Grafting of germanium phthalocyanine dichloride on poly(vinylidene fluoride) surfaces

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Room temperature ultrasonic surface modifications of poly(vinylidene fluoride) (PVDF) with germanium phthalocyanine dichloride in the presence of lithium lead to the formation of Ge-C bonds on the PVDF surfaces. Based on the analysis of attenuated total reflection Fourier transform infra-red, X-ray photoelectron spectroscopy (X.p.s.) and ultraviolet-visible (u.v.-vis.) spectra of the PVDF modified surfaces, it is shown that these species are chemically bonded through a central metal atom. This is demonstrated by the appearance of the 613 cm^{-1} band due to the Ge-C stretching mode, and a parallel disappearance of the C-F and C-H modes at 764, 1182 and 1209 cm^{-1}. Although more data are needed to establish mechanistic aspects of these reactions, X.p.s. and u.v.-vis. spectral analyses also indicate a removal of HF groups from the PVDF surface and the formation of C-Ge bonds.

(Keywords: surface modification; PVDF; spectroscopy)

INTRODUCTION

In recent years, the main interest in studying poly(vinylidene fluoride) (PVDF) surfaces was stimulated by the possibility of creating polymers with surface conductive properties. Although PVDF surfaces are non-conductive, proper modifications can lead to altering the surface dielectric properties. Although Kise and Ogata[1] and McCarthy and Dias[2] showed that controlled conjugated polyene structures can be formed through the elimination of hydrogen fluoride from PVDF surfaces, the research on thermal degradation of PVDF leading to dehydrofluorination was initiated by Lovinger and Freed[3] and Hagiwara *et al.*[4,5]. Although recently proposed new chemical methods utilizing phase-transfer catalysis (PTC) reactions[6,7], and ultrasonic PTC[8], were also successful, it became quite apparent that the length of the conjugation is heavily affected by the presence of head-to-head or tail-to-tail defects along the PVDF polymer backbone. These discouraging findings stimulated us to look for novel routes leading to surface modifications that would incorporate the main group elements containing phthalocyanines to partially conjugated polymer surfaces. However, because the main group metal phthalocyanine polymers require extreme conditions (high temperature), the first step in this study was to utilize ultrasonic energy in a one-step, room temperature synthesis of $[Si(Pc)O]_n$ (ref. 9). As a follow up of these studies, we reported similar room temperature ultrasonic synthesis of $[Ge(Pc)O]_n$ (ref. 10) polymers and ultrasonic grafting reactions of silicon phthalocyanine dichloride across the conjugated PVDF surface[11].

In our continuing efforts concerning main group polymer chemistry and polymer surface modifications, this study expands the scope of the previous experiments and it focuses on grafting germanium phthalocyanine dichloride ($GePcCl_2$) on PVDF surfaces. The primary motivation behind this study is that phthalocyanines exhibit inherent conductive properties. This, along with good chemical and thermal stability, creates an opportunity for synthesizing surfaces with new non-linear optical and electric properties. Similarly to our previous studies[11], a one-step Wurtz coupling grafting procedure will be used for the ultrasonic surface modification of the PVDF surfaces with $GePcCl_2$ in the presence of a lithium coupling reagent.

EXPERIMENTAL

Synthesis of $GePcCl_2$

Germanium phthalocyanine dichloride was prepared using the procedure described by Kenney and Joyner[12].

Grafting of $GePcCl_2$ on PVDF in the presence of Li

PVDF films (Westlake Plastics Co.) were degreased by Soxhlet extraction for 8 h with dichloromethane and vacuum dried to remove any residual processing aids. Strips of PVDF (~1 × 2 cm and 175 μm thick) were individually sonicated under nitrogen in 15 ml of freshly distilled tetrahydrofuran (THF) for 1 h at 25°C with 0.250 g (4×10^{-4} mol) $GePcCl_2$ and 0.056 g (8.07×10^{-3} mol) lithium powder (Aldrich). The sonically treated strips were rinsed with distilled water, acetone and ethanol and vacuum dried at room temperature overnight.

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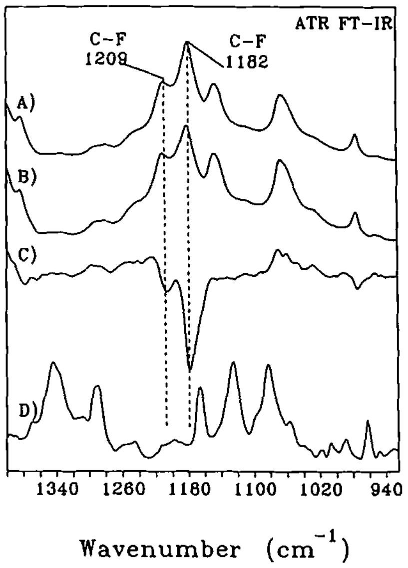

Figure 1 ATR *FT*i.r. spectra of: (A) non-sonicated PVDF; (B) sonicated PVDF in THF for 1 h with $GePcCl_2$ and lithium; (C) subtraction spectrum of A – B; (D) $GePcCl_2$

Analytical methods

Infra-red spectroscopy. Attenuated total reflectance Fourier transform infra-red (ATR *FT*i.r.) spectra were collected on a purged, air-purified (free of hydrocarbons, carbon dioxide, and water; Balston Filter Products) Digilab FTS-14B spectrometer equipped with a liquid nitrogen cooled MCT detector. The ATR attachment (cell no. 301; Spectra Tech, Inc.) was aligned at 45° and all spectra were recorded with a resolution of 4 cm^{-1} and an interferometer mirror speed of 0.3 cm s^{-1}. In order to enhance the signal-to-noise ratio, the spectra of all samples were obtained by coadding 400 single scans. Each resulting spectrum was ratioed against the spectrum of an aligned KRS-5 crystal (thallium bromide-iodide, 45° parallelogram: Spectra Tech Inc.), transferred to an IBM compatible computer, and analysed with the aid of Spectra Calc Software (Galactic Ind.).

The i.r. spectra of the metal phthalocyanine powders were obtained using photoacoustic Fourier transform infra-red (PA *FT*i.r.) spectroscopy. The detailed procedures involved in these measurements have been described elsewhere[11].

X-ray photoelectron spectroscopy. X-ray photoelectron spectra were obtained at the Regional Instrumentation Facility for Surface Analysis at the University of Minnesota (Minneapolis, MN) on a Perkin-Elmer PHI 5400 spectrometer using a 15 kV, MgKα source.

Ultraviolet-visible (u.v.-vis.) spectroscopy. Solid state u.v.-vis. spectra of the surface modified PVDF films were recorded on a multiple cell Hewlett-Packard 8451A diode array u.v.-vis. spectrophotometer equipped with a deuterium lamp. Untreated PVDF was used as a reference. Solution u.v.-vis. spectra of $GePcCl_2$ were obtained as previously described[11].

RESULTS AND DISCUSSION

As indicated in the Experimental section, grafting of metal phthalocyanines onto the PVDF surfaces was attempted by sonication of clean PVDF films in the presence of $GePcCl_2$ and lithium dispersed in THF. Although visual inspection after sonication indicated a distinct greenish-blue tint, usually not observed on ordinarily transparent PVDF films, to verify the presence of the germanium phthalocyanine on the PVDF, the films were analysed by ATR *FT*i.r. and u.v.-vis. spectroscopy.

The surface ATR *FT*i.r. spectrum of ultrasonicated PVDF surfaces with germanium phthalocyanine in the presence of lithium is displayed in *Figure 1B*. For reference purposes, an untreated PVDF film surface spectrum is shown in *Figure 1A*. Subtraction of spectrum B from A is shown in *Figure 1C* (multiplied by 10) and allows for detection of the spectral features that are usually not observable from direct measurements due to inherently low surface concentration levels. The analysis of the spectral changes shown in *Figure 1C* indicates that the PVDF surface dehydrofluorinates as a consequence of ultrasonication in the presence of germanium phthalocyanine and lithium. This is demonstrated by the presence of two negative bands at 1209 and 1182 cm^{-1} attributed to the C-F stretching modes of PVDF. Analysis of the spectral changes shown in *Figure 2C* also indicates a band at 613 cm^{-1}, which is attributed to the Ge-C stretching mode[13]. This band has a positive intensity indicating that the Ge-C bond is being formed. Band assignments for metal-containing phthalocyanine molecules can be found in ref. 14.

Figures 3A–D illustrate that the visual hue of the ultrasonicated PVDF surfaces is detectable by u.v.–vis. spectroscopy. For reference purposes, *Figure 3A* shows the spectrum of an untreated PVDF film referenced against itself. This spectrum illustrates that baseline fluctuations free electronic absorption can be obtained from the PVDF films. The u.v.-vis. spectra shown in *Figures 3B* and *C* illustrate the π-π^* electronic transitions of the $GePcCl_2$. The presence of two distinct electronic absorptions of the phthalocyanines Q band at 670 nm and the Soret band at 330 nm indicate that $GePcCl_2$ is present on the sonically treated PVDF surface. In addition, the u.v.-vis. data provide evidence that phthalocyanine is not readily absorbed or physically

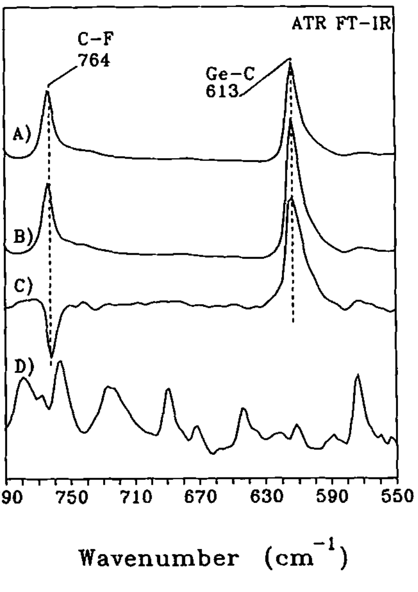

Figure 2 ATR *FT*i.r. spectra of: (A) non-sonicated PVDF; (B) sonicated PVDF in THF for 1 h with $GePcCl_2$ and lithium; (C) subtraction spectrum of A – B; (D) $GePcCl_2$

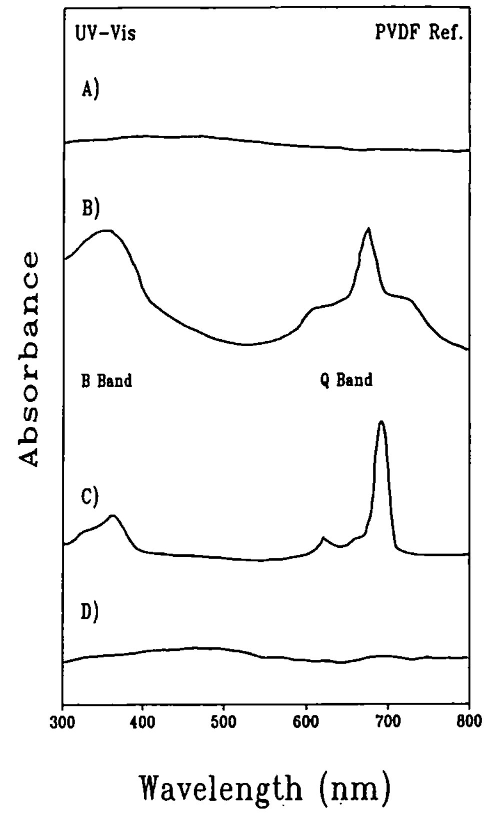

Figure 3 Electronic absorption spectra of: (A) PVDF referenced against itself; (B) $GePcCl_2$; (C) PVDF sonicated with $GePcCl_2$ and lithium in THF for 60 min; (D) PVDF sonicated with $GePcCl_2$ in THF for 60 min

embedded into the surface of the PVDF film by the ultrasonication process. Upon sonication of PVDF in the presence of $GePcCl_2$ and absence of lithium, the spectrum in *Figure 3D* has no electronic bands characteristic of germanium phthalocyanine. In summary, the u.v.-vis. spectra show that germanium phthalocyanine is present on the PVDF film when sonication with $GePcCl_2$ and lithium is performed, but the nature of the phthalocyanine bonding to the PVDF surfaces can be detected in the difference ATR spectrum (*Figure 2C*).

In an effort to provide further evidence for the bonding characteristics of germanium phthalocyanine to the PVDF film surfaces, X.p.s. spectroscopy was used. As illustrated in *Figure 4A*, the spectrum of $GePcCl_2$ shows the core electron position of Ge 2p. A comparison between sonically treated PVDF film (*Figure 4B*) and the powder spectrum of germanium phthalocyanine (*Figure 4A*) shows that the Ge 2p core electron for the germanium phthalocyanine sonicated PVDF films is relatively weak but detectable. This observation would tend to suggest that a relatively small amount of germanium phthalocyanine is present on the PVDF surface, which is indeed the case when one considers the small ratio of germanium to carbon atoms. In addition, there are sensitivity problems in this region; namely, the tendency of the PVDF film surfaces to be charged as the photoelectron energy increases[15,16], ultimately causing a low signal-to-noise ratio in this energy region. For these reasons, the weak Ge 2p core electron binding energy peak is observed.

If our claims that germanium phthalocyanine is bonded to the PVDF backbone are valid, the C 1s core electron peaks of the PVDF backbone should be also affected by the treatment. *Figure 5A*, shows the C 1s core electron peaks of the PVDF films with two distinct C 1s bands detected in the untreated PVDF film spectrum. The first peak at 293.2 eV (a) is assigned to the $\underline{C}$-F and the second at 287.5 eV (b) is assigned to the $\underline{C}$-H bonding[11]. Upon

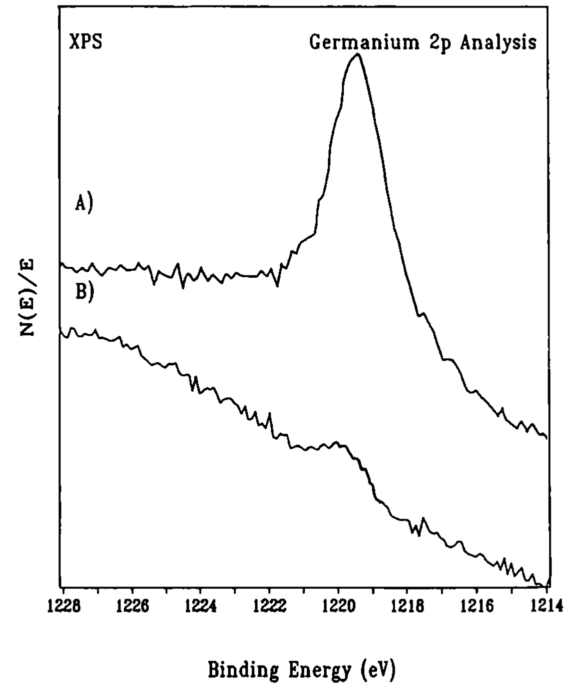

Figure 4 Electron spectroscopy for chemical analysis Ge 2p core electron band region of: (A) $GePcCl_2$; (B) PVDF film sonicated with $GePcCl_2$ and lithium in THF for 60 min

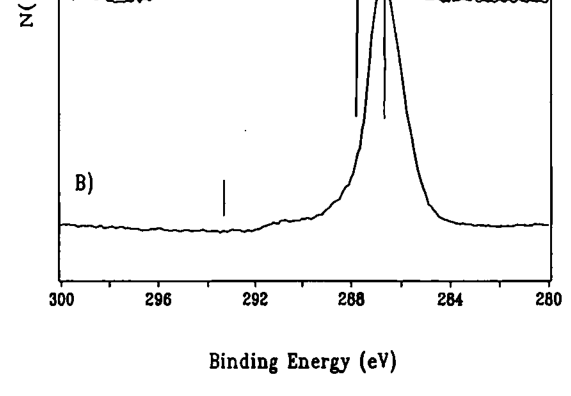

Figure 5 Electron spectroscopy for chemical analysis C 1s core electron band region of: (A) non-sonicated PVDF; (B) PVDF film sonicated with $GePcCl_2$ and lithium in THF for 60 min

Table 1 Electron spectroscopy for chemical analysis binding energies (eV) of various germanium compounds

Compound	Ge 2p	C 1s
$Ge(C_6H_5)_4$	1218.2	284.2
Ge	1218.8	286.2
GeO_2	1222.5	287.0
GeS_2	1220.8	285.8
GeF_2	1223.4	287.5

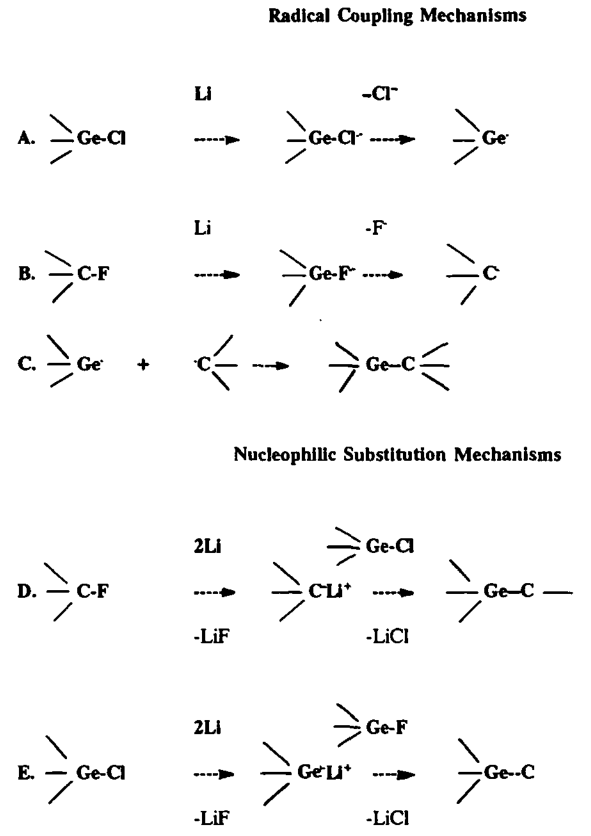

Figure 6 Several proposed Wurtz radical coupling and nucleophilic substitution reactions for the formation of a PVDF C-Ge phthalocyanine bond

sonication of the PVDF film in the presence of $GePcCl_2$ and lithium (*Figure 5B*), the C-F peak disappears while the C-H peak shifts to a lower energy at 286.4 eV. The C-F peak at 293.2 eV is eliminated because the surface of the PVDF film becomes dehydrofluorinated as the sonication reaction proceeds. On the other hand, the C 1s band at 287.5 eV shifts to lower energy because the PVDF surface not only becomes dehydrofluorinated, but also because germanium phthalocyanine reacts across the PVDF film surface. If the PVDF film surface was simply being dehydrofluorinated, the C 1s band would appear at 285.0 eV, as previously reported in the literature[17,18]. If the PVDF film surface is bound to the germanium of germanium phthalocyanine, the C 1s band would appear at 286.2 eV, as observed for other germanium compounds listed in *Table 1*[19]. As shown in *Figure 5B*, the C 1s peak appears at 286.4 eV and therefore, it is believed to be attributed to the germanium phthalocyanine bonded to PVDF surfaces.

With these data in mind, one would like to understand the mechanistic aspects of this reaction and how deep into the PVDF surface the reaction proceeds. Whereas the latter can be assessed based on the penetration depth of the ATR experiment, which in this case is ~4–6 μm, the former can be only speculated because in order to understand the Ge-C bond formation, additional experiments are needed. At this point, however, several plausible reaction schemes for the grafting of a $GePcCl_2$ monomer across the surface of PVDF can be postulated. They are schematically presented in *Figure 6*. We realized that the majority of the data pertaining to Wurtz coupling mechanisms have been gathered from homogeneous systems, but there are also reports for Si containing heterogeneous systems[20]. We will use this knowledge and try to rationalize the observations made in this study for $GePcCl_2$ using the Wurtz reactions which are based on radical coupling and/or nucleophilic substitution. In the case of radical coupling, the initial formation of radical anions followed by the expulsion of the respective halide anions is proposed. This is shown in *Figures 6A* and *B*, with the final step of coupling between alkyl and germanium radicals illustrated in *Figure 6C*. The second pathway may involve a halogen–metal exchange between the alkali metal and alkyl halide, i.e. PVDF ($-[CH_2CF_2]-$), which was reported to form an organometallic intermediate[21]. The alkyllithium intermediate can further react with a germanium halide, that is $GePcCl_2$, by nucleophilic substitution, to form the resulting C-Ge bond, such as that shown in *Figure 6D*. Another alternative is that a germanium lithium intermediate is formed and reacts with an alkyl halide, i.e. PVDF, to generate the C-Ge linkage. This is shown in *Figure 6E*. Although these reaction paths may occur simultaneously, it is believed that nucleophilic substitution (*Figure 6E*) is most likely to occur. This assessment is based on the fact that when PVDF is treated with CuPc in the presence of Li, the C 1s spectrum (not shown) is unchanged with respect to the untreated PVDF film surface. Similar observations were obtained for $SiPcCl_2$ when grafted onto PVDF.

CONCLUSIONS

A new, room temperature grafting methodology of $GePcCl_2$ with the aid of a lithium coupling agent to the surface of a PVDF film utilizing ultrasonic energy was developed. Based on the analysis of ATR *FT*i.r. spectra of the PVDF modified surfaces, germanium phthalocyanine is attached to the PVDF film substrate through bonding to carbon. This is demonstrated by the appearance of the 613 cm^{-1} band due to the Ge-C stretching mode, and parallel disappearance of the C-F and C-H modes at 764, 1182 and 1209 cm^{-1}. These data are supported by the C 1s X.p.s. spectral analysis which indicates that two processes may occur on the surfaces: dehydrofluorination and chemical bonding of germanium phthalocyanine across the surface.

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