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Ultrasonic PTC Modification of Poly(vinylidene fluoride) Surfaces and Their Characterization

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ABSTRACT: Attenuated total reflectance (ATR) and photoacoustic (PA) Fourier transform infrared (FT-IR) spectroscopy are used to characterize the surface of poly(vinylidene fluoride) (PVF_2) films upon dehydrofluorination. It is shown that HF groups are removed from the surface and C=C double bonds are formed. The reaction leads to substantial structural changes on the surface of the films. These changes are monitored by ATR and PA FT-IR spectroscopy. In addition to dehydrofluorination using phase-transfer catalysis (PTC) a new approach utilizing ultrasonic waves was examined. Two different sets of experiments were performed: temperature- and time-dependent reactions for both methods. It is shown that both approaches lead to substantial differences in the extent of the reaction as well as structural changes at the surface. UV–vis spectroscopy was utilized to determine the conjugation length of C=C units, while SEM was employed to estimate a thickness of the surface layer.

Introduction

The main interest in studying dehydrofluorination reactions arises from the possibility of creating polymers with conductive properties. Such conductive polymers may be obtained by modifying the surface of nonconductive PVF_2.[1,2] Originally, dehydrofluorinated polymers were obtained by thermal degradation of PVF_2.[3–6] The mere possibility of making conductive surfaces has spurred much interest in developing new methods of dehydrofluorination. Recently, several methods have been used to obtain dehydrofluorinated surfaces among which phase-transfer catalysis (PTC) reaction has proven to be the most successful.[1,2,7–9]

In the dehydrofluorination of PVF_2 the primary process is elimination of the HF units and formation of C=C double bonds in the polymer backbone. It has been proposed that the surface reaction proceeds according to a "zipper" mechanism, in which the elimination begins at a certain point and propagates along the chain.[3,7] Thus, a conjugated polyene chain is formed on the PVF_2 surface.[1,2,7,8] The presence of head-to-head (H–H) and tail-to-tail (T–T) defects determines the conjugation length of newly formed structures. The distance between the nearest defects in the polymer chain limits the length of conjugation and apparently causes premature termination of the propagating "zipper" reaction.

Although extensive spectroscopic research has been done on PVF_2 structure,[4,10–12] limited data are available concerning the actual changes that occur during dehydrofluorination. These changes can be monitored by using Fourier transform infrared (FT-IR) spectroscopy. In this work, we characterized surface-dehydrofluorinated PVF_2 films using attenuated total reflectance (ATR), and photoacoustic (PA) FT-IR spectroscopy. ATR spectroscopy is perhaps the most common IR technique used for surface characterization.[13–15] A newer technique that is gaining acceptance is photoacoustic (PA) FT-IR spectroscopy. This is mainly due to improved signal-to-noise ratio and ability to perform surface depth profiling studies.[16,17–19]

A further objective of this work was to establish how ultrasonic waves affect the surface modification of PVF_2. The use of ultrasonic waves in chemical synthesis is relatively new. For the most part, it has been applied in homogeneous inorganic reactions.[20,21] To our knowledge, the ultrasonic technique has not been used in polymer synthesis or modification.

Experimental Section

Sample Preparation. Polyvinylidene fluoride (PVF_2) films (127 μm thick and 1.76 g/cm^3 density) were obtained from Westlake Plastics. The following reagents were used in the synthesis: sodium hydroxide and tetrabutylammonium bromide (TBAB). A 25% w/w aqueous solution of sodium hydroxide was prepared by refluxing and cooling to ambient temperature. Tetrabutylammonium bromide (TBAB) (Baker Anal. Co.) was used as the phase-transfer catalyst (PTC) in the dehydrofluorination reactions. PVF_2 films were cut to a required size, and in order to eliminate impurities introduced during film processing, the specimens were washed in refluxing dichloromethane for 1 h under vigorous agitation. The films were vacuum dried for 24 h at 0.5 Torr. In order to limit the dehydrofluorination reaction to one side of the PVF_2 film, Teflon tape was applied to the other side.

The dehydrofluorination of the PVF_2 surfaces was achieved by modification of an earlier published method.[7,22] In a typical experiment, 25 mL of aqueous NaOH (25% w/w) and 0.4 g of TBAB were stirred for 10 min. The PVF_2 specimen was then immersed in the reaction mixture for the desired time. The dehydrofluorination reaction was carried out at 25 °C with the reaction time varying from 5 min to 6 h. Similar experiments were performed keeping the reaction time constant and varying the temperature from 25 to 45 °C. After the reaction, the PVF_2 films were washed several times with methanol and dichloromethane and vacuum dried (0.5 Torr) at room temperature for 24 h.

The same procedure was used to prepare specimens treated with ultrasonic waves. The vessel containing all reagents and the PVF_2 specimen was placed in a Branson B-12 (Branson Co.) ultrasonic bath as opposed to the use of magnetic stirring, described above.

Spectral Measurements. ATR FT-IR spectra were recorded on a Mattson-Cygnus 25 single-beam FT-IR spectrometer (Sirius 100) equipped with a He–Ne laser to provide an accuracy in frequency reading of 0.01 cm^{-1}. The ATR attachment (Mattson Instruments Inc.) with a KRS-5 crystal was aligned to a beam incidence angle of 45°. The interferometer mirror velocity was set at 0.316 cm/s. A total of 400 scans were collected to improve the signal-to-noise ratio. All spectra were ratioed against the reference (KRS-5). The instrument was purged with dry nitrogen gas.

The PA FT-IR spectra were recorded on a Digilab FTS-10 Fourier transform infrared spectrometer equipped with a PAS cell. All spectra were collected at 4 cm^{-1} resolution with a mirror velocity of 0.3 cm/s. In order to improve the signal-to-noise ratio, 400 scans were collected for each sample and ratioed against carbon black powder. The instrument was continuously purged with dry nitrogen. Each sample was placed in the PAS cell and purged with dry helium for 30 min prior to collecting the spectra. The flow rate was adjusted to maintain the same pressure inside the cell, about 0.2 psi. The PAS cell was stabilized at the temperature of the sample compartment prior to its use.

UV–vis spectra of the surface-treated PVF_2 films were obtained on a multiple cell Hewlett-Packard 8451A diode array UV–visible

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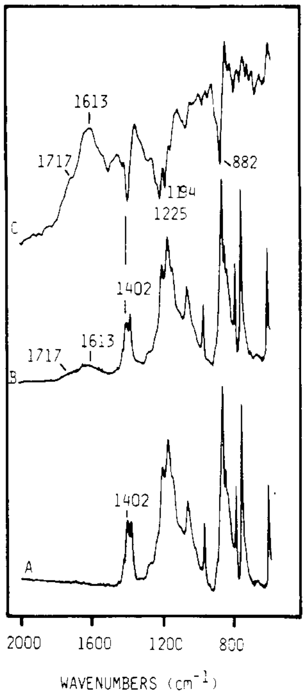

Figure 1. ATR FT-IR spectra of PVF_2 films: A, unreacted; B, dehydrofluorinated (2 h, 45 °C); C, difference spectrum (B − A).

spectrophotometer. Unreacted PVF_2 film was used as a reference.

Electron Microscopy. A JEOL 301 (JEOL Co.) scanning electron microscope (SEM) was used to obtain photographs of cross sections of treated films. The films were clamped to a special holder and placed inside the microscope. Pictures were taken at different locations on the cross section of the film at a magnification of 3300 applying 14 kV. A polaroid camera attached to the scanner was used to obtain the photographs.

Results

Temperature Studies. Figure 1A shows the ATR FT-IR spectrum of clean PVF_2 film surface. The observed vibrational modes are in agreement with previously reported bands in transmission spectra.[4,10-12] Because this work is focused on the surface dehydrofluorination of PVF_2, only bands that exhibit intensity changes upon the surface treatment will be examined and discussed. Trace B of Figure 1 shows the ATR FT-IR spectrum of PVF_2 surface reacted for 2 h at 45 °C. One could consider the observed changes, such as appearance of a broad band at 1613 cm^{-1} or slight intensity decrease of the 1402 cm^{-1} band, as rather insignificant. In fact, we do not expect large changes because the dehydrofluorination reaction leads to no more than several monolayers coverage of new structures on the PVF_2 surface. Therefore, to interpret these changes, it is useful to apply a method that will enhance the spectral information from the surface. One of the spectral processing operations widely used in polymer analysis is digital subtraction of the spectra in order to reveal subtle differences between two samples.[23] We utilized this approach to highlight the spectral information upon the structural changes on the PVF_2 surface caused by dehydrofluorination. The ATR spectrum of unreacted PVF_2 film was subtracted from the spectra obtained for the surface treated specimens. The resulting difference is shown in Figure 1C. It appears that, on subtraction, the bands show either positive or negative intensities. In this context, the difference spectra will show positive absorbances which reflect that new structures are formed during the surface treatment and negative absorbances indicating the loss of original structures. In the 1800–1500 cm^{-1} region the appearance of a positive band is observed upon the reaction. The maximum intensity of this band being at 1613 cm^{-1} suggests the formation of structures with C=C double bonds.[1,8] At elevated reaction temperatures this band becomes stronger.

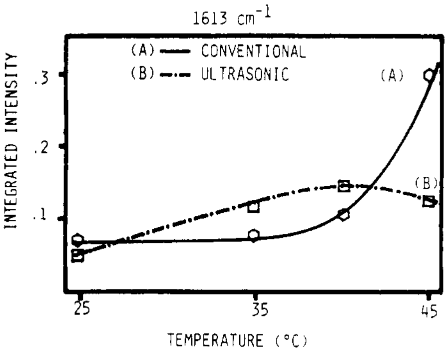

Figure 2. Integrated intensity of the 1613 cm^{-1} band plotted as a function of the reaction temperature: A, conventional PTC; B, ultrasonic PTC.

The band at 1402 cm^{-1} is also affected by the dehydrofluorination reaction. This band is associated with wagging and bending vibrational modes of the C–H units in PVF_2 backbone.[10,11] As the reaction proceeds, a decrease of the intensity of this band is observed. Other notable changes are observed for the bands at 1195 and 885 cm^{-1} that also appear to have negative intensities on subtraction. These bands are associated with the C–H, F–C–F, and C–F vibrational modes[10,11,24] reflecting a loss of the PVF_2 surface structures. The above spectral changes are indicative of the structural changes that occur on the surface of the polymer film upon dehydrofluorination.

So far, we have indicated qualitative spectral changes on the PVF_2 surface upon dehydrofluorination using a conventional synthetic method. Another approach to modify PVF_2 surfaces is to use a more powerful source of energy. In this work we utilized ultrasonic waves. This method has not been used in polymer synthesis or modification. Our premise is that this technique will open new routes in surface modification of polymers. An advantage of this approach is that when ultrasound waves are passed through the medium, the particles experience oscillations that create regions of compression and rarefaction. The negative pressure in the rarefaction region gives rise to the formation of bubbles that may be filled with a gas, the vapor of the liquid, or may be almost empty depending on the pressure and the forces holding the liquid together. The collapse of these bubbles, caused by the compression region of the ultrasonic waves, produces a powerful shock wave that is responsible for well-known processes such as dispersion and the erosion of metals. The energy output in the region of the collapsing bubble is considerable, with estimates of 2–3000 °C and pressures in the kilobar range for time periods in the nanoseconds.[20,21,25]

To establish differences in the surface treatment between conventional and ultrasonic methods, we prepared a series of surface treated PVF_2 films utilizing both conventional and ultrasonic approaches. An initial analysis of the spectra indicates that both methods lead to the same qualitative results. Although the spectral features observed in the subtraction spectra are similar, the analysis of integrated intensities shows substantial differences. Figures 2 and 3 plot integrated intensities of the 1613 and 1402 cm^{-1} bands as a function of reaction temperature. In the conventional procedure, as the reaction temperature is raised, an increase of the integrated intensity of the 1613 cm^{-1} band is observed (Figure 2A). At the same time, the 1402 cm^{-1} band is diminished (Figure 3A). Figures 2B and

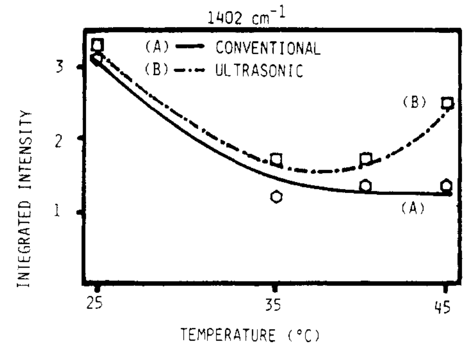

Figure 3. Integrated intensity of the 1402 cm^{-1} band plotted as a function of the reaction temperature: A, conventional PTC; B, ultrasonic PTC.

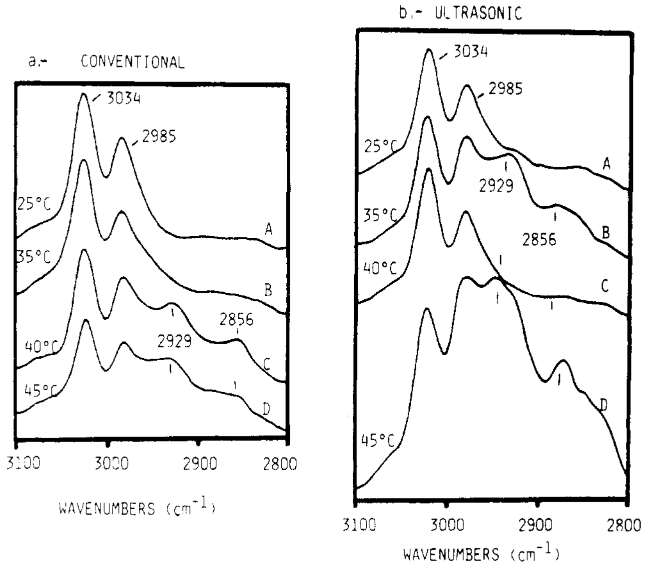

Figure 4. PA FT-IR spectra in the 3100–2800 cm^{-1} region (C–H stretching) for (a) conventional treatment and (b) ultrasonic treatment: A, 25 °C, 2 h; B, 35 °C, 2 h; C, 40 °C, 2 h; D, 45 °C, 2 h.

3B depict integrated intensities of the same bands as a function of temperature for the specimens treated with ultrasonic waves. Initially, as the reaction temperature increases to 40 °C, the 1613 cm^{-1} band increases much faster than the corresponding band in conventional treatment. This is accompanied by weakening of the 1402 cm^{-1} band. Above 40 °C, however, the 1613 cm^{-1} band is rapidly diminished and the band at 1402 cm^{-1} slightly increases. Thus, there are apparent differences between the conventional and the ultrasonic treatment.

The structures formed on the PVF$_2$ surface can be monitored by using photoacoustic (PA) FT-IR spectroscopy. A number of recent studies showed that this technique is also surface sensitive and offers several advantages.[13,14,17,18] The PA FT-IR spectra show similar features to those obtained by using the ATR technique.

Up to this point, we were concerned with the spectal changes that occur in the 1800–600 cm^{-1} region. If the dehydrofluorination reaction leads to a formation of new structures of the PVF$_2$ surface, we should be able to detect changes occurring in the C–H stretching region. As shown in Figure 4a, part A, the PA FT-IR spectrum of a treated PVF$_2$ surface (25 °C, 2 h) shows two bands at 3034 and 2985 cm^{-1}. As the reaction temperature increases, new bands at 2929 and 2856 cm^{-1} are observed, indicating again a formation of new structures. However, the nature of the changes for conventionally (Figure 4a) and ultrasonically (Figure 4b) treated specimens is substantially different.

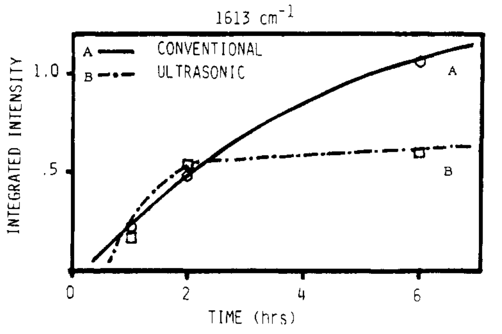

Figure 5. Integrated intensity of the 1613 cm^{-1} band plotted as a function of the reaction time: A, conventional PTC; B, ultrasonic PTC.

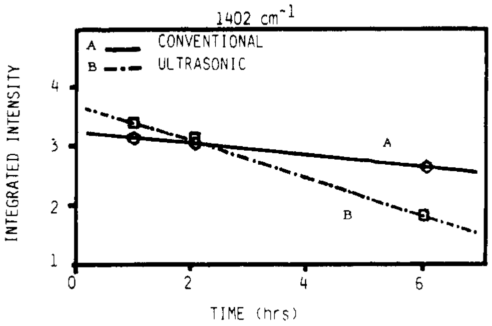

Figure 6. Integrated intensity of the 1402 cm^{-1} band plotted as a function of the reaction time: A, conventional PTC; B, ultrasonic PTC.

When the conventional method is applied, both bands appear to increase steadily with temperature. On the other hand, the ultrasonic treatment at 35 °C causes rapid increase of both bands (2929 and 2856 cm^{-1}). Further temperature increase to 40 °C results in a sudden intensity loss (Figure 4b, part C). As the temperature increases to 45 °C, both bands dominate this spectral region (Figure 4a, part D).

Kinetics of the Surface Treatments. In the previous section we described the spectral changes for both conventional and ultrasonic surface treatments as a function of temperature. In this part we will consider the results of kinetics of dehydrofluorination reaction and how one may control this surface process by extending the reaction time.

An extended reaction time leads to the appearance of bands at 1613 and 1717 cm^{-1} in both PA and ATR FT-IR spectra. Initial appearance and then further increase of both bands with time are observed. As the dehydrofluorination progresses, the 1402 cm^{-1} band is diminished, indicating that time- and temperature-dependent experiments lead to similar qualitative results.

Again, in order to evaluate the time-dependent experiments, we used bands at 1613 and 1402 cm^{-1}. Figures 5 and 6 show integrated intensities of both bands plotted as a function of the reaction time. For conventionally treated PVF$_2$ surfaces the band at 1613 cm^{-1} increases at constant rate (Figure 5A). On the other hand, when ultrasonic waves are applied, this band increases rapidly, and, when reaction time exceeds 2 h, its intensity levels off (Figure 5B). The 1402 cm^{-1} band decreases for both ultrasonically and conventionally treated surfaces (Figure 6, traces A and B, respectively). It seems, however, that upon ultrasonic treatment its intensity decreases at a greater rate.

In the 3100–2800 cm^{-1} region (C–H stretching region) the spectrum of clean PVF$_2$ surface exhibits two bands at 3034 and 2985 cm^{-1} due to asymmetric and symmetric C–H

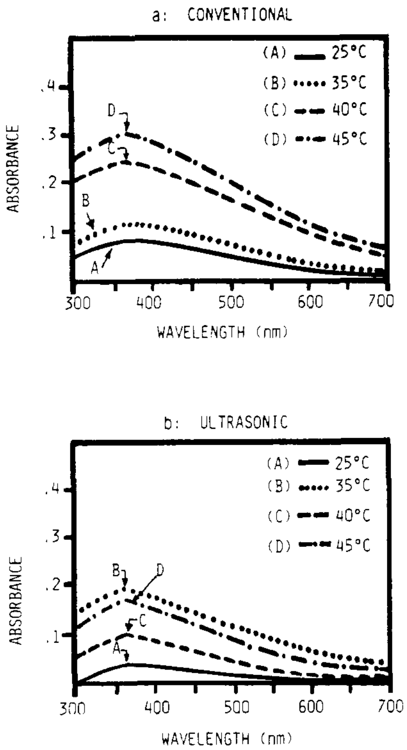

Figure 7. UV-vis spectra of dehydrofluorinated PVF_2 for (a) conventional treatment and (b) ultrasonic treatment: A, 1 h, 25 °C; B, 1 h, 35 °C; C, 1 h, 40 °C; D, 1 h, 45 °C.

stretching modes, respectively.[26,27] Similarly, we will compare the spectra obtained as a function of reaction time for both conventional and ultrasonic treatments. In conventional treatment, as the reaction time increases, a decrease of intensities of both bands is observed. The ultrasonic treatment leads to the appearance of new bands at 2929 and 2856 cm^{-1}. The same bands were observed when the reaction was run at elevated temperatures.

UV-Vis. The nature of newly formed structures on the PVF_2 surfaces can be monitored by using UV-vis spectroscopy. The UV-vis spectra of dehydrofluorinated PVF_2 films show electronic transition at 364 nm (λ_{max}) (Figure 7a, part A). As the reaction temperature increases from 25 to 45 °C the absorbance values at λ_{max} become greater. Their wavelength remains constant. For the films treated at constant temperature, prolonged reaction times give rise to an increase in the absorbance values (Figure 8a), whereas the wavelength of the electronic band at 364 nm remains unchanged.

The ultrasonic treatment at elevated temperatures leads to initial intensity increase of the absorbance of λ_{max}. However, when reaction temperature is raised to 40 °C, the band becomes weaker (Figure 7b). Similar observations were made in the infrared analysis for the 1613 cm^{-1} band. For a given temperature, extended reaction time leads to an increase of the absorbance values at 364 nm (Figure 8b). In both cases, varying time and temperature of the reaction, the values of λ_{max} apparently do not change.

Discussion

ATR and PA FT-IR analyses of the surface dehydrofluorinated PVF_2 films provide useful spectral information necessary to characterize new structures formed on the surface. In an attempt to elucidate structural changes occurring on the PVF_2 surface, first it is necessary to understand the origin of new bands associated and sensitive to the surface treatment. In the following section we will focus on the assignments of these bands.

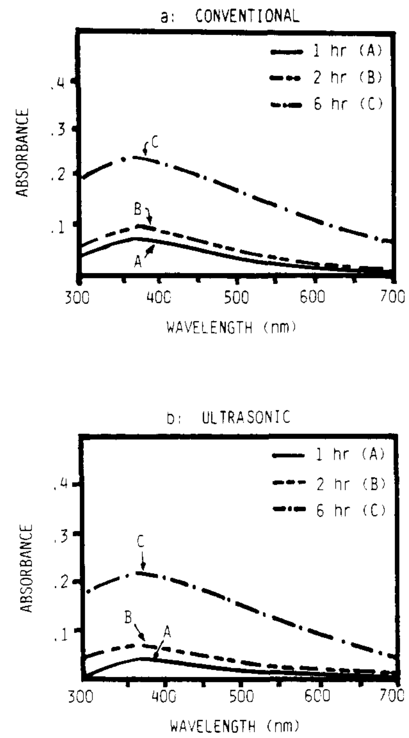

Figure 8. UV-vis spectra of dehydrofluorinated PVF_2 for (a) conventional treatment and (b) ultrasonic treatment: A, 25 °C, 1 h; B, 25 °C, 2 h; C, 25 °C, 6 h.

The band at 1613 cm^{-1} and a shoulder at 1717 cm^{-1} become stronger with temperature (Figure 1C) or prolonged time of the reaction. Wentink et al.[6] found two bands with maximum intensities at 1600 and 1715 cm^{-1} and assigned them to C=C double bonds formed along the polymer backbone in dehydrofluorinated PVF_2. For thermally degraded PVF_2, Hagiwara et al.[4,5] reported three bands in this region: at 1710 cm^{-1}, due to isolated C=C double bonds carrying a fluorine substituent, and two bands at 1620 and 1595 cm^{-1}, due to conjugated systems. Recently, Kise et al.[1] detected a strong band at 1590 cm^{-1} in the spectra of PTC dehydrofluorinated PVF_2 as a result of the formation of -C=C- double bonds on the surface. Although the reported frequencies vary, there is a general agreement that the bands in this region are due to C=C double bonds of newly formed structures on the PVF_2 surface.

In light of the above considerations the bands at 1613 and 1717 cm^{-1} are associated with the vibrational modes of C=C double bonds. The band at 1613 cm^{-1} is assigned to the C=C stretching vibrational mode of -(CH=CF)- units. The band at 1717 cm^{-1}, being much weaker than that at 1613 cm^{-1}, was recently assigned to the C=C stretching mode of -(CF=CF)- units.[22] The presence of these structures is possible because PVF_2 exhibits H-H or T-T defects. Due to a resonance between defects and the adjacent conjugated chains, this band corresponds to the -C=C- vibrations at H-H and T-T defect sites. Its low intensity, as compared to the 1613 cm^{-1} band, is proportional to the amount of defects present and depends on its symmetry. If the fluorine atoms occupied trans positions, this band would be infrared inactive. Hence, due to lower symmetry of the cis conformation the band at 1717 cm^{-1} is infrared active.

According to the "zipper" mechanism,[3,7] the reaction proceeds along the PVF_2 chain and leads to a formation of conjugated -(CH=CF)- units separated by carbon-carbon single bonds. In previous work we reported that H-H and T-T defects have significant effect on the efficiency of the dehydrofluorination reaction.[22] Approximately 10% of H–H and T–T defects are present in clean PVF_2.[22] Infrared bands characteristic of the H–H and T–T irregularities have been reported at 1453 and 678 cm^{-1}. Normal coordinate analysis calculations indicated that these bands correspond to the CH_2 bending and CF_2 wagging vibrational modes in the $-CH_2CH_2-$ and $-CF_2CF_2-$ units.[24] Apparently, their presence imposes limits on the length of conjugation. If the polymer backbone had no defects, the "zipper" reaction would probably propagate throughout the physical dimensions of the film leading to a long-chain conjugated backbone.

As the reaction propagates on the surface, the band at 1402 cm^{-1} becomes weaker. This band has been assigned to a combination mode of H–C–H, C–C–H, and C–C vibrations.[12,24] Its negative intensity in the difference spectrum (Figure 1C) and diminishing intensity with temperature (Figure 3, parts A and B) or prolonged reaction times (Figure 6, parts A and B) suggest a loss of hydrogens from the PVF_2 surface. Similar results are found for the bands at 1225, 1194, and 882 cm^{-1} that also appear to have negative intensities upon subtraction (Figure 1C). These bands are assigned[11,12,24] to the vibrational modes of F–C–F, C–C–F, and C–F species in the polymer backbone and become weaker as the reaction progresses. Such behavior indicates a loss of fluorines from the PVF_2 surface. Thus, the negative bands in the difference spectrum are associated with a loss of HF species from the surface.

Another observable change in the surface spectra is a partial loss of intensities of the bands at 3034 and 2985 cm^{-1}. They are assigned to the C–H stretching vibrations of the $-CH_2CF_2-$ groups. Due to the presence of highly electronegative fluorines attached to the adjacent carbon atoms both bands appear to have higher frequencies than that observed for the CH_2CH_2 backbone.[6,26,27] Both bands decrease in intensity as the reaction progresses. This process is accompanied by the appearance of two bands at 2929 and 2856 cm^{-1} indicating formation of $-(CF{=}CH)-$ species on the PVF_2 surface. As the HF units are eliminated from the PVF_2 backbone, the C–H force constant becomes weaker that is manifested by lower vibrational frequencies of the C–H stretching modes.

Conventional PTC Reaction. As the reaction temperature increases, the spectral changes described above become more pronounced. For example, the band at 1613 cm^{-1} increases in intensity. Figure 2A depicts integrated intensity of this band plotted as a function of temperature. This intensity increase indicates that greater amounts of $-(CF{=}CH)-$ structures are being formed on the surface which, in turn, implies that the newly formed surface layer becomes thicker. A diminishing intensity of the 1402 cm^{-1} band along with bands at 1225, 1194, and 882 cm^{-1} (Figure 3A) suggests that higher temperatures activate hydrogen and fluorine elimination from the surface. Hence, a loss of the HF units from PVF_2 backbone leads to a formation of the C=C double bonds.

Similar results are found when dehydrofluorination of the PVF_2 surface was carried out maintaining the reaction temperature constant and increasing the time of the treatment. As the reaction time is extended to few hours, the 1613 cm^{-1} band becomes stronger (Figures 5A and 6B), indicating a thicker $-(CF{=}CH)-$ layer formed on the PVF_2 surface. As expected, the bands at 1402, 1225, 1194, and 882 cm^{-1} show an opposite behavior. Above observations indicate that as the reaction time increases, the layer formed on the surface becomes thicker.

It has been shown in earlier studies that the length of C=C conjugation can be estimated by using UV–vis spectroscopy.[28-30] One may monitor both wavelength and intensity of the absorption band responsible for the electronic transition in C=C units. The wavelength (λ_{max}) of the band is related to the length of the polyene conjugation, whereas its intensity to the amount of new structures formed (Beer's law).[28,30] As the temperature of the reaction increases, the electronic band at 364 nm becomes stronger (Figure 7a). This band, associated with π–π^* transition in the polymer backbone, increases because a greater amount of the C=C species is formed on the surface. The temperature variations do not affect its wavelength. The 364-nm band corresponds to an average sequence length of conjugated –C=C– double bonds of 7–8 units.[28,30] Thus, regardless of the reaction conditions, the length of C=C conjugation remains unchanged. The reaction starts at a certain point of the polymer backbone and continues until the H–H or T–T defects terminate the process ("zipperlike" propagation). The analysis of UV–vis spectra supports the results obtained by FT-IR spectroscopy.

Ultrasonic PTC Reaction. Searching for new ways to obtain better control of the thickness of the layer, we utilized a modified method for carrying out the dehydrofluorination reaction. Namely, ultrasonic waves were applied to the reaction media. Upon ultrasonic treatment the intensity changes of the bands at 1613, 1402, 1194, and 882 cm^{-1}, as well as the bands in the 3100–2800 cm^{-1} region do not follow the pattern observed for conventionally treated films. The results for selected bands are depicted in Figures 2, 3, 5, and 6.

For ultrasonically treated surfaces, the intensity of the 1613 cm^{-1} band associated with a formation of $-(CF{=}CH)-$ structures increases with temperature. This intensity increase suggests a faster reaction when ultrasonic waves are applied to the PTC dehydrofluorination, as compared to the conventional PTC method. However, when the reaction temperature reaches 40 °C, the intensity suddenly drops. The intensity of the 1402 cm^{-1} band follows the trend for conventional treatment up to 40 °C. Above that temperature, the band becomes stronger. In the C–H stretching region, initially, two bands at 3034 and 2985 cm^{-1} due to the C–H stretching of CH_2CF_2 units are observed. As the temperature of the reaction increases, the intensities of both bands are diminished and new bands at 2929 and 2856 cm^{-1} appear. Thus, the high-energy input provided to the system has a significant impact on the nature of the conjugated chains formed on the PVF_2 surface. At first glance one might suggest a nonuniformity of the ultrasonic media due to the compression and rarefaction regions which create locally nonidentical reaction conditions such that the dehydrofluorination is inhomogeneous. This is perhaps correct because PVF_2 exhibits a uniquely distinct pattern of degradation.[3,6,31] Using optical microscopy Lovinger et al.[3] observed an uneven discoloration of PVF_2 upon thermal treatment indicating inhomogeneity of the process which, in its nature, is rather thermal than oxidative. A unique feature of the degradation comes from the fact that crystalline regions preferentially undergo discoloration.[3] In an attempt to rationalize our spectroscopic observations it is necessary to address the question as to why and how ultrasonic waves terminate the PTC reaction on the surface. First, let us compare ultrasonic and conventional treatments. Ultrasonic waves provide a high-energy input to the surface for short periods of time. This treatment accelerates the reaction initially. Thus, if the ultrasonically accelerated PTC reaction was fully terminated, one would expect only

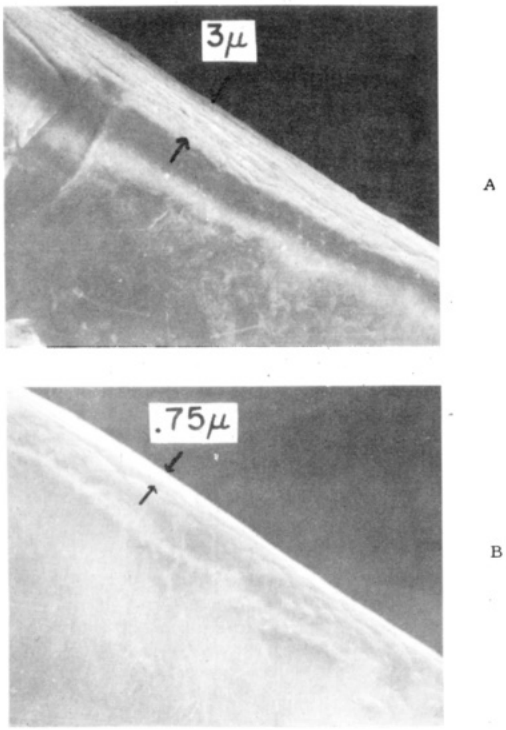

Figure 9. Electron micrographs of dehydrofluorinated PVF_2 film cross sections: A, conventional PTC, 6 h, 25 °C; B, ultrasonic PTC, 6 h, 25 °C.

thermal degradation of the surface, especially at higher reaction temperatures. However, thermal degradation would also lead to a formation of polyene sequences. Although the above appears to be a reasonable rationalization, this explanation does not satisfy our results because the intensity of the 1613 cm^{-1} band is diminished when the reaction is run above 40 °C. However, an important factor in the above justification is missing. Namely, the stability of the newly formed polyenic layer. One should realize that the energy input to the system is rather high (elevated temperature and ultrasonic energy), and therefore, we might anticipate a partial decomposition of the layer. At elevated temperatures this factor can conceivably play a role which is manifested by the intensity decrease of the 1613 cm^{-1} band. On the other hand, the effect of prolonged reaction time (Figure 5) on a formation of the polyenic layer is distinguishably different. The 1613 cm^{-1} band increases rapidly, and after 2 h of PTC ultrasonic treatment its intensity remains unchanged. Because of lower temperature (25 °C vs 40 °C) a newly formed layer has higher thermal stability. Hence, the following scenario is possible. The reaction proceeds in such a way that the thickness of the layer formed increases with time, and, as the temperature is raised, the surface layer is partially washed away and another layer is subsequently formed. As a result, its thickness remains essentially constant. From a macroscopic point of view this kind of treatment may be beneficial if one desires to obtain well-defined thickness of the layer on the surface. An advantage of the ultrasonic treatment is depicted in Figure 5. At a given temperature, when reaction time increases, the intensity of the band at 1613 cm^{-1} increases very rapidly, indicating a faster initial reaction rate than that for conventional treatment under the same conditions. Thus, with the use of ultrasonic waves the process proceeds much faster. Further prolongation of reaction time leads to a formation of the surface layer with a constant thickness. This is manifested by the intensity of the 1613 cm^{-1} band which remains unchanged as reaction progresses.

The UV–vis spectra for ultrasonically treated surfaces show similar patterns of variation of the electronic band. That is, as the reaction temperature increases, the absorbance of the electronic band due to $\pi-\pi^*$ transition changes. These changes agree with those found in the infrared analysis. Because the wavelength remains unchanged, the length of conjugation is the same for above reaction conditions. Such observation supports an evidence for the surface clean up process when the reaction is carried out in the presence of ultrasonic waves. On the other hand, changes in the absorbance values indicate that the amount of species on the surface at a given stage of the reaction varies, perhaps due to nonuniformity of the dehydrofluorination on the film surface. As depicted in Figure 7b, initially, the absorbance increases with temperature and then is diminished. In the time-dependent experiments, the λ_{max} for both ultrasonically and conventionally treated specimens remains the same, indicating nonchanging conjugation length on the surface.

Thickness of the Surface Layer. In order to support the spectroscopic data, we measured the thickness of polyenic layers by using scanning electron microscopy (SEM). Figure 9, parts A and B, shows cross-section photographs of specimens treated by using identical conventional and ultrasonic PTC conditions (6 h, 25 °C). As seen in photograph 9A (conventional method) the thickness of the surface layer is 3 μm. This value for ultrasonically prepared specimens (Figure 9B) was found to be 0.75 μm.

Conclusions

In this work we utilized ATR and PA FT-IR spectroscopy for characterization of surface-dehydrofluorinated PVF_2 films. Both techniques are sensitive to the structural changes occurring on the film surface upon dehydrofluorination.

The thickness of the surface layer formed upon dehydrofluorination increases with an increase in the time and/or temperature of the reaction for samples treated by using a conventional PTC reaction.

The use of ultrasonic waves for PTC dehydrofluorination provides faster initial reaction rates and more controllable thickness of the surface layer, as indicated in the kinetic studies. After certain reaction time, the thickness of the newly formed C=C layer remains constant regardless of further extent of the reaction time. Apparently a new polyene layer is formed and partially washed away such that its thickness remains constant. A constant C=C conjugation length on the surface can be obtained, regardless of the reaction conditions.

Earlier studies suggestd that PVF_2 degradation products may include not only the formation of polyenic sequences but also other types of structures due to chain scission, cross-linking, or cyclization.[3,4,6,31] The PTC reaction itself may produce nonuniform surface reaction on PVF_2, especially at elevated temperatures.[9] Because ultrasonic waves provide transitory high-energy local environments it is possible that different degradation processes may occur on the PVF_2 surface. At higher temperatures, a chain cleavage may become competitive with dehydrofluorination resulting in the formation of fluoroaliphatic compounds.[31,32] Although no evidence for a formation of products other than polyenic sequences on the surface of the films was found, these mechanisms should not be neglected.

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References and Notes

(1) Kise, H.; Ogata, H. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 3443.
(2) Dias, A. J.; McCarthy, T. J. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1057–1061.
(3) Lovinger, A. L.; Freed, D. J. *Macromolecules* **1980**, *13*, 989–944.
(4) Hagiwara, M.; Ellinghorst, G.; Hummel, D. O. *Makromol. Chem.* **1977**, *178*, 2901–2912.
(5) Hagiwara, M.; Ellinghorst, G.; Hummel, D. O. *Makromol. Chem.* **1977**, *178*, 2913–2926.
(6) Wentink, T., Jr.; Willwerth, L. J.; Phaneuf, J. P. *J. Polym. Sci.* **1961**, *55*, 551–562.
(7) Hahn, B.; Percec, V. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 783.
(8) Dias, A. J.; McCarthy, T. J. *Macromolecules* 1984, *17*, 2529–2531.
(9) Faingold-Murshak, V.; Karvaly, B. *Polym. Commun.* **1986**, *12*, 301–302.
(10) Bachmann, M. A.; Koenig, J. L. *J. Chem. Phys.* **1981**, *74*(10), 5896–5910.
(11) Kobayashi, M.; Tashiro, K.; Takodoro, H. *Macromolecules*, **1975**, *8*(2), 158–171.
(12) Boerio, S.; Koenig, J. L. *J. Polym. Sci., Polym. Chem. Ed.* 1974, *9*, 1517.
(13) Koenig, J. L. *Adv. Polym. Sci.* **1983**, *54*, 89–154.
(14) Krishnan, K. *Appl. Spectrosc.* **1981**, *35*, 549.
(15) Urban, M. W.; Koenig, J. L., to be submitted for publication.
(16) Salazar-Rojas, E.; Urban, M. W. *Polym. Prep.* **1987**, *28*(1), 1–2.
(17) Urban, M. W.; Koenig, J. L. *Appl. Spectrosc.* **1986**, *40*(7), 994–998 and references therein.
(18) Urban, M. W. *J. Coat. Technol.* **1987**, *59*(745), 29 and references therein.
(19) Graham, J. A.; Grim, W. M., III; Fateley W. G. In *Fourier Transform Infrared Spectroscopy: Applications to Chemical Systems*; Ferraro, J. R., Basile, L. J., Eds.; Academic: FL, 1985.
(20) Shoh, A. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; Wiley: New York, 1981; Vol. 16.
(21) Brown, B.; Goodman, J. E. *High Intensity Ultrasonics-Industrial Applications*; Van Nostrand: Princeton, 1965.
(22) Kuhn, K.; Hahn, B.; Percec, V.; Urban, M. W. *Appl. Spectrosc.* **1987**, *41*(5), 843.
(23) Koenig, J. L. *Appl. Spectrosc.* **1975**, *29*, 293.
(24) Painter, P. C.; Coleman, M. M.; Koenig, J. L. *The Theory of Vibrational Spectroscopy and Its Application to Polymeric Materials*; Wiley: New York, 1982.
(25) Sehgal, C.; Sutherland, R. G.; Verall, R. E. *J. Phys. Chem.* **1980**, *84*, 396.
(26) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; 3rd ed., Chapman and Hall: London, 1975.
(27) Colthup, N. B.; Daly, L. H.; Wiberly, S. E. "*Introduction to Infrared and Raman Spectroscopy*", 2nd ed.; Academic: New York, 1975.
(28) Leijenaar, S. R.; van der Heuvel, C. M. J.; Huysmans, W. *Macromolecules* **1985**, *186*, 1549–1553.
(29) Barton, S. S.; Boulton, G.; Harrison, B. *Faraday Soc. Trans.* **1971**, *67*, 3534–3539.
(30) Lewis, G. N.; Calvin, M. *Chem. Rev.* **1939**, *25*, 273–311.
(31) Montaudo, G.; Plugisi, C.; Scamporrino, E.; Vitalini, D. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 301–316.
(32) Ballistreri, A.; Foti, S.; Montaudo, G.; Scamporrino, E. *J. Poly. Sci., Polym. Chem. Ed.* **1980**, *18*, 1147–1153.

Solid-State Cross Polarization/Magic Angle Spinning ^{13}C NMR Study of Thermotropic Aromatic Polyester Containing a Flexible Spacer in the Main Chain

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ABSTRACT: The solid-state structure of a thermotropic aromatic polyester containing an aliphatic flexible spacer based on terephthalic acid and 4,4′-dihydoxy-1,6-diphenoxyhexane has been investigated by high-resolution solid-state CP/MAS (cross polarization/magic angle spinning) ^{13}C NMR. Samples of the polymer with different thermal histories, i.e., an original sample as obtained by low-temperature solution polymerization and once-melted samples with different cooling conditions, have been prepared in order to study the effect of the thermal history on the solid-state structure of the polymer. For the original sample, the solid-state spectrum shows that a conformation of the hexamethylene spacer is all-trans in the plane of the phenoxy group and that the ester linkage is nearly perpendicular to the plane of the aromatic ring. For the once-melted sample, it has been found that the conformations of the hexamethylene spacer and the ether linkage are a function of thermal history but that no appreciable change takes place about the ester linkage. The thermotropic aromatic ester compound bis(4-butoxyphenyl) terephthalate has also been characterized by solid-state and solution NMR. The conformation of the model compound is similar to that of the original sample of the polyester.

Introduction

Thermotropic polyesters have attacted much attention[1-3] because of their high potential as materials with excellent mechanical properties. It is very important to obtain information about their solid-state structures since thermotropic polyesters are utilized in the solid state. Moreover, many useful thermotropic polyesters show too low a solubility to allow measurements of the chemical structure in solution.

Recently, high-resolution CP/MAS (cross polarization/magic angle spinning) NMR has become a powerful tool for characterizing polymers in the solid state.[4-6] A thermotropic polyester is one of the best subjects for solid-state NMR study since there is great interest in the relationship between the solid-state structure and properties. Such information as chemical structure, molecular packing, molecular order, molecular motion, and conformation of a polymer can be obtained by means of solid-state NMR. However, very little work has been reported on solid-state NMR studies of thermotropic polyesters.[7,8]

In the present work, solid-state structures of thermotropic polyester 1 containing a flexible spacer[9] are inves-