C vibrational stretching band of the indoline ring shifts from 1431 to 1425 cm^{-1}. Due to the in-plane bond length changes, the C–H bond deformations are also altered. This is illustrated by the shift of the C–H in-plane and out-of-plane deformation bands at 1057 and 904 cm^{-1}, respectively.

In an effort to illustrate the effect of axial ligand replacement, the intraligand C=N stretching band intensity at 1512 cm^{-1} was monitored as a function of sonication time. As shown in *Figure 2*, the replacement of an axially postioned chlorine atom in $Ge(Pc)Cl_2$ to oxygen in $[Ge(Pc)O]_n$ during polymerization is demonstrated by the shift of the C=N band from 1512 to 1502 cm^{-1}. Traces A–E illustrate that, after approximately 2 h of sonication, the intraligand substitution, and therefore polymerization, appear to be complete. During this process, the chlorine ligand is replaced by a more electronegative oxygen ligand. The electronegativity increase will facilitate a withdrawal of the electron density away from the germanium atom, upon which back-donation of electrons is possible through the inner N atoms. As a result, strengthening the Ge–N bond while weakening and lengthening the C=N bond will occur. This is again illustrated in *Figure 2* by the C=N intraligand band shift to a lower wavenumber.

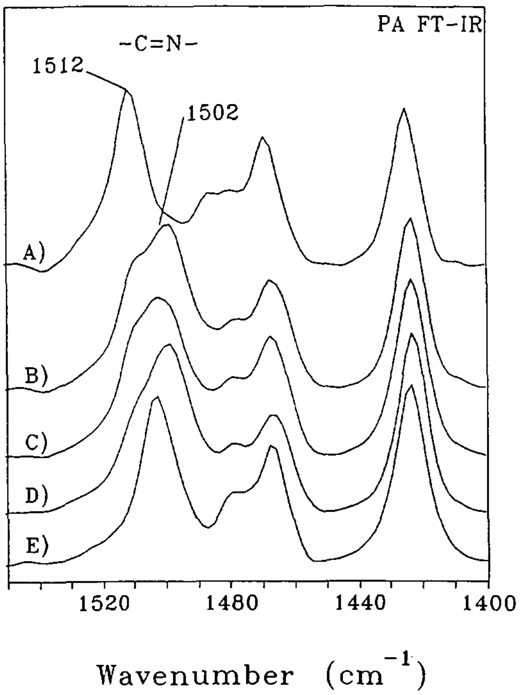

Figure 2 PA *FT*i.r. spectra of $GePcCl_2$ sonicated with sodium telluride for periods of: A, 0 min; B, 15 min; C, 30 min; D, 60 min; E, 120 min

Table 2 Typical metal phthalocyanine ligand π–π^* transitions

Label	Transition	Absorbance (nm)
Q	$a_{1u} \rightarrow e_g$	660
B	$a_{2u} \rightarrow e_g$	320
N	$a'_{2u} \rightarrow e_g$	275
L	$a_{1u} \rightarrow e'_g$	245

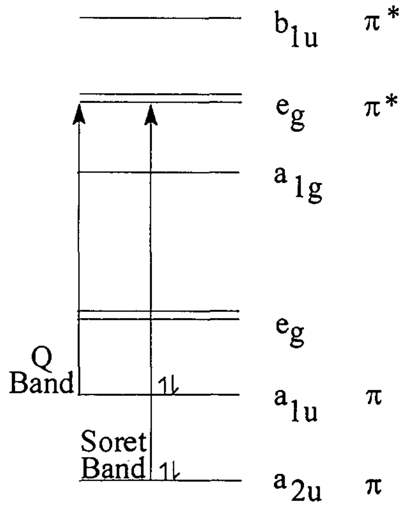

Figure 3 Molecular orbital energy levels of a phthalocyanine macrocycle

As a result of electron density changes during polymerization, these changes will also be reflected in the changes of electronic transitions. Most metallophthalocyanines belong to the point group D_{4h} (ref. 28). As theoretically predicted for D_{4h} molecular symmetry, monomeric phthalocyanines in solutions typically exhibit four characteristic electronic transitions in the u.v.–vis. spectra[27,29]. *Table 2* provides approximate energies of the absorptions along with the molecular orbital (MO) designation for the transitions. Of particular interest are the electronic transition at ~320 nm, referred to as the B band (Soret band), and the transition at ~660 nm, referred to as the Q band. The B and Q electronic bands arise primarily from the $\pi \rightarrow \pi^*$ transitions within the delocalized Pc ring system. *Figure 3* shows a scheme of the origin of the Q and Soret bands and the energy levels in a typical metallophthalocyanine[30]. According to Gouterman and co-workers[31–34], the HOMO orbital is $a_{1u}(\pi)$ and the next low-lying filled orbital is $a_{2u}(\pi)$, and the LUMO is $e_g(\pi^*)$. Transitions from a_{1u} and a_{2u} to e_g are responsible for the two π–π^* transitions labelled as the Q and Soret bands, characteristic of the spectra of all metallophthalocyanine species. The N electronic Pc transition is expected to occur near the B band, and thus is responsible for the broadening of the absorption maximum in this region[27]. The Q band is responsible for the inherent opaque blue/green colour of the phthalocyanines and is sensitive to molecular symmetry changes[35].

Further evidence for the ultrasonic formation of poly(phthalocyanato) germanium oxide and electron density changes associated with it can be found in the analysis of the u.v.–vis. spectra of germanium phthalocyanine dichloride monomer as a function of sonication time. As the sonication time increases, a blue

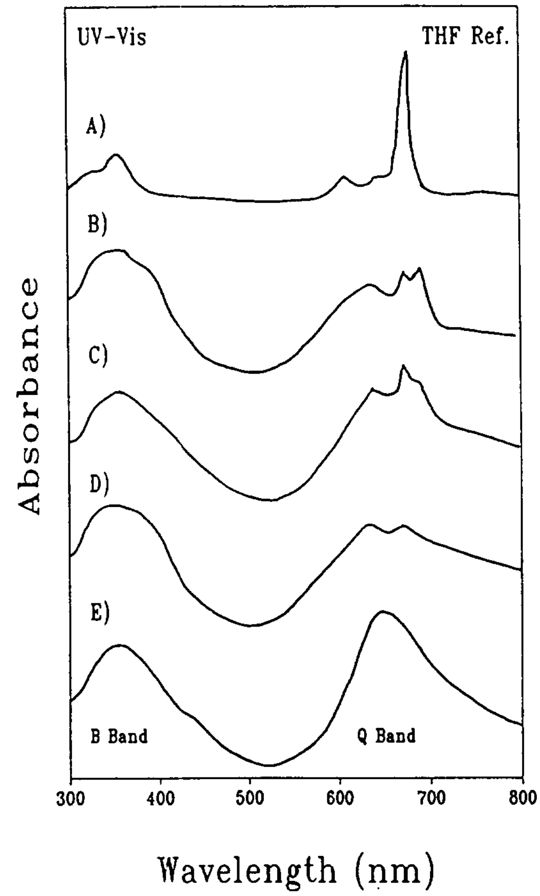

Figure 4 Electronic absorption spectra of $GePcCl_2$ sonicated with sodium telluride for periods of: A, 0 min; B, 15 min; C, 30 min; D, 60 min; E, 120 min

hypsochromic shift of the Q band from 690 to 640 nm is observed. This is shown in *Figure 4*, traces A–E. This phenomenon results from a change of the molecular orbital energy states such that higher energy is required for the electronic transition to occur. This could correspond to the lowering of the HOMO energy level, which would exhibit a decrease of the electron density on the phthalocyanine ring, subsequently raising the energy required to undergo the electronic transition.

Additional evidence for the ligand replacement and axial polymerization is documented in *FT*i.r. spectra which indicate the formation of Fe–O–Ge bridges and parallels the disappearance of the Ge–OH entity. This is illustrated in *Figure 5*, traces A–E, where the appearance of the band at 872 cm^{-1}, attributed to the Ge–O–Ge normal stretching vibrations, and the disappearance of the band at 642 cm^{-1}, assigned to the Ge–OH asymmetric stretch, is observed as sonication proceeds. A comparison of traces E and F indicates that the difference in the band area of the Ge–O–Ge and Ge–OH stretching modes, corresponds to the different degrees of polymerization for the two syntheses. The average degree of polymerization, determined by end-group analysis[36,37], for the ultrasonicated sample is approximately 15 ($n = 15$) while the thermally prepared sample is approximately 45 ($n = 45$). The above result is lower than that determined for the ultrasonicated poly(phthalocyanato) silicon oxide ($n = 48$).

A comparison of the silicon and germanium oxide polymer spectra is shown in traces A and B of *Figure 6*. As indicated earlier, due to the size and electronegativity differences of the metal, the C=N vibrational band shifts from 1518 to 1502 cm^{-1}. The metal-oxygen (M–O) vibrational stretching mode in the M–O–M bridge of $[Ge(Pc)O]_n$ appears at a lower frequency than that of the silicon phthalocyanine polymer. The increase of molecular mass, while going from silicon to germanium, affects the M–O vibrational energy even if the force constants remain unchanged. This is reflected in a lower

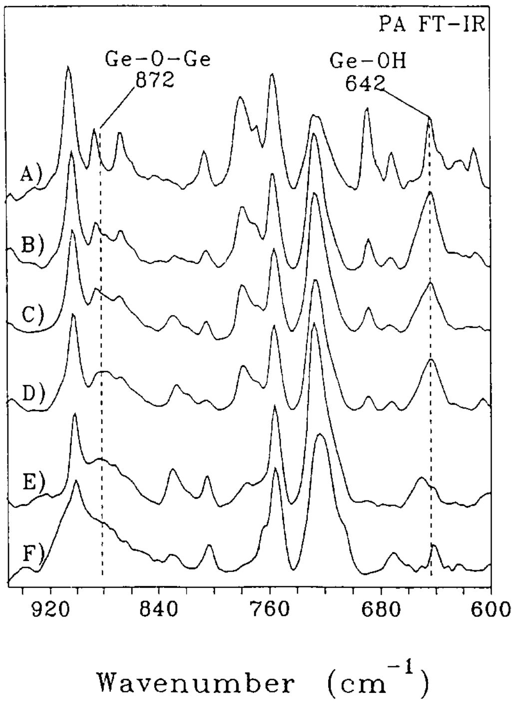

Figure 5 PA *FT*i.r. spectra of $GePcCl_2$ sonicated with sodium telluride for periods of: A, 0 min; B, 15 min; C, 30 min; D, 60 min; E, 120 min; F, a thermally polymerized poly(phthalocyanato) germanium oxide $[GePcO]_n$

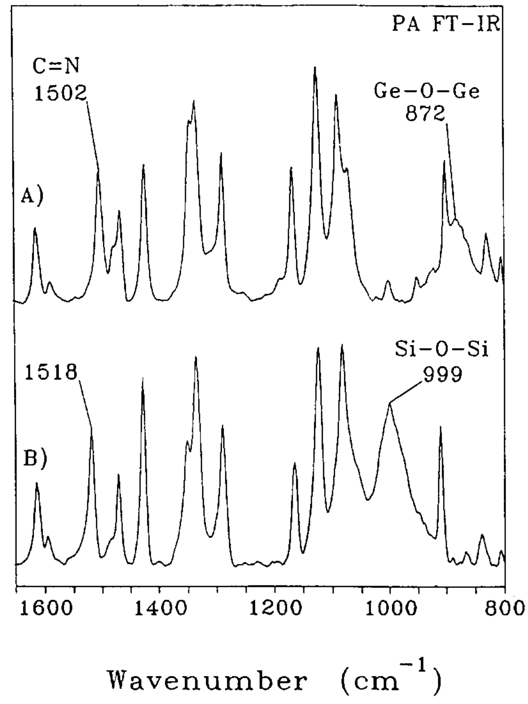

Figure 6 PA *FT*i.r. spectra of sonically polymerized: A, poly(phthalocyanato) silicon oxide; B, poly(phthalocyanato) germanium oxide

vibrational energy in *Figure 6*, as the Ge–O–Ge stretching band appears at 872 cm^{-1} while the corresponding Si–O–Si stretch is detected at 999 cm^{-1}.

Further evidence for the different effects of germanium and silicon metal atoms in phthalocyanine polymers is reflected in the u.v.–vis. spectra shown in *Figure 7*. As illustrated by *Figure 7*, traces A–D, a shift in absorbance is not detected for metal phthalocyanines containing different metal atoms. However, the shift from 690 to 640 nm occurs due to the replacement of the chlorine ligands by oxygen.

If the role of oxygen is to form an M–O–M bridge, one question that needs to be addressed is the source of oxygen. Previous n.m.r. analysis has shown that the oxygen atom probably does not come from the solvent THF breaking apart during ultrasonication[38]. Since a reasonably easy source of oxygen could be atmospheric air, oxygen was bubbled into the sonicated reaction and the end products did not appear to exhibit any differences. As a matter of fact, the reaction appeared to proceed much more slowly. Due to the apparent rate reduction of the reaction, the possibility of oxygen being incorporated from the air was ruled out.

Another source could be water which is added at the end of the ultrasonication process. In an effort to determine whether water is indeed incorporated into the phthalocyanine, a series of reactions was carried out, in which D_2O was added at different times to the sonication process. The resulting PA *FT*i.r. spectra of the selected reaction products are shown in *Figures 8* and *9*, traces A–D. A comparison of traces A and D in *Figures 8* and *9* shows that the bands of particular interest include 3495 cm^{-1} (GeO–H stretching mode), 2582 cm^{-1} (GeO–D stretching mode), 743 cm^{-1} (GeO–D bending mode) and 632 cm^{-1} (Ge–OD asymmetric stretching mode). As shown in *Figure 8*, trace B, addition of a small amount of D_2O to THF before sonication of $GePcCl_2$ for 15 min shows the presence of the OD stretching band at 2582 cm^{-1} assigned to the GeO–D stretching mode. Furthermore, addition of D_2O after sonicating the

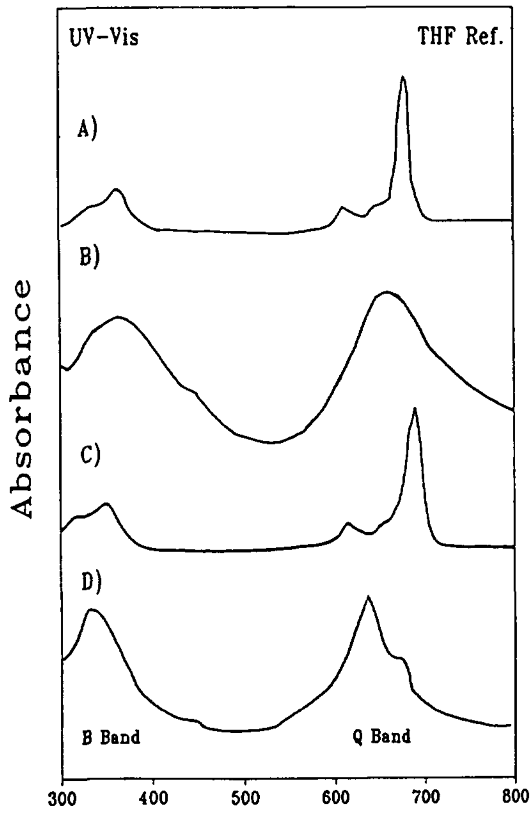

Figure 7 Electronic absorption spectra: A, $GePcCl_2$; B, sonically polymerized $[GePcO]_n$; C, $SiPcCl_2$; D, sonically polymerized $[SiPcO]_n$

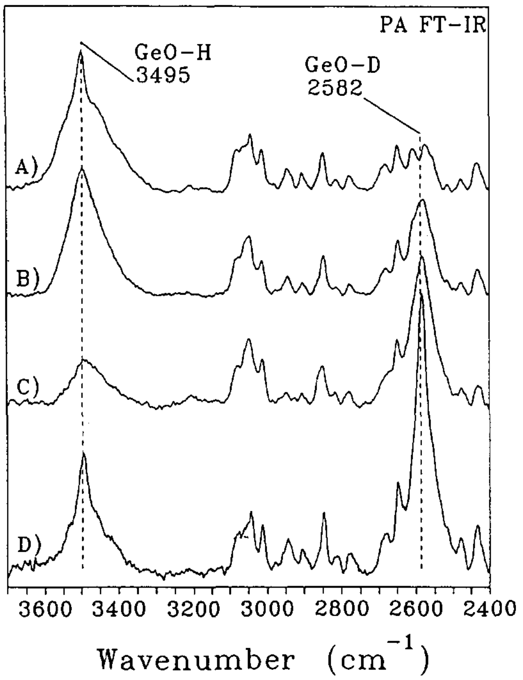

Figure 8 PA *FT*i.r. spectra: A, $GePc(OH)_2$; B, $GePcCl_2$ sonicated for 15 min in THF/D_2O; C, $GePcCl_2$ sonicated for 15 min in THF and worked up with D_2O; D, $GePcCl_2$ sonicated for 60 min in THF and worked up with D_2O

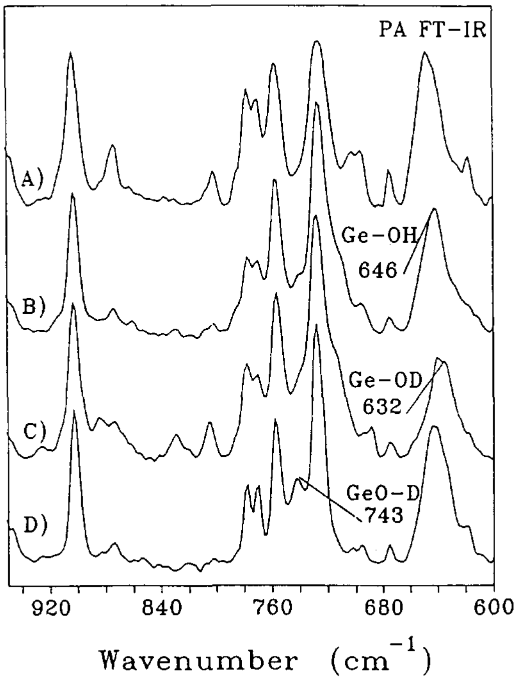

Figure 9 PA *FT*i.r. spectra: A, $GePc(OH)_2$; B, $GePcCl_2$ sonicated for 15 min in THF/D_2O; C, $GePcCl_2$ sonicated for 15 min in THF and worked up with D_2O; D, $GePcCl_2$ sonicated for 60 min in THF and worked up with D_2O

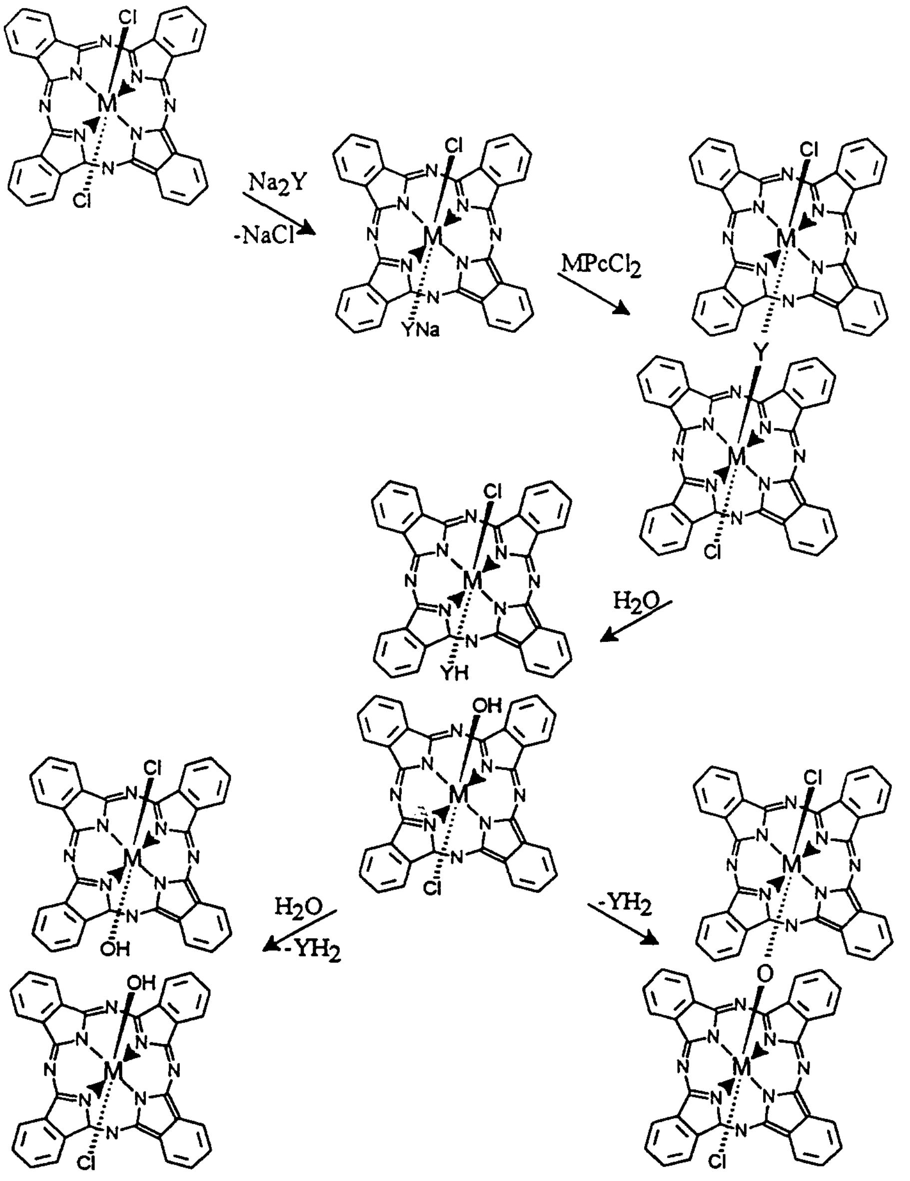

Figure 10 A proposed mechanism for the ultrasonic synthesis of poly(phthalocyanato) germanium oxide

$GePcCl_2$ mixture for 15 min (*Figure 8*, traces C and D) results in a decrease of the band at 3495 cm^{-1} (GeO–H stretching) while the GeO–D band at 2582 cm^{-1} increases. According to this data, water appears to be the most probable source of the oxygen.

Analysis of the above experimental data suggests that the mechanism depicted in *Figure 10* may be responsible for the polymerization of $[GePcO]_n$. Upon sonication of $GePcCl_2$ in the presence of a sodium chalcogenide (Na_2Y), the axially bound chlorine undergoes nucleophilic displacement with NaY. The sodium chalcogenide intermediate can react with another $GePcCl_2$ to form a chalcogenide-bridged phthalocyanine oligomer. Upon addition of water, hydrolysis of the chalcogenide-bridged oligomer can occur, forming both a hydroxy and hydrogen chalcogenide axially bound phthalocyanine. At this point, two competing reactions can occur. Either the oxygen-bridged phthalocyanine oligomer can be formed by loss of H_2Y, or the hydrogen chalcogenide phthalocyanine can undergo further hydrolysis to form another hydroxy-terminated phthalocyanine. As stated previously, although the role of ultrasound is not clearly understood, it is thought that ultrasonication increases the solubility of the phthalocyanines in THF; the reactive intermediates are brought into closer proximity and thus are more likely to react.

Conclusions

These studies show that poly(phthalocyanato) germanium oxide can be prepared via a one-step room temperature synthesis utilizing ultrasonication. Upon ultrasonication of $Ge(Pc)Cl_2$ in the presence of a sodium chalcogenide, a cofacially stacked poly(phthalocyanato) germanium oxide product was obtained. PA *FT*i.r. and u.v.–vis. data provided evidence that the cofacially stacked polymer was indeed formed. The presence of water is thought to play an important role in the polymerization in that it is thought to be the source of the oxygen bridging atoms between phthalocyanine rings.

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