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Selective Oxidation of Para-Substituted Polystyrenes during Surface-Enhanced Raman Scattering

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ABSTRACT: Selective oxidation of para-substituted polystyrene films on silver substrates has been observed during surface-enhanced Raman scattering (SERS). It is proposed that primary oxidation occurs by a Norrish type II reaction, resulting in chain scission and the formation of aryl ketone and olefin end groups. When the substituent in the para position is electron donating, as in the case of poly(4-fluorostyrene), poly(4-chlorostyrene), poly(4-bromostyrene), and poly(4-methylstyrene), further oxidation occurs rapidly by a Norrish I reaction, resulting in formation of para-substituted benzoic acids. When the substituents are electron withdrawing, as in the case of poly(4-sulfonate styrene) and poly(4-nitrostyrene), the rate of the Norrish I reaction is low. Further oxidation takes place by a Diels–Alder addition process between the aryl ketone and olefin end groups, ultimately leading to the formation of graphitelike species.

I. Introduction

Surface-enhanced Raman scattering (SERS) was first reported in 1977 for pyridine adsorbed onto an electrochemically roughened silver electrode.[1] Since that time, SERS has been reported from a large number of low molecular weight compounds. An excellent review of the work done in this field prior to 1982 has been given.[2]

Relatively few investigations of polymers have been reported. Murray and Allara[3] reported SERS from poly(*p*-nitrostyrene) (PPNS) in an "overlayer" configuration in which silver island films were deposited onto polymer films that were spin-coated onto aluminum substrates. They showed that the intensity of the strongest lines in the SERS spectra was approximately 5000 counts/s. By comparison, the intensity of the strongest lines in the normal Raman spectra of PPNS films spun onto aluminum to a thickness of about 1000 Å was only about 100 counts/s.

Parry and Dendramis[4] investigated the Raman scattering from thin polystyrene (PS) films spin-coated onto silicon wafers. They were unable to observe normal Raman scattering from films that were about 350 Å in thickness. However, when silver island films were evaporated onto the PS films in an overlayer configuration similar to that used by Murray and Allara, SERS spectra were obtained that were more intense than the Raman spectra of bulk PS.

Allara, Murray, and Bodoff[5] reported SERS from polystyrene in an "underlayer" configuration in which the polymer was spin-coated onto silver island films deposited onto glass slides. They reported that the morphology of the silver controlled the depth into the polymer film from which Raman scattering enhanced by the electromagnetic mechanism was observed. When the silver films had sharp features, SERS was observed only from the first few tens of angstroms of polymer at the silver interface. However, when the silver had large features, SERS was observed from several hundred angstroms into the polymer, suggesting that SERS might be a useful technique for depth profiling at polymer surfaces.

Lee and Meisel[6] observed SERS from silver and gold colloids stabilized by polymers, including poly(vinyl alcohol), poly(ethylene oxide), and poly(vinylpyridine), but were not able to observe normal Raman scattering from the same polymers. They observed the strong band characteristic of the totally symmetric ring breathing vibration near 1014 cm^{-1} in SERS spectra of poly(vinylpyridine) adsorbed onto silver sol particles. There was no indication of the band near 1025 cm^{-1}, which is usually attributed to a pyridinium ion or to pyridine chemisorbed at Lewis acid sites, and it was concluded that poly(vinylpyridine) was physisorbed by bonding through the π system and with the pyridine rings parallel to the substrate. Lee and Meisel[6] also suggested that poly(ethylene oxide) was adsorbed through the oxygen atoms and that poly(vinyl alcohol) was adsorbed through residual carbonyl groups that were present because of incomplete hydrolysis of the poly(vinyl acetate) from which the poly(vinyl alcohol) was made.

Boerio and Roth[7] showed that poly(4-vinylpyridine) (PVP) was adsorbed onto silver island films through the nitrogen atoms and that the rings were perpendicular to the surface. In normal Raman spectra of PVP, the ring breathing mode was observed as a strong band near 997 cm^{-1}. However, in the SERS spectra, this mode was split into components near 1000 and 1020 cm^{-1}. The component at the highest frequency was attributed to rings that were either coordinated through the nitrogen atom or protonated while that at lower frequencies was attributed to rings that were physisorbed or not adsorbed.

One of the most important problems associated with SERS of polymers concerns degradation of the samples to form graphitelike substances during laser irradiation. This degradation is characterized by the appearance of a pair of intense bands near 1575 and 1375 cm^{-1}. These bands have been observed in SERS spectra of polymers[4,5] and small molecules.[5,8–10] Originally, the bands near 1375 and 1575 cm^{-1} were assigned to carbonates.[8] However, similar bands have been observed in the normal Raman spectra of graphitelike materials[9] and in SERS spectra of surface species containing little oxygen,[9] supporting their assignment to graphitic species.

Oxidative degradation of polymers during SERS experiments can be reduced in several ways. Parry and Dendramis obtained excellent spectra of polystyrene by holding samples under vacuum during laser irradiation.[4] Boerio et al. showed that the oxidation of poly(α-methylstyrene) could be inhibited by blending a small amount of an antioxidant with the polymer.[11]

Boerio and Roth[7] showed that the degradation could be reduced by applying a thin film of a polymer with a low Raman scattering cross section, such as poly(methyl methacrylate) (PMMA), on top of the PVP films Excellent SERS spectra of PVP were obtained without interference from Raman lines of PMMA.

In a subsequent investigation, Venkatachalam, Boerio, and Roth[12] considered SERS from "bilayers" consisting of

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thin films of polystyrene (PS), poly(4-vinylpyridine) (PVP), or diglycidyl ether of Bisphenol A (DGEBA) overcoated with much thicker films of poly(4-styrene sulfonate) (PSS), which has a large Raman scattering cross section. Excellent SERS spectra of PS, PVP, and DGEBA could be obtained from such samples with little evidence of degradation. Moreover, no SERS was observed from the PSS overlayers as long as the PS, PVP, or DGEBA films exceeded a certain minimum thickness of perhaps 100 Å even though PSS has a large Raman cross section and the PSS overlayers were 1 order of magnitude thicker than the PS, PVP, and DGEBA films. It was suggested that the overlayers inhibited the degradation by restricting the supply of oxygen at the metal/polymer interface.

It has been speculated that the degradation of polymers during SERS experiments to form graphitelike substances involves a photoinitiated, silver-catalyzed oxidation process.[4] There have been several other reports of catalysis by SERS-active metals. Roth, Venkatachalam, and Boerio[13] investigated SERS from *p*-nitrobenzoic acid (PNBA). The spectra obtained at low laser powers were very similar to the normal Raman spectra of the sodium salt. However, when the laser power was increased, a strong band appeared near 1460 cm^{-1} that was not observed in the spectrum of either PNBA or its sodium salt. The changes observed in SERS spectra of PNBA during laser irradiation at high powers were related to reductive coupling of adsorbed molecules to form azodibenzoate, and the strong band near 1460 cm^{-1} was assigned to the stretching mode of the N=N bond.

Subsequently, Venkatachalam, Boerio, and Roth showed that azodibenzoate was also formed during SERS experiments from *p*-aminobenzoic acid (PABA) adsorbed onto silver island films. However, in that case, moisture was required for the reaction to proceed.[14] Azodibenzoate was formed if PABA was adsorbed onto silver island films and exposed to atmospheric moisture before or during SERS experiments. When similar samples were stored in a desiccator or held under vacuum during the SERS experiment, azodibenzoate was not formed. Since azodibenzoate was not formed during laser irradiation of bulk PNBA or PABA, it was concluded that the silver substrate was catalytically active.[14]

Dorain and co-workers[15] reported SERS from finely divided silver powder exposed to SO_2 gas. When SERS spectra were obtained in a helium atmosphere from freshly prepared powder using a low laser power (40 mW, for example), the broad bands characteristic of graphitic species were observed near 1350 and 1550 cm^{-1}. A sharp but weak band was observed near 1050 cm^{-1} and assigned to adsorbed NO_3^- (the silver powder was prepared by reduction of $AgNO_3$). After exposure of the powder to a brief pulse of SO_2, new bands appeared near 615 and 925 cm^{-1}, which were assigned to adsorbed SO_3^{2-}. This assignment was confirmed when bands were observed near the same frequencies in the normal Raman spectra of Ag_2SO_3 powder. When the laser power was increased to 500 mW, a new band appeared near 962 cm^{-1}, which was attributed to SO_4^{2-} formed by oxidation of SO_3^{2-}.

In the present paper, we present some interesting structural effects that appear to control the course of the oxidation process in polystyrene and its para-substituted derivatives. We have observed that the presence of electron-donating substituents (F, Cl, Br, and CH_3) in para position to the benzene ring induces a selective oxidation of the backbone yielding para-substituted benzoic acids. The presence of electron-attracting substituents (NO_2, SO_3H) leads to the formation of graphitelike species, as is the case of unsubstituted polystyrenes.

To the best of our knowledge, this is the first report of the formation of specific compounds from the substrate-catalyzed oxidation of polymers during SERS experiments. Furthermore, the results obtained appear relevant to the general understanding of the mechanisms of thermal and photooxidation processes occurring in polystyrene. In fact, they provide new and detailed information regarding the structural factors (i.e., substituent effects) that control the kinetics of the various (competitive) oxidation reactions involved in the process.

II. Experimental Section

Samples for SERS were prepared as follows. Glass slides were etched in chromic acid–sulfuric acid, rinsed in distilled water, and dried. Island films were deposited on the slides by slow thermal evaporation of silver in a glass bell jar at a pressure of approximately 10^{-6} Torr. The thickness of the films was controlled at about 43 Å using a quartz-crystal oscillator thickness monitor.

Poly(4-chlorostyrene), poly(4-bromostyrene), and poly(4-methylstyrene) were purchased from Aldrich Chemical Co. and used as received. Poly(4-fluorostyrene) was synthesized in our laboratory. 4-Fluorostyrene obtained from Aldrich was washed with a 0.2 M solution of KOH in water, dried over anhydrous Na_2SO_4, and distilled under vacuum. Free-radical polymerization of the monomer was carried out in toluene at 60 °C using azobis(isobutyronitrile) as initiator. The polymer was purified by reprecipitation from methanol several times.

Thin films of the para-substituted polystyrenes were deposited on the silver films by spin coating from dilute solutions in methyl ethyl ketone (MEK). Surface-enhanced Raman spectra were obtained using a spectrometer equipped with a Spectra-Physics 165 argon ion laser, Spex 1401 double monochromator, ITT FW-130 photomultiplier tube, and Harshaw photon-counting detection system. The monochromator was equipped with ruled gratings (1200 g/mm), which were blazed at 5000 Å and worked in the first order. The time constant, scan rate, and slit width were 10 s, 50 cm^{-1}/min, and 400 μm, respectively. All of the spectra were obtained using the green line (5145 Å) of the laser at powers ranging from 10 to 100 mW as measured at the laser head. Plasma lines were removed from the spectra by placing a narrow-band-pass filter between the laser and the sample. The SERS samples were placed in the laser beam so that the angles between the incident and scattered beams and the normal to the sample surface were 30° and 60°, respectively. All of the SERS spectra were obtained with the samples exposed to the atmosphere.

Normal Raman spectra were obtained using the same instrument by irradiating a small amount of the sample powder supported in a glass capillary tube. However, the time constant and slit width were 2 s and 200 μm, respectively.

III. Results and Discussion

Normal Raman spectra of the para-substituted polystyrenes are presented in Figure 1. As expected, the spectra are dominated by bands due to vibrations of the substituted benzene rings. Differences in the spectra are mostly related to the masses of the substituents in the para position. Spectra of poly(4-methylstyrene) and poly(4-fluorostyrene) are similar since in those cases the substituents are "light" and spectra of poly(4-chlorostyrene) and poly(4-bromostyrene) are similar since the substituents in those cases are "heavy". Assignments of most bands in the spectra can be discussed in terms of the numbering system of Wilson.[16]

The strongest bands in the spectra of poly(4-chlorostyrene), near 1603 and 1101 cm^{-1}, are assigned to $\nu(8a)$ and $\nu(1)$, tangential ring stretching and breathing modes, respectively. Medium intensity bands near 1013 and 647 cm^{-1} are assigned to $\nu(18a)$, a CH in-plane bending mode, and $\nu(6b)$, a radial ring stretching mode, respectively. The medium intensity band near 805 cm^{-1} is assigned to $\nu(10a)$,

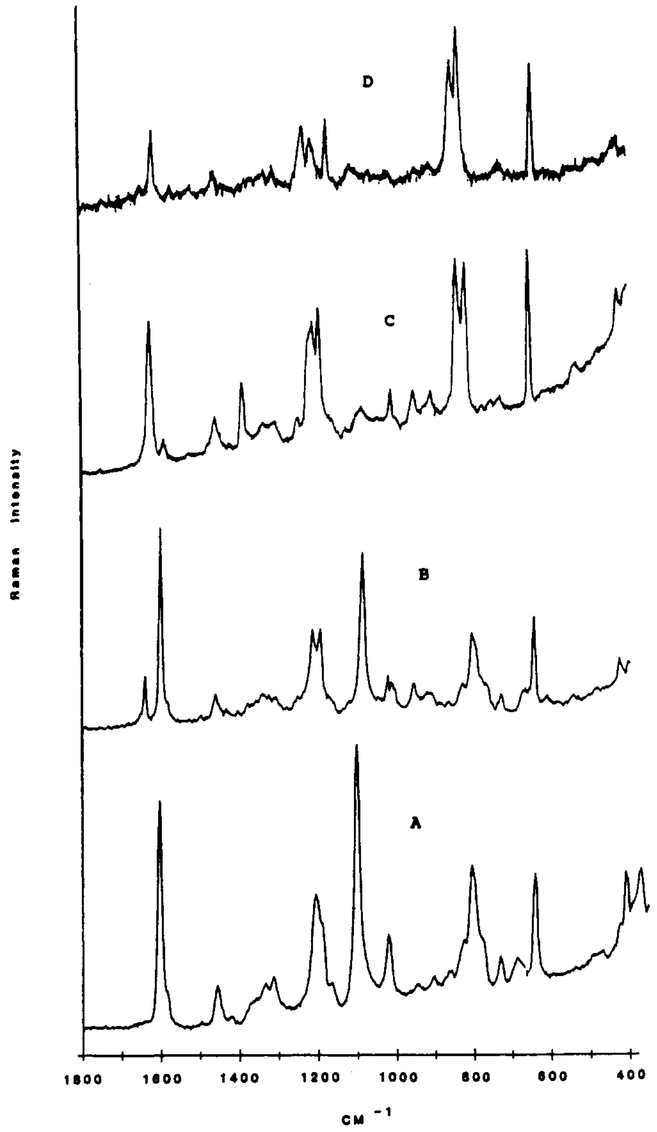


Figure 1. Normal Raman spectra of (A) poly(*p*-chlorostyrene), (B) poly(*p*-bromostyrene), (C) poly(*p*-methylstyrene), and (D) poly(*p*-fluorostyrene).

a CH out-of-plane bending mode. The pair of bands near 1203 and 1195 cm^{-1} is attributed to $\nu(13)$ and $\nu(9a)$, which are C–X stretching and CH in-plane bending modes, respectively, while the weak band near 1455 cm^{-1} is assigned to $\nu(19a)$, another tangential ring stretching mode. Spectra of poly(4-bromostyrene) are very similar to those of poly(4-chlorostyrene) except that $\nu(1)$ is shifted downward in frequency to about 1085 cm^{-1}.

As indicated above, spectra of poly(4-methylstyrene) and poly(4-fluorostyrene) are somewhat different from those of poly(4-chlorostyrene) and poly(4-bromostyrene) since the substituent in the para position is light in the former case and heavy in the latter case. Spectra of poly(4-methylstyrene) are dominated by strong bands near 1615, 1195, 845, 810, and 655 cm^{-1}. The bands near 1615 and 1195 cm^{-1} are attributed to $\nu(8a)$ and $\nu(9a)$, respectively, and the band near 655 cm^{-1} is assigned to $\nu(6b)$. One of the bands at 845 and 810 cm^{-1} is assigned to $\nu(1)$ while the other is related to $\nu(10a)$.

Several weak bands are observed, which can also be assigned to modes of the substituted benzene ring. Bands near 1590 and 1458 cm^{-1} are assigned to $\nu(8b)$ and $\nu(19a)$, additional tangential ring stretching modes. The sharp band near 1011 cm^{-1} is assigned to $\nu(18a)$. The broad band centered at about 1210 cm^{-1} actually consists of two overlapping bands related to the C–X stretching vibrations $\nu(7a)$ and $\nu(13)$. The only band in the spectrum that may be related to the methyl substituent on the ring is that near 1390 cm^{-1}, which may be due to the symmetric deformation or "umbrella" mode.

Spectra of poly(4-fluorostyrene) are remarkably similar to those of poly(4-methylstyrene). Strong bands near 851 and 840 cm^{-1} are assigned to $\nu(1)$ and $\nu(10a)$. That near 648 cm^{-1} is attributed to $\nu(6b)$. The sharp bands near 1610 and 1165 cm^{-1} are assigned to $\nu(8a)$ and $\nu(9a)$, respectively. Bands near 1215 and 1204 cm^{-1} are related to $\nu(13)$ and $\nu(7a)$, respectively. The weak band near 1455 cm^{-1} is assigned to $\nu(19a)$.

The SERS spectra of the para-substituted polystyrenes spin-coated from dilute solutions onto silver island films varied as a function of laser power. However, there was little tendency for the polymers to oxidize to graphitelike species as occurred for polystyrene and poly(α-methylstyrene). Instead, the para-substituted polystyrenes oxidized to form para-substituted benzoic acids. The SERS spectra of the para-substituted benzoic acids, which will be discussed in detail elsewhere,[17] are shown in Figure 2.

Oxidation of para-substituted polystyrenes to para-substituted benzoic acids was clearly shown when SERS spectra of poly(4-chlorostyrene) spin-coated onto a silver island film from a 1% solution in methyl ethyl ketone were obtained as a function of laser power (see Figure 3). Spectra obtained at a laser power of 10 mW were characterized by medium intensity bands near 1600, 1400, 946, and 630 cm^{-1} and by weak bands near 1209, 1175, 1103, and 1010 cm^{-1}. The band near 1600 cm^{-1} is related to both $\nu(8a)$ and $\nu_a(COO^-)$ while that near 1400 cm^{-1} is related to $\nu_s(COO^-)$. Bands near 1209 and 1175 cm^{-1} are assigned to $\nu(13)$ and $\nu(9a)$, respectively. Bands near 1103 and 1010 cm^{-1} are assigned to $\nu(1)$ and $\nu(18a)$, respectively. Those near 946 and 630 cm^{-1} are related to sulfite species resulting from reduction of sulfate contaminants at the silver surface.[11]

When the laser power was increased to 50 mW, the band near 1600 cm^{-1} increased rapidly in intensity and new bands appeared near 1150, 850, and 550 cm^{-1}. Bands near 1209, 945, and 630 cm^{-1} decreased in intensity, and those near 1175, 1100, and 1010 cm^{-1} increased. The spectra obtained at a laser power of 100 mW were dominated by the bands near 1600, 1150, 1100, and 850 cm^{-1} and were remarkably similar to SERS spectra of 4-chlorobenzoic acid (see Figure 2A).

Very similar results were obtained for the other polymers. As shown in Figure 4, SERS spectra of poly(4-bromostyrene) spin-coated onto silver islands were more similar to SERS spectra of 4-bromobenzoic acid (see Figure 2B) than to normal Raman spectra of the polymer. Bands characteristic of $\nu(8a)$ and $\nu_a(COO^-)$ and of $\nu_s(COO^-)$ were observed near 1598 and 1397 cm^{-1}, respectively. $\nu(9a)$ and $\nu(10a)$ were shifted from near 1195 and 801 cm^{-1} in normal Raman spectra of the polymer to near 1149 and 848 cm^{-1}, respectively, in SERS spectra. $\nu(1)$ was observed near 1080 cm^{-1} in SERS spectra of poly(4-bromostyrene), very near its position in normal Raman spectra of the polymer and SERS spectra of 4-bromobenzoic acid. Weak bands related to $\nu(18a)$ and $\nu(12)$ were observed near 1010 and 503 cm^{-1} in SERS spectra of poly(4-bromostyrene) and were very close to their positions in SERS spectra of 4-bromobenzoic acid.

SERS spectra of poly(4-methylstyrene) spin-coated onto silver islands were much different from normal Raman spectra but were very similar to SERS spectra of 4-methylbenzoic acid (toluic acid) (see Figures 5 and 2C).

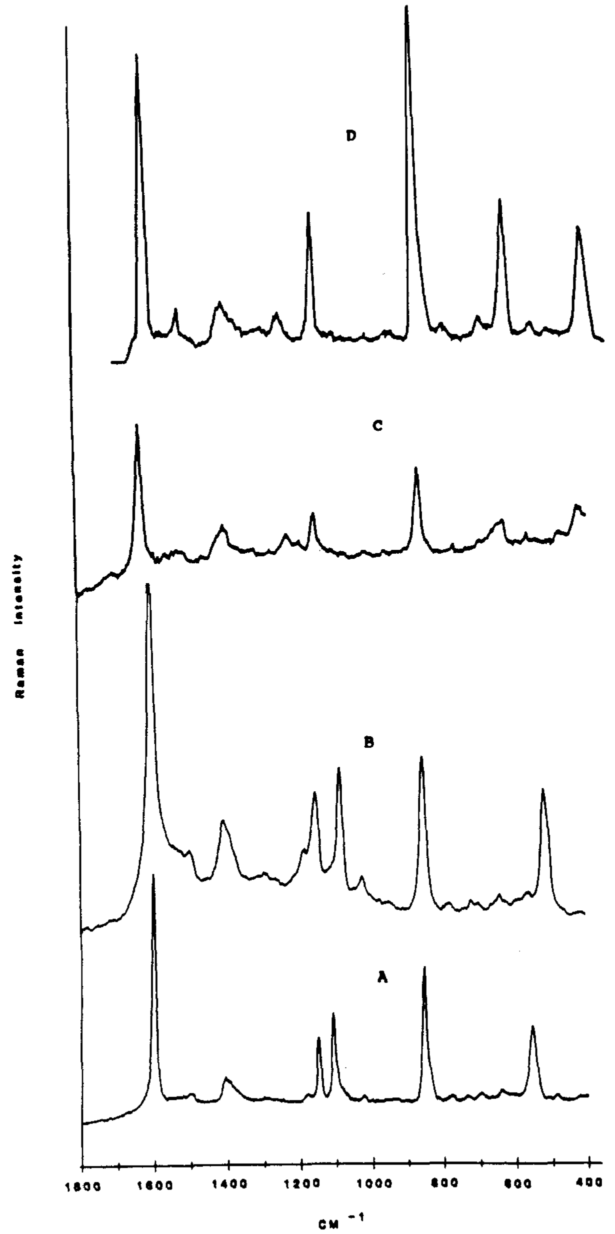


Figure 2. SERS spectra of (A) *p*-chlorobenzoic acid, (B) *p*-bromobenzoic acid, (C) *p*-methylbenzoic acid, and (D) *p*-fluorobenzoic acid spin-coated from dilute solutions onto silver island films.

A strong band assigned to ν(8a) was observed near 1612 cm^{-1} in SERS spectra of the polymer. Weaker bands related to ν(9a) and ν(1) were found near 1148 and 861 cm^{-1}, respectively. Broad bands related to ν_a(COO$^-$) and ν_s(COO$^-$) were observed near 1585 and 1400 cm^{-1}, respectively. These bands are all within a few wavenumbers of their positions in SERS spectra of toluic acid shown in Figure 2C.

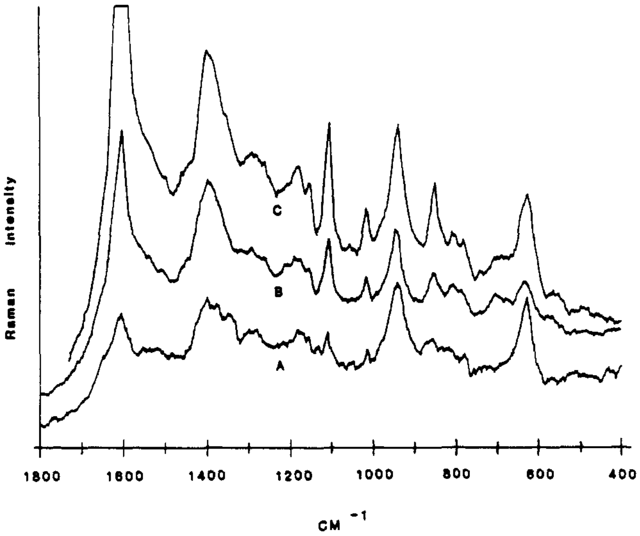


Figure 3. Surface-enhanced Raman scattering from poly(*p*-chlorostyrene) spin-coated onto a silver island film from a 1% solution in methyl ethyl ketone. The laser power was (A) 10, (B) 50, and (C) 100 mW.

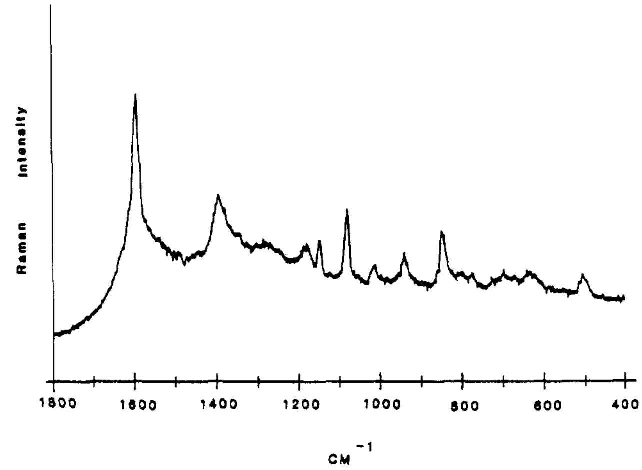


Figure 4. Surface-enhanced Raman scattering from poly(*p*-bromostyrene) spin-coated onto a silver island film from a 0.2% solution in methyl ethyl ketone. The laser power was 100 mW.

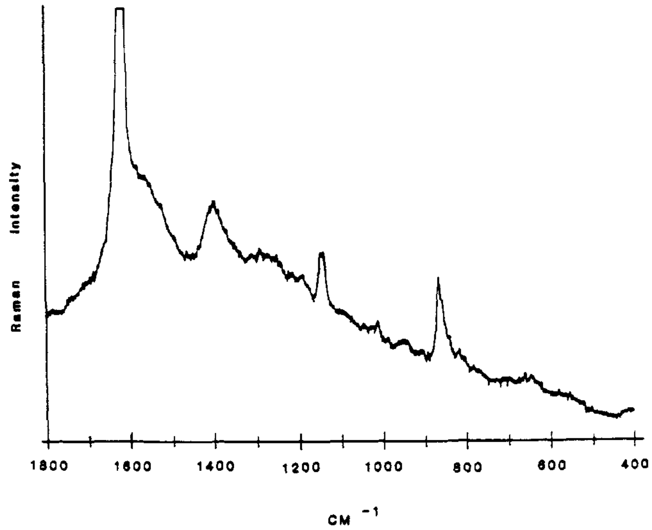


Figure 5. Surface-enhanced Raman scattering from poly(*p*-methylstyrene) spin-coated onto silver island films from a 0.1% solution in methyl ethyl ketone. The laser power was 100 mW.

SERS spectra obtained with a laser power of 100 mW from a thin film of poly(4-fluorostyrene) spin-coated from a 1% solution in toluene onto a silver island film resembled SERS spectra of 4-fluorobenzoic acid (see Figure 6). A strong band assigned to ν(8a) and to ν_a(COO$^-$) was observed near 1613 cm^{-1} and a weaker band related to ν_s(COO$^-$) was observed near 1403 cm^{-1}, very near the corresponding bands in SERS spectra of 4-fluorobenzoic acid (see Figure 2D). Bands assigned to ν(9a) and ν(1), which are CH in-plane bending and ring breathing modes, respectively, shifted from near 1161 and 838 cm^{-1} in normal Raman spectra of poly(*p*-fluorostyrene) to near 1148 and 863 cm^{-1} in SERS spectra, which are virtually identical with their positions in SERS spectra of 4-fluorobenzoic acid. Similarly, ν(13) shifted from near 1230 cm^{-1} to near 1248 cm^{-1},

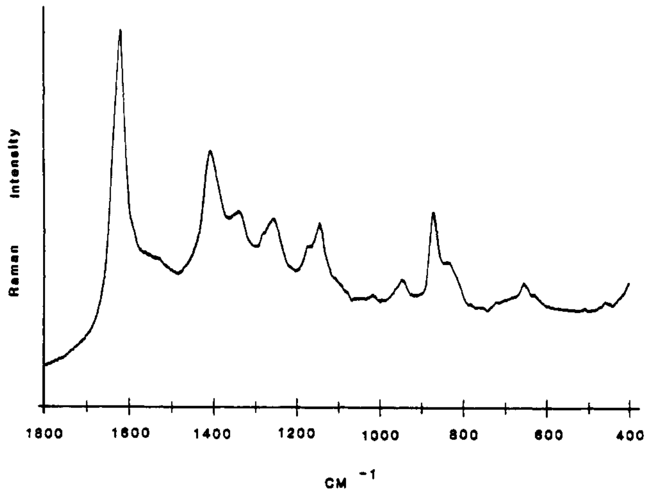
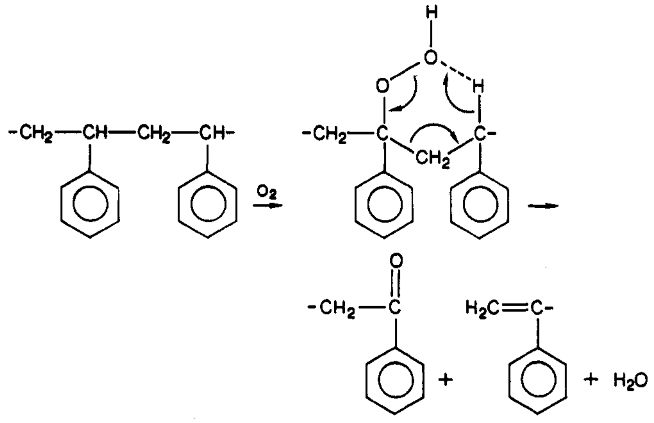


Figure 6. Surface-enhanced Raman scattering from poly(*p*-fluorostyrene) spin-coated onto a silver island film from a 0.1% solution in toluene. The laser power was 100 mW.

Scheme I
Primary Oxidative Degradation of Polystyrene (Norrish Type II Reaction)



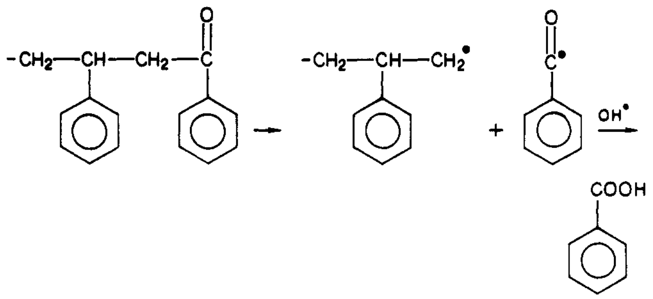
very close to its position in SERS spectra of 4-fluorobenzoic acid.

It is clear that the degradation of polystyrene to form graphitelike species at the silver surface is related to thermally induced oxidation of the polymers. Remarkably, the effect of electron-attracting substituents such as NO_2 and SO_3H is to increase the rate of graphitization. Electron-donating substituents such as F, Cl, Br, and CH_3 are able to stop the formation of graphitelike products and to induce a selective oxidation of the polymer backbone to yield 4-substituted benzoic acids.

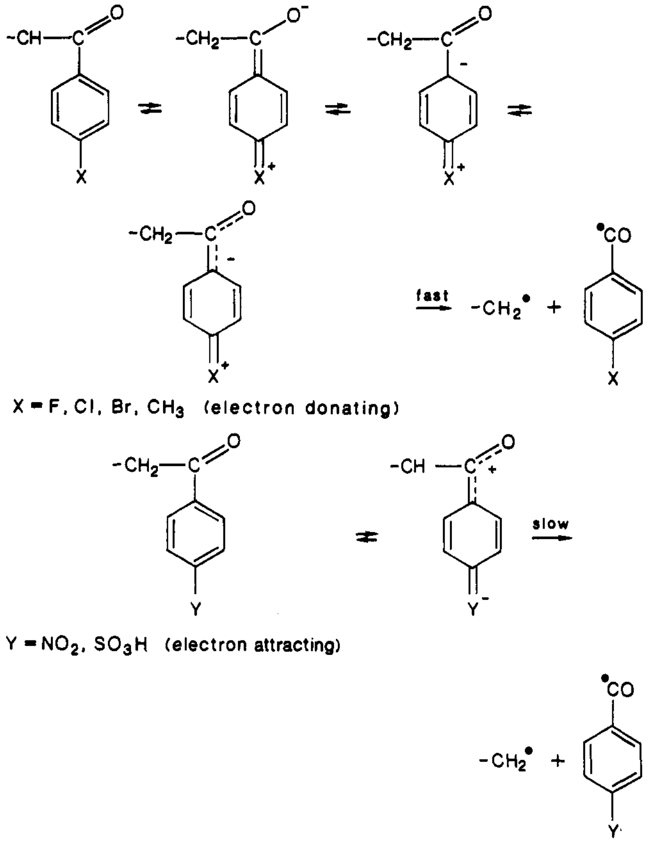
The interpretation of the above results proves to be quite challenging since it stimulates the extension of current theories on the thermal and photooxidative processes occurring in polystyrene[18-23] to include the occurrence of substituent effects as factors controlling the kinetics of the various oxidation reactions involved in the process. In the following section, a discussion of possible reaction mechanisms is reported in an attempt to explain the observed facts and to provide a detailed framework for the polystyrene oxidation theory.

The important role of hydroperoxides in the photooxidation of polystyrene is generally agreed,[18-21] and Grassie and Weir[19] have proposed that the decomposition of the hydroperoxide occurs by a Norrish type II reaction (Scheme I) with formation of olefin and aryl ketone end groups. The subsequent oxidation steps have been proposed to occur by the intermediacy of singlet oxygen[22,23] since the triplet states of vinyl ketones are known to be quenched by oxygen, resulting in the formation of singlet oxygen molecules, and the olefin produced in Scheme I would be quite reactive toward singlet oxygen attack.[24]

Scheme II
Selective Oxidation (Norrish Type I Reaction)



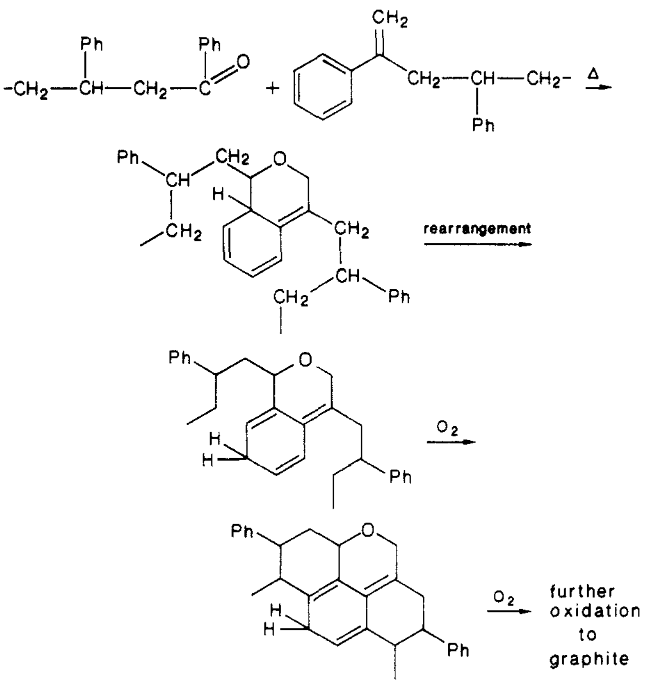
Scheme III
Effect of Para Substitution on Oxidation Products (Norrish Type I Reaction)



This mechanism would remain a valid possibility if it were able to explain also the ability of para substituents to orient the oxidation of polystyrene toward the production of graphitelike species or of benzoic acids, respectively.

The latter evidence appears to imply the existence of at least two competitive processes susceptible to substituent effects. In our view, the selective oxidation of para-substituted polystyrenes to benzoic acid derivatives may occur by a Norrish type I reaction as shown in Scheme II. This process is likely to be very much influenced by substituents. Electron-donating groups are expected to enhance the rate of formation of benzoic acids while electron-attracting groups are expected to lower it (Scheme III). In fact, the rate-determining reaction in benzoic acid production is believed to be the homolytic cleavage of the CH_2–CO bond, which is resonance stabilized or destabilized according to the nature of the substituent (Scheme III).

Scheme IV
Graphitization Process (Diels–Alder Addition)



As far as the graphitization process is concerned, all the mechanisms involving cross-linking of the polymer backbone through olefin reactions appear suitable, in principle. Among them it is worth mentioning the possibility that the olefin and ketone end groups react immediately after being formed by a Diels–Alder addition process, favored by a "cage effect" due to the small diffusion rates of the end groups in the polymer matrix (Scheme IV).

A Diels–Alder dimerization of styrene is believed to be responsible for the initiation of the thermal polymerization of styrene in the bulk,[25-27] similar to the initial process described in Scheme IV, and cage effects have been found to take place in the photooxidation of polystyrene.[28]

What makes the latter attractive is its competitiveness to the reaction leading to the formation of benzoic acids (Schemes II and III). In fact, graphitization would occur only if the homolytic cleavage of the CH_2–CO bond is slow enough to allow the Diels–Alder reaction to take place. If the cleavage reaction is fast, the overall products of the process will be benzoic acids. The tentative nature of these propositions should be stressed once more, however.

IV. Conclusions

Selective oxidation of para-substituted polystyrene films on silver substrates has been observed during surface-enhanced Raman scattering (SERS). It is proposed that primary oxidation occurs by a Norrish type II reaction, resulting in chain scission and the formation of aryl ketone and olefin end groups. When the substituent in the para position is electron donating, as in the case of poly(4-fluorostyrene), poly(4-chlorostyrene), poly(4-bromostyrene), and poly(4-methylstyrene), further oxidation occurs rapidly by a Norrish I reaction, resulting in formation of para-substituted benzoic acids. When the substituents are electron withdrawing, as in the case of poly(4-sulfonate styrene) and poly(4-nitrostyrene), the rate of the Norrish I reaction is low. Further oxidation takes place by a Diels–Alder addition process between the aryl ketone and olefin end groups, ultimately leading to the formation of graphitelike species.

As mentioned above, this appears to be the first observation of formation of specific compounds from the substrate-catalyzed oxidation of polymers during SERS experiments. Furthermore, the selective oxidation of para-substituted polystyrenes has not been reported before. The results reported here stress the importance of SERS as a powerful technique to detect oxidative processes which might escape the scrutiny of more conventional methods of surface analysis.

There are frequent references in the literature to significant differences between normal Raman spectra of organic compounds and their SERS spectra. The results of this research, and results reported elsewhere regarding catalytic effects of SERS-active substrates, make it clear that one of the reasons for these differences is that the compounds themselves are modified during SERS experiments by oxidation reactions. Once those reactions are brought under control, SERS should be quite useful as a technique for at least some types of surfaces analysis.

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Registry No. Poly(4-chlorostyrene), 24991-47-7; poly(4-bromostyrene), 24936-50-3; poly(4-methylstyrene), 24936-41-2; poly(4-fluorostyrene), 24936-47-8.

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