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Structural effects of phenols on the photooxidative degradation of polybenzoxazines

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Abstract

The photooxidative behavior of a series of polybenzoxazines based on various phenols, upon exposure to ultraviolet (UV) radiation (>290 nm), is examined. Substituted benzoquinone has been demonstrated in a previous study to be generated in cured 6,6′-bis(2,3-dihydro-3-methyl-4H-1,3-benzoxazinyl)isopropylidene (BA-m) resin when exposed to UV radiation. In the present work, a comparison study is conducted on polybenzoxazines, all of which contained the same amine (methylamine), but with phenolic units that had different substituents on the *para*-positions of the phenyl rings. BA-m is shown to have the highest degree of substituted benzoquinone formation followed by those polymers derived from hydroquinone, 4,4′-(hexafluoroisopropylidene)diphenol, 4,4′-thiodiphenol, 4,4′-dihydroxybenzophenone, *p*-cresol and phenol. The nature of the *para*-position phenolic substituent appears to have an impact on the oxidation process affecting the degrees of substituted benzoquinone formation. Reasons for the differing rates of oxidation are discussed, as well as secondary reactions that occur as a result of photooxidation. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Photooxidation; Polybenzoxazine; Ultraviolet

1. Introduction

When ultraviolet (UV) radiation is absorbed by polymer systems, the results are typically destructive changes, usually centered at the polymer surface [1]. The UV radiation reaching the Earth's surface, which may then react with the polymers [2], is UVA and UVB, which cover a wavelength range of 400–315 and 315–289 nm, respectively. Upon absorption of this radiation, radical species may be produced at various points throughout the polymer matrix [1]. The radicals may then react with oxygen or oxygen-containing radical species resulting in the formation of oxidation products. Direct photolysis may also occur within the polymer leading to various internal structural changes. With continued exposure to UV energy, the radical formation, oxidation reactions, and structural rearrangements may continue with time resulting in polymer fracture, discoloration, or a combination of the two. The polybenzoxazine class of phenolic resin is in need of critical evaluation in order to determine the fundamental properties inherent to this material, one of these properties being the stability to the UV radiation. Benzoquinone structures have been identified previously to form in various polymers upon UV exposure [3–6], and the mechanisms suggested for the formation of these oxidation products were based upon accepted chemical concepts. However, detailed studies as to the effects that different structural compositions can have on the degrees of oxidation, as well as the possible roles these structural units can play in the oxidation mechanisms, are more rare. The unique nature of polybenzoxazine phenolic resin chemistry allows this material to be tailored for specific performances in different applications by substituting key structural elements with new species of slightly differing structures. This being the case, it is possible to gain direct insight as to the influence that specific polybenzoxazine components have on the nature of the oxidation process and may, as a result, give more complete evidence as to what photooxidation mechanisms are actually operating. The purpose of this work is to determine the role *para*-substituted phenolic structures play in the photooxidative degradation of polybenzoxazines as well as to investigate if any other secondary reactions occur as a result of UV absorption. In the process of trying to eliminate damage due to UV radiation, it is necessary to first understand the complete mechanism at work by identifying which structural makeups are more susceptible to UV exposure and

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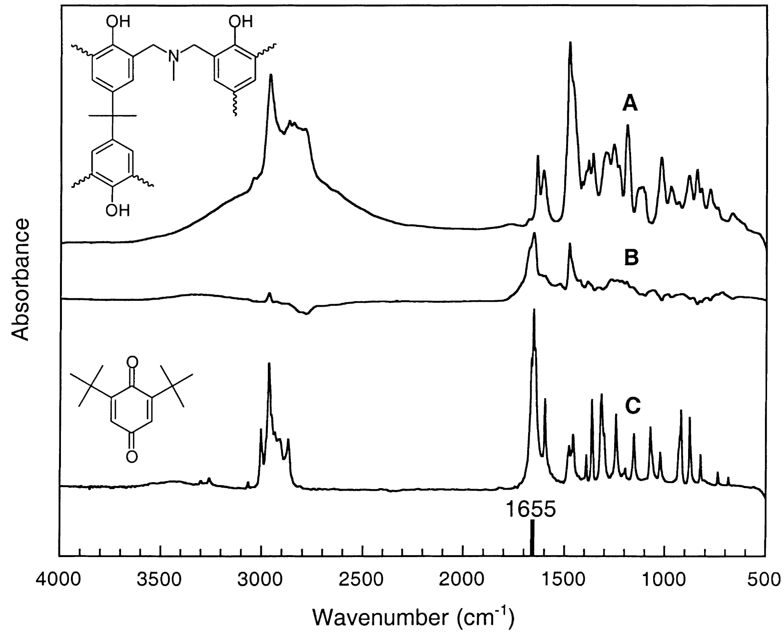


Fig. 1. (A) FTIR spectra and structures: unirradiated BA-m polymer spectrum and structure; (B) difference spectrum of BA-m polymer irradiated for 500 h; and (C) substituted benzoquinone model compound spectrum and structure.

why. As substituted benzoquinone has already been identified as the primary oxidation product in BA-m polybenzoxazine, a study of the formation of this species in other polybenzoxazines of similar structures will be used as a benchmark for radiation damage.

2. Experimental

Chemicals purchased from Aldrich Chemical Company included formaldehyde (37% in water), methylamine (40% in water), 4,4′-(hexafluoroisopropylidene)diphenol (97%), 4,4′-thiodiphenol (99%), 4,4′-dihydroxybenzophenone (99%), hydroquinone (99%), *p*-cresol (99%) and phenol (99%). Polycarbonate grade 4,4′-isopropylidenediphenol (bisphenol-A) was obtained from Shell Chemical Company. All chemicals were used as received. Benzoxazine monomers were synthesized using methylamine and the following phenols: bisphenol-A, 4,4′-(hexafluoroisopropylidene)diphenol, 4,4′-thiodiphenol, 4,4′-dihydroxybenzophenone, hydroquinone, *p*-cresol, and phenol. All monomers were synthesized in dioxane from the particular phenol, formaldehyde, and methylamine in a 1:4:2 mole ratio (1:2:1 for *p*-cresol and phenol) as described in previous studies [7,8]. A medium pressure mercury vapor arc lamp and absorption sleeve were purchased from Ace Glass, Inc. The sleeve of Pyrex glass filtered all wavelengths of radiation shorter than approximately 290 nm. Samples were placed at a specific distance from the source so as to receive 80 W m^{-2} of radiation in the 290–400 nm range. UV exposure was carried out in ambient air at room temperature. The UV lamp was tested periodically throughout the irradiation experiments to ensure that it was functioning properly. All irradiated samples were amorphous so that oxygen could diffuse into and potentially interact with the material. A Bomem Michelson MB110 single beam Fourier Transform Infra Red spectrometer (FTIR) was used to monitor the changes that occurred in irradiated samples during exposure to UV radiation. Spectra were displayed in the absorbance mode and obtained from 100 co-added scans taken at a resolution of 4 cm^{-1} with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector with a specific detectivity, D^*, of 1×10^{10} cm $Hz^{1/2}$ W^{-1}. Prior to each acquisition, the spectrometer was purged with dry nitrogen gas for 20 min. Thin films of cured polybenzoxazines for FTIR analysis were prepared, without initiators or catalysts, on potassium bromide (KBr) plates. A sample-holding KBr plate was placed face down on a glass plate, which had first been treated with a minimum amount of dichlorodimethylsilane. A curing oven was then preheated to 120°C where a monomer sample was allowed to melt between the glass and KBr plate. A weight was then added to the top of the KBr plate in order to ensure that a thin sample cured in the absence of air and moisture, to avoid any unnecessary and premature oxidation reactions, would be obtained. The cured sample on the KBr plate was separated from the glass plate and then permanently affixed in a special FTIR mount that held the cured polymer film–KBr combination in a precise position relative to the FTIR beam path when the entire mounting unit was placed in the FTIR spectrometer. All cured polymer films were clear with a slight yellow color, except for HQ-m, which had a darker yellow color. It was not possible to cure each of the thermosetting polymer films to exactly the same thickness so that the

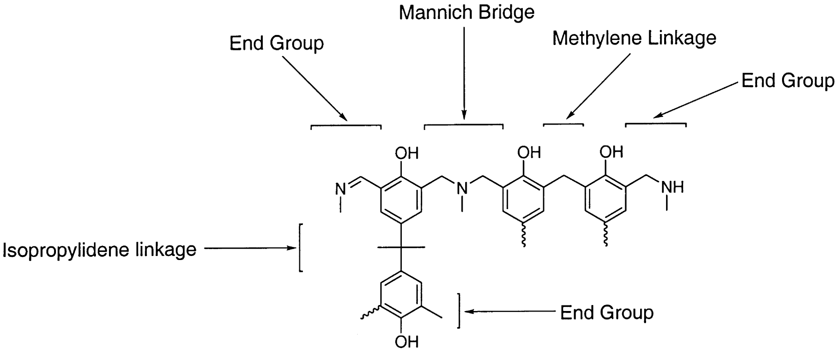


Fig. 2. Representative “molecule” containing all strucures known or highly speculated to exist in cured polybenzoxazines.

absorbed intensities of the same structures within the various samples would be identical. However, all the raw polymer spectral intensities were such that the maximum peak heights fell below a value of 1.00 on the FTIR absorbance scale. And, because the samples were precisely positioned in the FTIR spectrometer, the identical sample locations were examined for each raw spectrum collected, thus allowing difference spectra of each polymer to be obtained that tracked the degradation process over time. The subtle changes that occurred in the raw irradiated polymer spectra were not accurately characterizable without the use of the spectral subtraction technique. Raw absorbance that did not change due to UV irradiation subtracted to the baseline in the difference spectra while absorbance of newly appearing species grew upwards and the absorbance of disappearing species grew downwards. The actual concentrations of the characterized oxidation product that appeared in each polymer are unknown, yet all experiments are measured against the previous arbitrary results obtained for BA-m polymer as a reference.

3. Results and discussion

In a previous study on BA-m polybenzoxazine [9], it was determined that a molecular modification occurs in this polymer, upon exposure to the UV radiation in air at room temperature, as is shown in the irradiation difference spectrum in Fig. 1B. The spectrum of the unirradiated polymer (A) is presented along with the difference spectrum (taken after 500 h of exposure) to indicate which raw absorbance is being effected by UV radiation. As can be seen, a number of different changes apparently occurred in the difference spectrum, so as a result, a second UV exposure study was undertaken on BA-m polymer to determine if any of the observed difference peaks were due to the oxidation reactions. The second irradiation study was carried out in the absence of oxygen and moisture, and the changes that resulted in the molecular structure were tracked by FTIR difference spectra. The results of this experiment indicated that no definitive or characterizable molecular changes occurred in the difference spectrum due to nonoxidative photolysis reactions, thus suggesting that the majority of the changes that occurred in BA-m polymer in air were, therefore, related to the oxidative chemical modification. In addition, this result also suggested that the principal oxidation reaction involved was likely a surface phenomenon. UV radiation reaching the interior of polymer films can be absorbed in nondestructive manners by distribution of the energy to nearby domains, and in this way, nonoxidative chain scission reactions can be reduced. This type of energy distribution reaction may pertain especially to the current polybenzoxazines as these materials are thermosetting polymers, and so any chains cleaved by the UV energy within the film have a very high probability of nondestructively recombining due to cage effects [10] that may thereby account for the observed lack of UV-induced changes in the oxygen-free experiment.

With this determination, the next task was to evaluate where oxidation could be occurring in the polymer structure. A representative “molecule” containing all the structures either known, or highly speculated to exist in cured BA-m polymer resin, is shown in Fig. 2. Each structure in this molecule was systematically studied for both evidence of oxidative and nonoxidative UV-induced molecular modification (even though reactions not related to oxidation are insignificant). The peak occurring at 1655 cm^{-1} in the BA-m polymer difference spectrum (Fig. 1B) was speculated to be the main peak attributed to an oxidation product, as it grew very strongly and fell within the range of a number of strongly absorbing carbonyl-containing species (which are typical products resulting from the UV irradiation of polymers in air) including aldehydes, amides, benzophenones, and quinones. Through model compound analyses and representative UV exposure experiments, end group structures were determined not to oxidize or to otherwise change, resulting in products A and B shown in Fig. 3, as the FTIR frequencies of these species did not match the suspected BA-m FTIR oxidation peak frequency. The same was true for the methylene linkages (Fig. 3C–E) and the Mannich bridge (Fig. 3G and H). Finally, the isopropylidene linkage was investigated, and it was found that a number of possible oxidation products that could form without chain cleavage (Fig. 3I and J) also did not have carbonyl

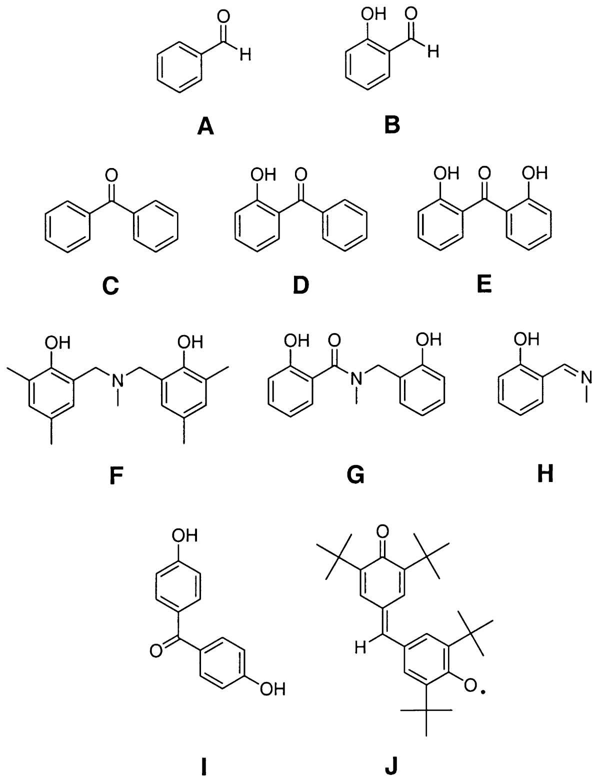
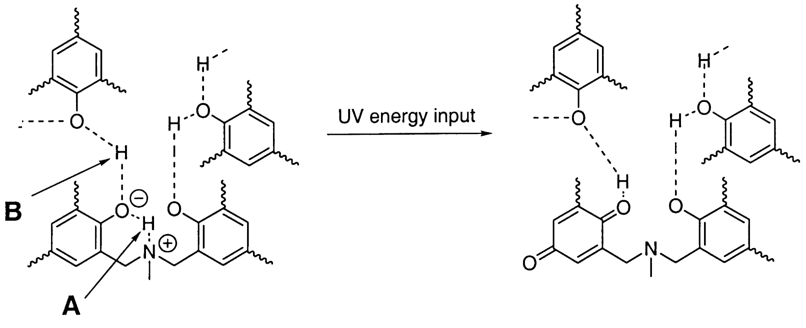


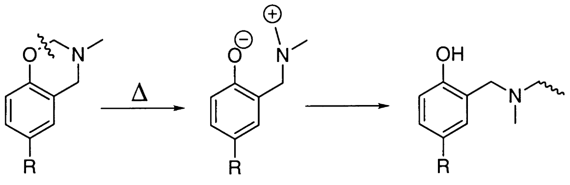
Fig. 3. Various structures evaluated in the study of the effects of UV radiation on polybenzoxazines.

peaks approximately matching the 1655 cm^{-1} peak in BA-m polymer. A final benzoquinone model compound was then considered, which could form if the *para*-substituted isopropylidene linkage cleaved, upon oxidation of that site, to produce substituted benzoquinone (SB). The FTIR spectrum and the structure of the SB model compound are compared with the difference spectrum of BA-m polymer in Fig. 1C, and as can be seen, the carbonyl peak for SB very nearly matched the strongest-forming peak in BA-m polymer at 1655 cm^{-1}. In addition, the general appearance of the SB model compound spectrum matched that of the BA-m polymer difference spectrum (with the carbonyl peak being the most prominent and distinct feature aside from the intense C–H stretching region in the SB model compound from the *t*-butyl groups), thus leading to the conclusion that SB is the primary photooxidation product species formed in polybenzoxazines.

When BA-m polymer was irradiated in air, it was found that there was a resulting interruption in the general hydrogen bonding architecture. The intermolecular hydrogen bonding absorbance in polybenzoxazine FTIR spectra falls at approximately 3390 cm^{-1} and the intramolecular hydrogen bonding absorbance can be found in the range of 3100–2250 cm^{-1} [11]. In the FTIR difference spectrum for BA-m polymer (Fig. 1B), it can be seen that UV irradiation results in a decrease in the intramolecular hydrogen bonding region and an increase in the intermolecular region. It is suspected that SB formation must, therefore, impact the hydrogen bonding architecture in a specific manner. The verified configuration of the pre-UV irradiation hydrogen bonding interactions in the cured resins [12] is represented in Scheme 1 (Loss of intramolecular hydrogen bonding and increase in intermolecular hydrogen bonding in the verified pre-UV-irradiated polymer hydrogen bonding interactions upon formation of the SB oxidation product.). Knowing the pre-irradiation hydrogen bonding scheme in BA-m, along with the fact that SB forms in this polymer following irradiation, it is logical to conclude that the reaction in Scheme 1 is occurring wherein an existing intramolecular hydrogen bond (A) is lost while the intermolecular hydrogen bonding (B) is either left unaffected, or may increase (experimentally observed) if there is a new interaction involving the carbonyl of the newly-formed SB species. As will be seen later, similar changes occur in the hydrogen bonding architectures for all the presently evaluated polymer samples. In addition to the aforementioned growth of the SB oxidation peak and the effects on hydrogen bonding, other significant changes were evident in the BA-m difference spectrum, which were not fully explained in the previous study, including the decrease in the C–H stretching region at 2900 cm^{-1} and the increase in the aromatic C–C stretching absorbance at approximately 1470 cm^{-1}. The primary goal of the previous paper, however, was to determine the nature of the structure leading to the absorbance peak at 1655 cm^{-1}. With more polymer difference spectra to compare and contrast with BA-m in the present work, the molecular changes that cause these other spectral phenomenon will, therefore, be discussed later.

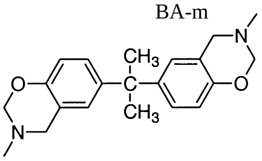
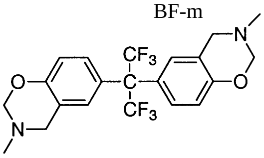
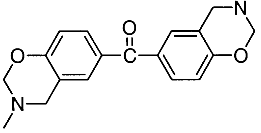
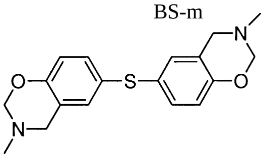
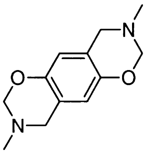
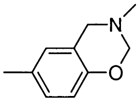
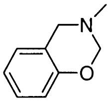


Scheme 1.



Scheme 2.

Table 1
Monomer structures, abbreviations used for the corresponding polymers and the curing conditions employed to create the various polybenzoxazine samples

Monomer	Polymer abbreviation	Curing conditions	
	BA-m	195 2 h	210 2 h
	BF-m	195 2 h	210 2 h
	44O-m	190 2 h	200 2 h
	BS-m	175 2 h	190 2 h
	HQ-m	180 2 h	195 2 h
	PC-m	175 2 h	190 2 h
	P-m	175 2 h	190 2 h

The monomer precursors of polybenzoxazines are synthesized from three reactants: phenols (which can be of differing structures), amines (which can be of differing structures), and formaldehyde. Once produced, monomers are thermally cured in a ring-opening reaction to form polybenzoxazines, as is illustrated in Scheme 2 (General ring-opening curing reaction for polybenzoxazine resin.), resulting in Mannich bridge structures (Fig. 2) linking the phenolic units of the new polymer chains together. As there are an abundance of different amine and phenol combinations, it is possible to synthesize many different polybenzoxazines without altering the basic synthetic chemistry. This advantage, coupled with the fact that polybenzoxazine films are typically clear, allows for the unique FTIR study of the polymer structure–UV stability relationships. Because the *para*-substituted diphenolic isopropylidene linkage of BA-m polymer must be severed in order for SB to form, it was thought that the nature of the oxidation reaction could be further deduced by substituting the linkage for some other substituents at the *para*-positions of the phenyl rings while leaving the rest of the polymer structures unchanged. It is, therefore, the goal of the present work to: (1) determine if these different substituents, in particular, their differing *para*-position bond strengths, could be correlated with the degree to which SB is observed to form in each material; and (2) to investigate the FTIR difference spectra in a detailed manner in an effort to correlate all the observed spectral changes with possible reactions leading to the changes.

The structures of the monomer precursors, the curing conditions employed to form the corresponding polymers, and the abbreviations used for the polymers derived from these monomers, are listed in Table 1. The present polybenzoxazine samples were irradiated in an identical fashion to that of the BA-m polymer sample in the previous study and the photooxidation profiles for SB formation obtained, the results of which are presented in Fig. 4. As can be seen, each material had a unique oxidation profile, so it was initially suspected that the final observed degrees of oxidation in the polymers were indeed dependent upon reaction mechanisms which were effected by the structure of the *para*-position substituents. In Fig. 5, the difference spectra hydrogen bonding regions for all of these polymers are compared to one another. As can be seen, SB formation apparently has the same effect on hydrogen bonding in all these samples, so it is concluded that the general reaction shown in Scheme 1 is correct and applies to all the present materials. Also, the peaks in each of the polymer difference spectra corresponding with the carbonyl stretching of the SB oxidation product do not all appear at the $1655\ \mathrm{cm}^{-1}$ of the SB model compound like BA-m, but absorb at various frequencies well within the typical range of the quinone carbonyl stretching vibration (Fig. 6). As FTIR spectral peaks are due to the vibrational modes of molecular bonds, characteristic peak frequencies can be effected by factors which cause

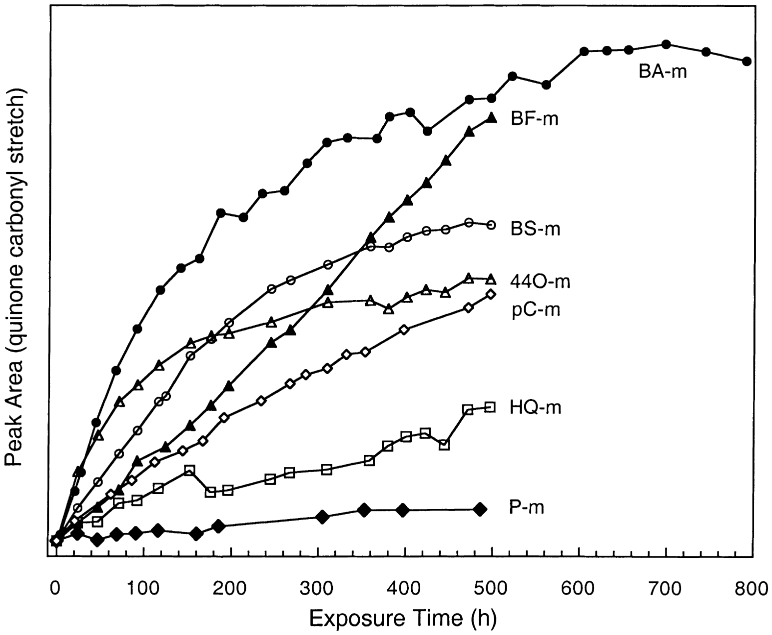


Fig. 4. Oxidation profiles of irradiated polybenzoxazine samples: growth of quinone carbonyl stretching peak.

the molecular bonds to vibrate in different ways. It is well-known that the stretching frequencies of carbonyl functionalities may be effected by a number of factors including the physical state of the system, electronic and mass effects of the neighboring substituents, conjugation, hydrogen bonding (intermolecular and intramolecular) and ring strain [13]. A disruption in the hydrogen bonding architecture was already correlated with SB formation, so the observed carbonyl frequency ranges primarily could be due to the new hydrogen bonding interactions among the samples. As a result, it is unlikely that the vibrational variations are the result of different chemical reactions occurring from polymer to polymer. There was a concern, however, that SB product peak intensity variations, due to peak overlap or other structural effects, could potentially misrepresent the relative degrees to which photooxidation is observed to occur among these polymers. However, the oxidation product absorbance peaks were located in the relatively

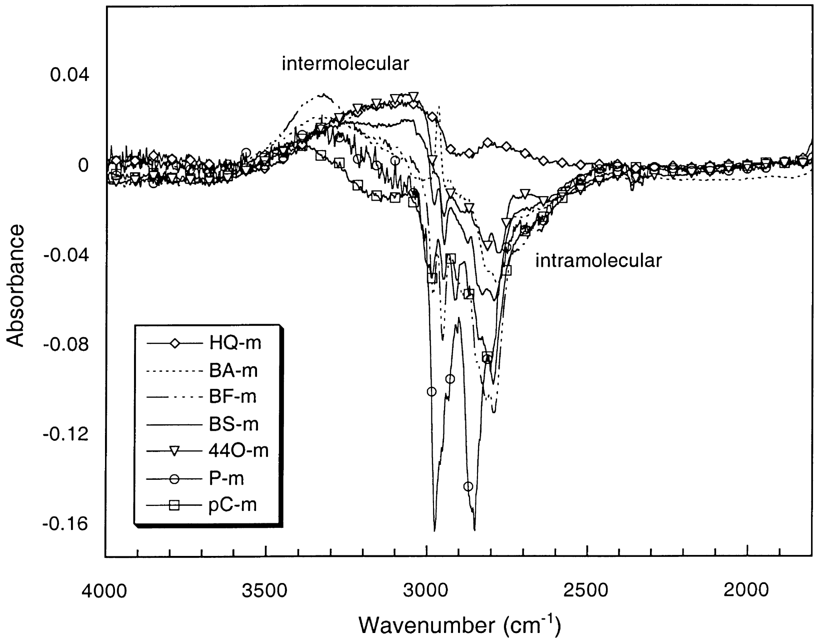


Fig. 5. FTIR difference spectra at 500 h of UV exposure; decrease in intramolecular and increase in intermolecular hydrogen bonding upon UV irradiation among the presently evaluated polymers.

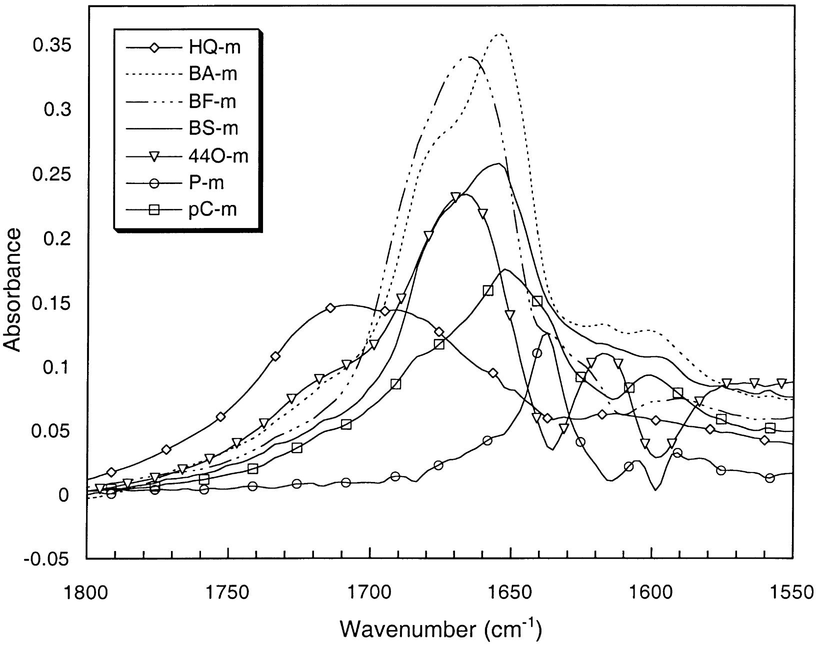


Fig. 6. FTIR difference spectra at 500 h of UV exposure: variability of quinone carbonyl stretching absorbance frequency among the presently evaluated polymers.

isolated areas of the FTIR spectra, which naturally minimized potential problems with peak overlap. In addition, the newly forming carbonyl stretching absorbance characterized in each polymer gave very strong and regularly growing absorbance peaks that, therefore, likely overwhelmed any small intensity fluctuations. Nevertheless, as will be seen later, there does appear to be a pattern to the final observed degrees of carbonyl formation for these polymers, which suggests that the possible presence of random intensity fluctuations do not invalidate the general character of the photooxidation profiles and the information they provide.

In order for SB to form (and as a possible rate-limiting reaction step in the photooxidation process), a particular phenyl ring converting to SB must have the ability to lose whatever substituent is situated at the *para*-position, whether it be a hydrogen (for phenol) or some larger unit. Unless the substituent present at the *para*-position cleaves, there is no chance that a carbonyl will form at the *para*-position. From a chemical point of view, the strength of the bond (bond dissociation energy) between the particular oxidizing phenyl ring and the *para*-position substituent potentially plays a key role in determining the degree to which SB forms in each of the presently evaluated polymer samples. It was thought that the favored SB oxidation product would be formed more rapidly if it were: (1) not necessary to cleave a substituent from the *para*-position of a phenyl ring; and (2) if an oxygen substituent were already present at the *para*-position prior to UV irradiation. As a result, a unique polybenzoxazine, derived from hydroquinone (HQ-m), was first chosen for investigation, the phenolic unit of which consists of one phenyl ring and two hydroxyl groups situated *para*- to one another. The FTIR spectrum of uncured, unirradiated HQ-m monomer, the unirradiated polymer, and the corresponding polymer difference spectrum (taken at 500 h) are shown in Fig. 7. The spectrum of the unirradiated polymer sample (B), appears to include a very large carbonyl stretching absorbance (indicated by an asterisk) apparently corresponding to SB formation that is present prior to UV irradiation. The only polymer with a naturally existing carbonyl absorbance prior to irradiation is 44O-m, which has a carbonyl diphenolic linkage. The spectrum of HQ-m monomer (A) illustrates that there are no oxidized species in this material prior to curing. Upon irradiation of the polymer, however, the suspected SB oxidation product peak continues to grow with exposure in air (C), thus confirming the identity of SB. In order to prevent premature oxidation during curing, all the polymer samples were cured in the absence of atmosphere and moisture. For these samples, including hydroquinone, oxygen was not able to interact with the resin at the curing temperatures and so SB should not have been inadvertently formed. Yet, due to the unique hydroquinone phenolic unit of HQ-m monomer, this material was able to be converted during the curing process to the typical UV-induced SB product, possibly by the mechanism presented in Scheme 3 (Proposed mechanism of SB formation in HQ-m polymer upon cure.). When closed oxazine rings of polybenzoxazine monomers are thermally cleaved and opened in the first step of curing, phenoxy anions are believed to result [14]. In HQ-m monomer, therefore, phenoxy anions may then lead, by electron withdrawal from the oxygen to the phenyl rings, to initial carbonyl formation by means of a cyclohexadienyl-like reaction intermediate as in other similar

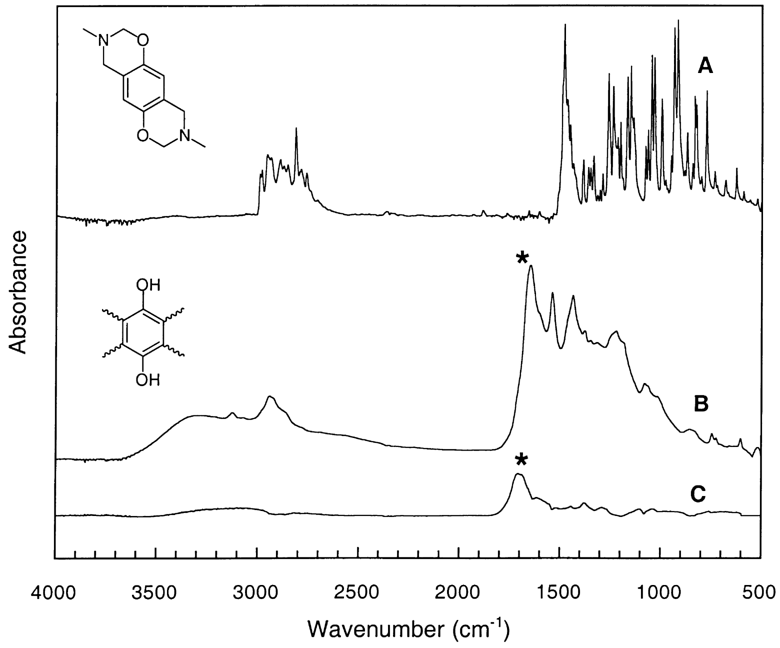
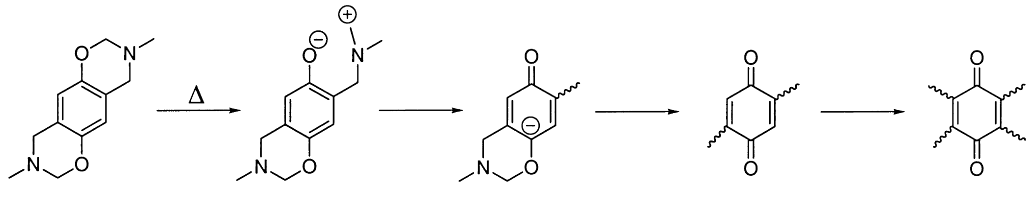


Fig. 7. (A) FTIR spectra and structures: unirradiated HQ-m monomer spectrum and structure; (B) unirradiated HQ-m polymer spectrum and structure; and (C) difference spectrum of HQ-m polymer irradiated for 500 h.

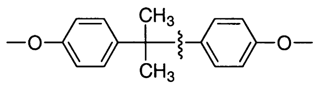
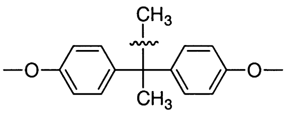
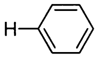
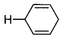
polymer UV irradiation studies [6,15]. In the *para*-position of the ring relative to the new, first-formed carbonyl, there is already oxygen substitution. This second oxygen needs only to further convert to a double bond, by electronic rearrangement, which then results in the typical SB oxidation product. Those HQ-m monomer units which thermally ring open and survive curing to polymerize in the typical manner are apparently then susceptible to UV exposure and oxidation. The formation of SB during curing is not surprising for a phenolic structure initially so similar to the SB photooxidation product, as thermooxidative and photooxidative reaction processes can be very similar in nature, the only significant differences being the rates of reaction and the energy inputs [16]. The presence of di-oxygen substitution on the phenyl ring of hydroquinone prior to irradiation sets the actual reaction occurring in this material upon UV exposure apart from the one occurring in BA-m where a second oxygen must be acquired from an outside source (air), so whether or not an anion or radical mechanism primarily operates upon UV exposure is still yet to be confirmed. Nevertheless, the photooxidation profile data alone as a measure of SB formation in HQ-m is misleading, as it does not take into account the pre-irradiation SB formation.

The bulk of di-hydroxy phenolic polybenzoxazines are synthesized from diphenols that have one hydroxyl group per phenyl ring, unlike the above discussed HQ-m polymer. Therefore, an assortment of typical polybenzoxazines with slightly differing *para*-substituents, either in the form of linkages joining diphenolic units (BA-m, BF-m, BS-m and 44O-m) or as units on monophenols (pC-m and P-m), were examined. A comparison of each of these polymer samples is presented in Table 2 along with the actual *para*-ring bonds under investigation, some representative molecular bonds, the bond dissociation energies of the representative molecular species [17], and the comparative degrees of photooxidation in each polymer in order from the highest (1) to the lowest (6) in keeping with the data shown in Fig. 4. HQ-m is not included in this list as it is not representative of typical polybenzoxazines (having *para*-oxygen substitution), and so is not directly applicable. For the isopropylidene linkage of the previously irradiated BA-m polymer sample, an actual bond dissociation energy reported in the literature [18] is given for the *para*-position bond under investigation. As this material experienced the highest degree of SB formation, it was theorized that the particular bond strength indicated is the weakest of any of the presently evaluated



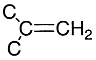
Scheme 3.

Table 2
Comparison of phenyl ring *para*-substituent bond strength to the observed degree of photooxidation among the presently evaluated polymer samples

Polymer	Actual bonds	Representative bonds	Bond dissociation energies (ΔH_{f298} kJ mol^{-1})	Oxidation degrees
A BA-m	$(CH_3)_2C$–phenyl		83	1
B BF-m	$(F_3C)_2$–phenyl	 $H_3C—CH_3$ $H_3C—CF_3$	60	2
		$H_3C–CH_3$	368	
		$H_3C–CF_3$	423	
C BS-m	S–phenyl	$(C_6H_5)S\text{-}CH_3$	285	3
		C–C	607	
		C–S	699	
D 44O-m	CO–phenyl	$C_6H_5CO–COC_6H_5$	277	4
E pC-m	H_3C–phenyl	$C_6H_5–CH_3$	389	5
F P-m	H–phenyl		431	6
			310	

para-position substituent bonds. With this bond dissociation energy as a reference, the representative bonds and the corresponding bond strengths for the other polybenzoxazines should be adjusted in order to estimate the approximate values for the actual bonds in question for comparison to BA-m. For the fluorinated isopropylidene linkage of BF-m, the structural change appears to have an effect on the rate of SB formation, yet the final degree of photooxidation approaches that of BA-m at 500 h of exposure. As can be seen from the representative bond energies for this polymer, fluorination strengthens the C–C bond to the fluorinated species. In BF-m polymer, however, the fluorination is not on the carbon directly bonded to the *para*-position of the phenyl ring, as it is in the representative fluorinated species, but to the quaternary carbon of the isopropylidene linkage. The actual bond energy of the hydrogenated methyl bond to the isopropylidene linkage carbon is given in Ref. [18], and when considering the resulting increase in bond strength upon fluorination, along with the indirect effect the increased bond strength has on the actual carbon–phenyl bond in question; it seems likely that the carbon–phenyl bond strength would be increased slightly over that in BA-m. The photooxidation data appears to confirm this bond strength conclusion as BA-m and BF-m are very similar in their final degrees of photooxidation. For the remaining polybenzoxazines, the oxidation profiles resemble more closely that of BA-m with a gradually slowing rate of SB formation leveling off by the end of the experiment. BS-m, 44O-m, and pC-m polymers each have approximate final degrees of SB formation even though BS-m and 44O-m are diphenolic while pC-m is monophenolic. When considering the representative bond energies of these three materials, it can be seen that: (1) the bond energies of each of these polymers are clearly greater than those of BA-m and BF-m; and (2) that the adjusted bond energies fall within a relatively close range to one another, both in general keeping with the respective photooxidation profiles. For the final monophenolic P-m polymer, the representative bond dissociation energy for this material is the highest of any listed, and the photooxidation data bears out the fact that this material also photooxidized the least. Therefore, it is concluded that there is indeed a relationship between the *para*-substituent–phenyl ring bond strength and the final degree of photooxidation, with the stronger *para*-substituted bonds leading to lower degrees of SB formation and weaker bonds allowing larger amounts of SB to be produced.

Table 3
Frequencies of various products that could result from oxidation and other reactions of severed *para*-substituent intermediate species in the presently evaluated polybenzoxazines

Wavenumber (cm^{-1})	Structure
1065–1030	Aryl Sv O
1400–1300	SO_2
1200–1100	
1230–1120	Hydrated sulfonic acid
1715–1680	Benzoic acid
1280–1120	CF_2
3100–3070	 $(C)(C)C{=}CH_2$

When SB forms in *para*-substituted polybenzoxazines, the *para*-substituents must be cleaved and so reactive intermediates are created. The cleaved substituents may harbor ionic or radical species, yet the actual nature of these reactive intermediates have not been determined and the ultimate fate of these cleaved intermediate species have not been addressed. ESR experiments could help to deduce the exact nature of the reactive intermediates; however, experiments of this kind are beyond the scope of this study. Nevertheless, the high-energy ends will seek to be stabilized in some manner; either by reacting further with other molecules or by simply reacting within themselves. It is entirely possible that these species could oxidize (like the phenyl rings they were formerly bonded to) or change in other ways, resulting in the products shown in Table 3, which have very strong and characteristic absorbance frequencies in the FTIR difference spectra. These species range from benzoic acids to unsaturated double bond-containing materials, yet none of the strong absorbance frequencies associated with these products can be found in the difference spectra of any of the present polymer samples. This analysis is very significant as it suggests that the *para*-ring substituents can remain chemically unchanged after their cleavage from the *para*-positions of the rings upon formation of SB, possibly by re-reacting within the polymer matrix and re-establishing the previous molecular bonding.

If bond reformation reactions occur in the diphenolic polybenzoxazine samples, then it is logical to believe that other existing bonds within these polymers must be severed to make way for the re-established bonds. Since the *para*-substituents are severed initially from the phenyl rings, there is a strong possibility that they reconnect to ring structures, and if true, then ring C–H bonds must be lost in the process. As is shown in Fig. 8, significant and variable decreases do occur consistently in each of the polymer difference spectra in the C–H stretching area of 3000–2800 cm^{-1} (except in HQ-m). In Fig. 9, the C–H stretching regions of the unirradiated polymer spectra are compared to one another. These spectra have been normalized by the use of an internal C–N–C vibrational peak at 855 cm^{-1}, corresponding to the Mannich bridge backbone, which is the same in all the samples (to make general comparisons possible). As can be seen, each sample had a variable degree of absorbance in this region prior to oxidation and as a result contributed to the resulting variabilities in the absorbance decrease after oxidation that, relatively, were not in keeping with the final degrees of SB formation (Fig. 4). The reactions leading to the decrease in the C–H stretching regions of the difference spectra may be understood by first considering the specific cases of mono-phenyl HQ-m and P-m polybenzoxazines. The reactions that must occur in each of these materials in order for SB to form are illustrated in Scheme 4 (Differences

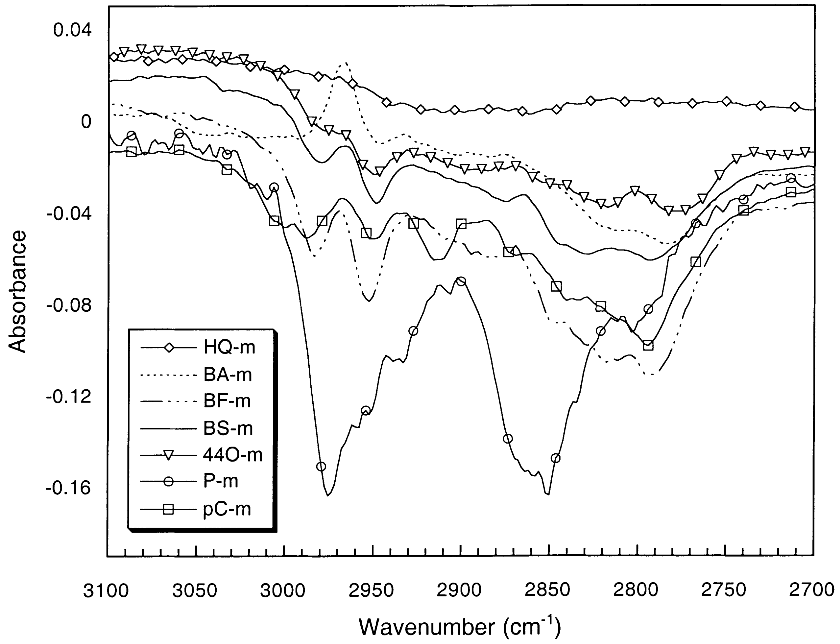


Fig. 8. FTIR difference spectra at 500 h of UV exposure: decrease in C–H stretching region upon UV irradiation among the presently evaluated polymers.

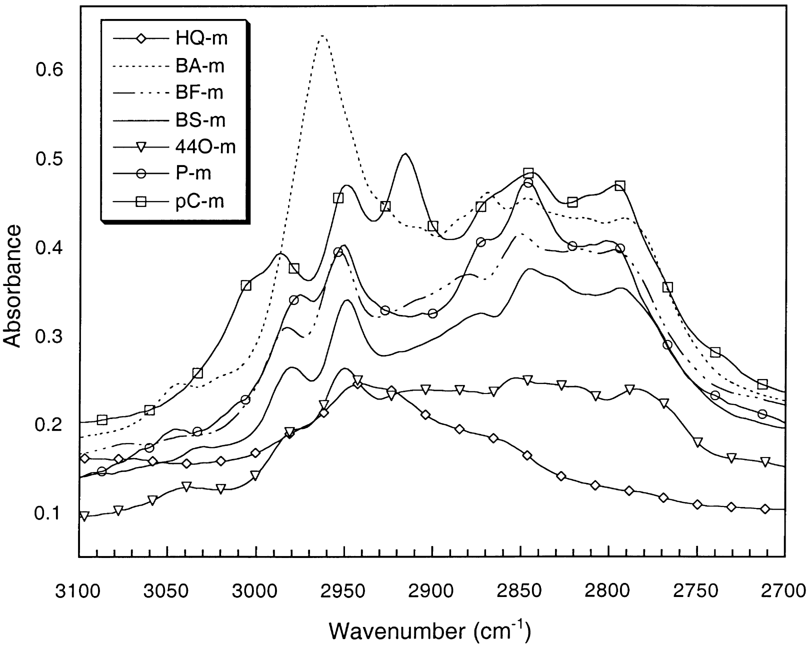
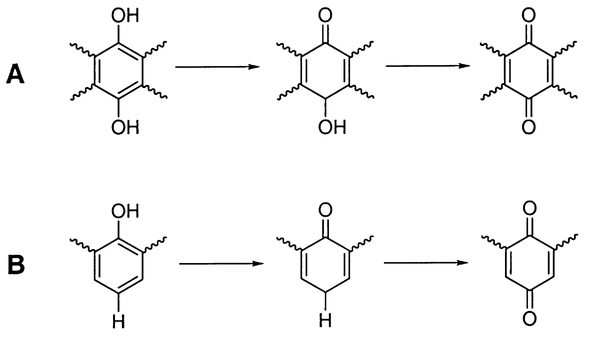


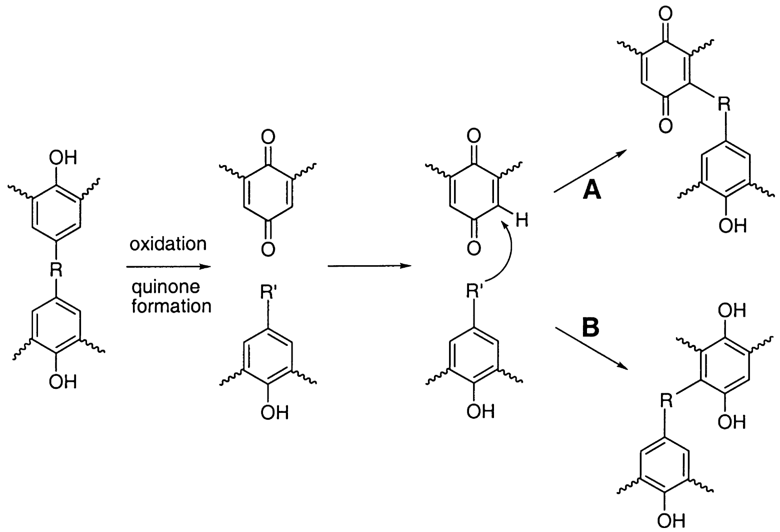
Fig. 9. FTIR spectra: C–H stretching absorbances prior to UV irradiation among the presently evaluated polymers.

in the UV-induced SB formation reaction between HQ-m (A) and P-m (B).). As is shown, SB can appear in HQ-m polymer (A) without the necessity of losing a *para*-C–H bond from a ring. In addition, the unique polymeric structure formed in this material upon curing naturally minimizes the amount of ring C–H bonds, which could be lost in the material overall. Therefore, the initial C–H stretching absorbance for this unirradiated polymer (Fig. 9) is due primarily to the CH_2's of the Mannich bridge structures and the CH_3 of the methylamine substituent. As a result, the C–H stretching region of the FTIR difference spectrum (Fig. 8) for this polymer is almost unchanged when the hydroquinone unit is converted to SB and ring aromaticity is lost. For P-m, however (Scheme 4B), the SB formation sequence is quite different as a *para*-substituted phenolic hydrogen must be cleaved from the ring to make way for oxygen. The difference spectrum for this material in Fig. 8 shows that there is a clear decrease in the C–H stretching region upon SB formation. P-m, like HQ-m, does not have a large *para*-position substituent, which may secondarily react within the polymer and possibly further decrease the intensity of C–H stretching. Therefore, the loss of C–H intensity in P-m is only due to the loss of the C–H bond from the *para*-position of the ring upon SB formation, and not to the loss of C–H from the Mannich bridge methylenes or the methylamine substituent. Also shown in Fig. 8 is monophenolic pC-m and the diphenolic polybenzoxazines that, in addition to P-m, experienced clear decreases in the C–H stretching region upon irradiation. The primary difference between P-m and these other polymers is that there is no *para*-position C–H bond to be lost upon SB formation, as different substituents are *para*-substituted on the phenyl rings of these polymers prior to UV irradiation. Therefore, because the decrease in C–H stretching absorbances in BA-m, BF-m, BS-m, 44O-m, and pC-m are so similar to P-m (which lost one C–H bond from each oxidizing ring), it is concluded that a C–H bond is also lost from rings in these polymers. The loss is not due to SB formation, however, but is proposed to be caused by the severed *para*-position substituents that reconnect, after cleavage from SB formation, to the newly-formed SB rings at the expense of nearby SB ring C–H bonds in accordance with the mechanism proposed in Scheme 5A (Proposed mechanism of severed *para*-substituent re-establishment in *para*-substituted polybenzoxazines: reconnection to the SB oxidation product (A), reconnection to an unoxidized aromatic phenyl ring (B).). Aromatic phenyl rings (B) are, theoretically, susceptible to attack from severed *para*-substituents, but whether or not aromatic rings are involved in the process will be discussed later.



Scheme 4.

As the formation of SB in polybenzoxazines is a reaction that involves the metamorphosis of an aromatic phenol into a nonaromatic SB ring, it was predicted that there would be



Scheme 5.

a variable, yet observable decrease in the aromatic C–C stretching vibration for all these polymer samples. A given decrease in the aromatic C–C stretching region of a polymer, however, was not expected to be equal in intensity to the increase in the SB carbonyl stretching absorbance peaks, as these two different species absorb to different degrees. The specific assignment of the aromatic C–C stretching in polybenzoxazines to the peaks present at approximately 1470 cm^{-1} in the normalized, unirradiated polymer spectra (Fig. 10) was made by the use of the dimer model compound shown in Fig. 3F. This molecule is an ideal model compound for FTIR analysis, yet it was previously determined through FTIR and NMR analysis that amorphous samples of this material did not photooxidize. Neither did this material remain intact when subjected to GCMS analysis. Therefore, this model compound could not be utilized to determine directly the nature of the room temperature photooxidation reactions of the present thermosetting polybenzoxazines, which themselves could not presently be directly evaluated by any other means than FTIR analysis. The aromatic C–C stretching region of the FTIR difference spectra around 1470 cm^{-1} for all the present polymer samples is shown in Fig. 11. As can be seen, the changes that occurred in these absorbances following irradiation did not follow a predictable pattern of decrease, as was expected by the initial raw

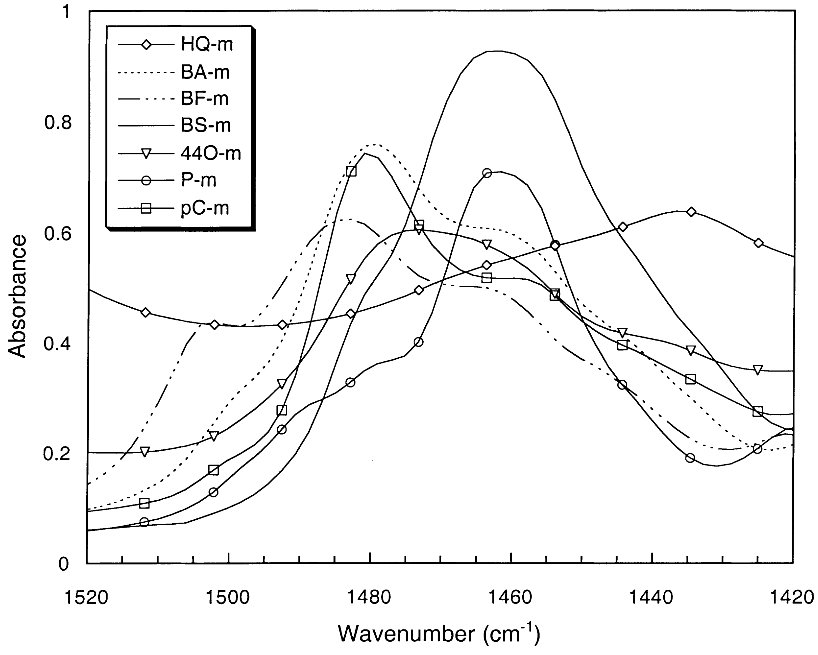


Fig. 10. FTIR spectra: C–C stretching absorbances prior to UV irradiation among the presently evaluated polymers.

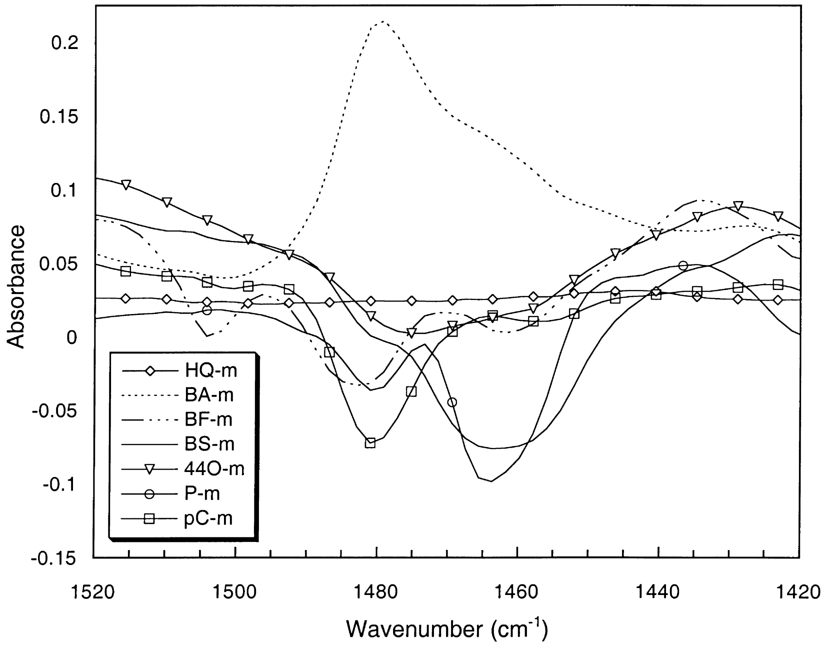


Fig. 11. FTIR difference spectra at 500 h of UV exposure: changes in the C–C stretching region upon UV irradiation among the presently evaluated polymers.

peak variabilities. More importantly, however, the predicted decrease in the peak absorbances were not observed for all the samples. Variable aromatic C–C stretching absorbance decrease did occur in BF-m, BS-m, 44O-m, pC-m, and P-m polymers, yet HQ-m and BA-m polymers had different absorbance behaviors as the peak in HQ-m remained unchanged while increasing in BA-m.

In an effort to explain the overall C–C stretching behavior in all of these polymers, the behavior of the mono-phenyl samples of HQ-m and P-m will, again, be considered first as these polymers do not contain *para*-ring substituents, which could complicate the spectral interpretations. For the atypical phenolic structure of HQ-m, the loss of aromaticity in this polymer upon formation of SB apparently had no effect on the aromatic C–C stretching absorbance. The reason for this behavior may lie with the fact that the hydroquinone unit and the SB product formed are very similar in structure, both having oxygen substituents on the rings *para*- to one another both before and after irradiation (Scheme 4A). Therefore, the simple change from an aromatic to a nonaromatic ring species may not critically affect the C–C stretching absorbance in this material. For the more typical case of P-m, however, it is necessary for this polymer to gain *para*-oxygen substitution on a ring in order for SB to form (Scheme 4B). The significant structural difference that occurs in going from an aromatic structure without *para*-oxygen substitution to nonaromatic SB with *para*-oxygen is appreciable and, therefore, responsible for the observed change in the aromatic C–C absorbance. As a result, P-m polymer, lacking a large *para*-substituent, illustrates that the formation of SB in typical polybenzoxazines will result, at a minimum, in a decrease in the aromatic C–C stretching absorbance.

With the exception of the aromatic C–C stretching peak behavior, all of the diphenolic polymers presently tested, as well as the monophenolic pC-m, had strikingly similar difference spectral characteristics with that of P-m polymer. In the previous discussion of the severed *para*-substituent reconnection reaction, it was concluded that the *para*-substituents re-establish themselves on SB rings at the expense of C–H bonds, but whether or not aromatic rings or newly-formed SB rings lose the C–H bonds in order to receive the new linkage bonds is still unconfirmed. It has presently been shown that the addition of different *para*-substituents on the 1,2,4,6-tetra-substituted phenyl rings of these polybenzoxazines results in intensity fluctuations of the raw aromatic C–C stretching absorbances in the FTIR spectra of the unirradiated materials (Fig. 10). The further addition of a severed *para*-substituent to an aromatic ring in polybenzoxazines would, therefore, be expected to further effect the intensity of the aromatic C–C stretching region in the present difference spectra. In contrast, the same addition reaction to a SB ring would not be expected to result in the same degree of effect on the aromatic C–C stretching absorbance as SB is a nonaromatic species. Only one of the presently evaluated polymers (BA-m) experienced an increase in the aromatic C–C stretching following UV irradiation, while the other polymer samples had clear decreases in this region of the FTIR difference spectrum. It is, therefore, proposed that the severed diphenolic linkage of BA-m reconnects more preferentially to aromatic rings within the polymer matrix causing the atypical aromatic C–C stretching increase. In contrast, the severed linkages of the other diphenolic polymers (and the severed methyl group of pC-m) add more preferentially to the nonaromatic SB species, as the aromatic C–C stretching decrease in these materials is similar to that of P-m polymer, which lacks large *para*-substituents and so, naturally, cannot effect the aromatic stretching behavior of nonoxidized aromatic ring species.

4. Conclusions

It has been demonstrated through FTIR analysis that the degree of SB formation in the polybenzoxazines presently tested, upon irradiation in air at room temperature, is directly related to the structure of the phenolic units employed. The formation of a nonaromatic SB species from an aromatic phenolic unit necessitates the cleavage of the existing *para*-substituted phenolic group (unless the group is oxygen as in the case of HQ-m), and it is apparent that the stronger the *para*-substituent bond to the phenyl ring, the lesser the final degree of photooxidation. Once severed, these substituents are neither observed to oxidize nor convert to unsaturated products, but remain vibrationally unchanged after irradiation and SB formation, indicating that the former bonds are likely re-established within the polymer matrix. Through analysis of the representative polymer samples, the observed loss of intensity in the C–H stretching regions of the FTIR difference spectra for all the non-oxygen *para*-substituted polymers was determined to be primarily due to the loss of C–H bonds from SB ring species; locations where severed *para*-substituents can be re-established. In addition, basic decreases in the aromatic C–C stretching absorbances for all the typical polybenzoxazines occurred from the loss of the phenyl ring aromaticity upon nonaromatic SB formation, except in BA-m, thus suggesting that a unique reaction occurs in BA-m. The re-establishment of severed *para*-substituent groups to nonaromatic SB rings at the expense of C–H bonds does not effect aromatic C–C stretching absorbances. The majority of the *para*-substituted polymers register an overall decrease in the aromatic C–C stretching absorbance from the loss of ring aromaticity, so the severed substituents preferentially connect to SB. For BA-m, however, the C–C stretching absorbance increases after oxidation, which suggests that the severed *para*-substituents can reattach, at the expense of C–H bonds, more readily to nonoxidized aromatic rings within the polymer, unlike the other samples, and re-establish the former molecular linkage.

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