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Structural effects of amines on the photooxidative degradation of polybenzoxazines

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Abstract

The photooxidative behavior of a series of polybenzoxazines based on various amines with the same phenolic unit (bisphenol-A), upon exposure to ultraviolet (UV) radiation ($\lambda > 290$ nm), is examined. BA-m polymer (containing methylamine) is shown to have the highest degree of substituted benzoquinone formation followed by those polymers derived from ethylamine, propylamine, cyclohexylamine, aniline, and *meta*-toluidene, the latter five of which had the same rate and degree of photooxidation. Fourier transform infrared spectroscopy studies suggest that the intramolecular hydrogen bonding interaction between the hydroxyl group of the phenolic unit and the nitrogen of the amine can play a key role in ionizing the oxygen of the phenolic hydroxyl group when conditions are advantageous, thus leading to high relative degrees of photooxidative degradation. In addition, model compound studies demonstrate that various degrees of non-intramolecularly bound hydrogen density around the phenolic hydroxyl group may impact upon the efficiency of the intramolecular interactions. Other model compound studies suggest that the size of the amine functionality is another critical factor influencing the degrees of photooxidation. A mechanism of UV-induced molecular modification involving contributions from the amine functionality is proposed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Amine; Hydrogen bonding; Ionization

1. Introduction

The interaction of ultraviolet (UV) radiation with polymeric materials has long been known to result in destructive changes within polymer matrices. The UV radiation which causes the most destructive changes in polymers is that which falls within the 295–400 nm frequency range of the electromagnetic spectrum. Sunlight is made up of many different, high-energy wavelengths of UV radiation, but the longer wavelength UV energy is what is able to interact with polymers on the surface of the Earth [1].

In a previous Fourier transform infrared (FTIR) spectroscopy study of the effects of UV radiation on a particular polybenzoxazine (BA-m), it was determined that the peak appearing in the FTIR difference spectrum at approximately 1655 cm^{-1} was due to the carbonyl stretching absorbance of substituted benzoquinone (SB) [2]. The raw spectrum of unirradiated BA-m polymer, the difference spectrum of the irradiated polymer (obtained after 500 h of UV exposure), and the raw spectrum of an SB model compound, are compared to one another in Fig. 1. As can be seen, the carbonyl stretching peak of the SB model compound and the 1655 cm^{-1} peak in the BA-m polymer difference spectrum are nearly identical in frequency. This type of quinone structure has been demonstrated to be produced in other various phenolic materials, due to oxidative degradation upon exposure to UV radiation [3–6]. But despite this initial confirmation of a possible oxidation product, a second BA-m polymer UV exposure experiment was then conducted in the absence of oxygen and moisture to determine if the 1655 cm^{-1} peak was due to non-oxidative and/or direct photolysis reactions. The result of this experiment was that no detectable oxidative or other molecular changes occurred in the polymer matrix in the absence of oxygen and moisture, so the 1655 cm^{-1} peak was indeed due to oxidation. In an effort to confirm that SB was the primary oxidation product, many other model compounds were irradiated and investigated for carbonyl-containing aldehyde, amide, benzophenone, and quinone products (Fig. 2). Fig. 3 shows various structures either known or highly speculated to exist in BA-m polymer. However, the carbonyl peak frequencies of these products were not similar to the 1655 cm^{-1} peak appearing in the BA-m difference spectrum. The peak was,

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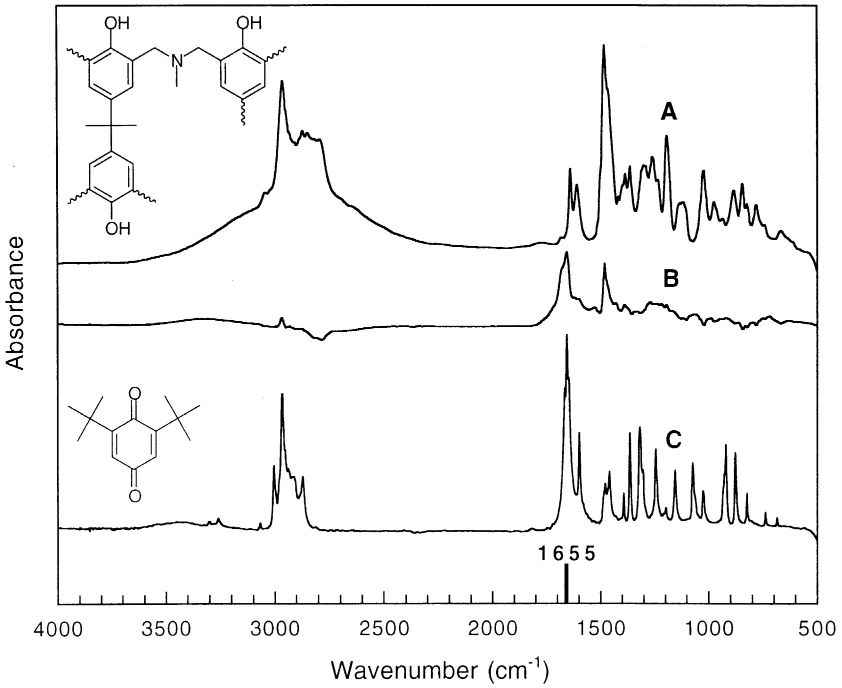


Fig. 1. FTIR spectra and structures: unirradiated BA-m polymer spectrum (A) and structure, difference spectrum of BA-m polymer irradiated for 500 h (B), substituted benzoquinone model compound spectrum (C) and structure.

therefore, due only to the carbonyl stretching absorbance of the non-aromatic SB oxidation product formed from the phenols of the polymer.

Polybenzoxazines are synthesized from three components: phenols (which can be of differing structures), amines (which can be of differing structures), and formaldehyde. This being the case, it is possible to make an array of different polymeric materials with a range of different properties (generic mechanistic schemes denote phenols as (X) and amines as (Y)). This advantage, coupled with the fact that polybenzoxazine films are clear, allowed for further systematic FTIR difference spectral studies as to the effects, which these specific interchangeable molecular structures have on the photooxidative behavior of the corresponding polymers. In later UV studies, it was shown that SB forms to varying degrees in different polybenzoxazines depending upon the structures of the phenolic units incorporated therein [7]. It was determined through the comparative evaluation of the difference spectral peak increases and decreases observed in these polymers that the strength of the *para*-position bond (X) in Scheme 1, step 4 generally correlated with the degree of photooxidation with stronger bonds leading to less quinone formation. Following *para*-bond cleavage and oxidation, it was concluded that the severed *para*-substituent (X) bond is reestablished to a new position on the quinone product (Scheme 1, steps 5,6). It was apparent that the same general reaction sequences occurred in each polymer and so the SB product formation profiles of each sample could be directly compared with one another. The changes, which occurred

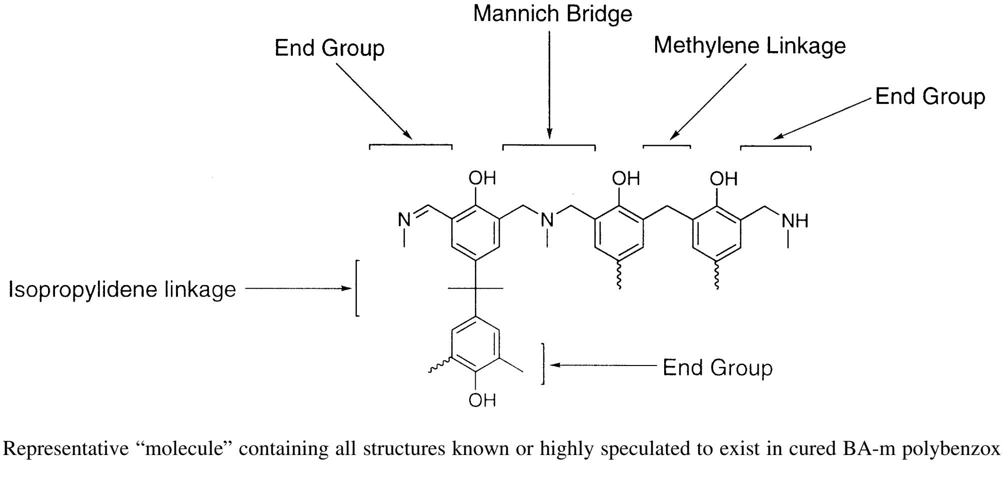


Fig. 2. Representative "molecule" containing all structures known or highly speculated to exist in cured BA-m polybenzoxazine.

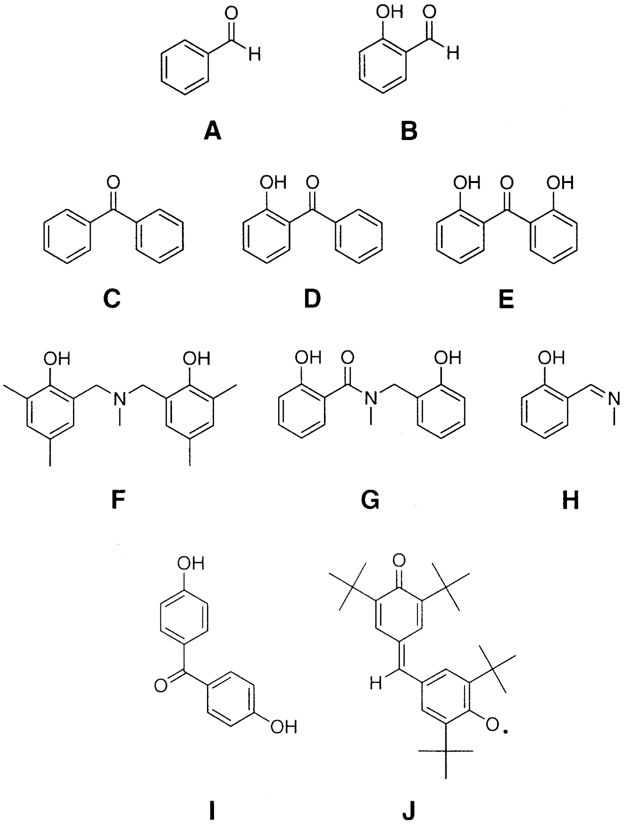


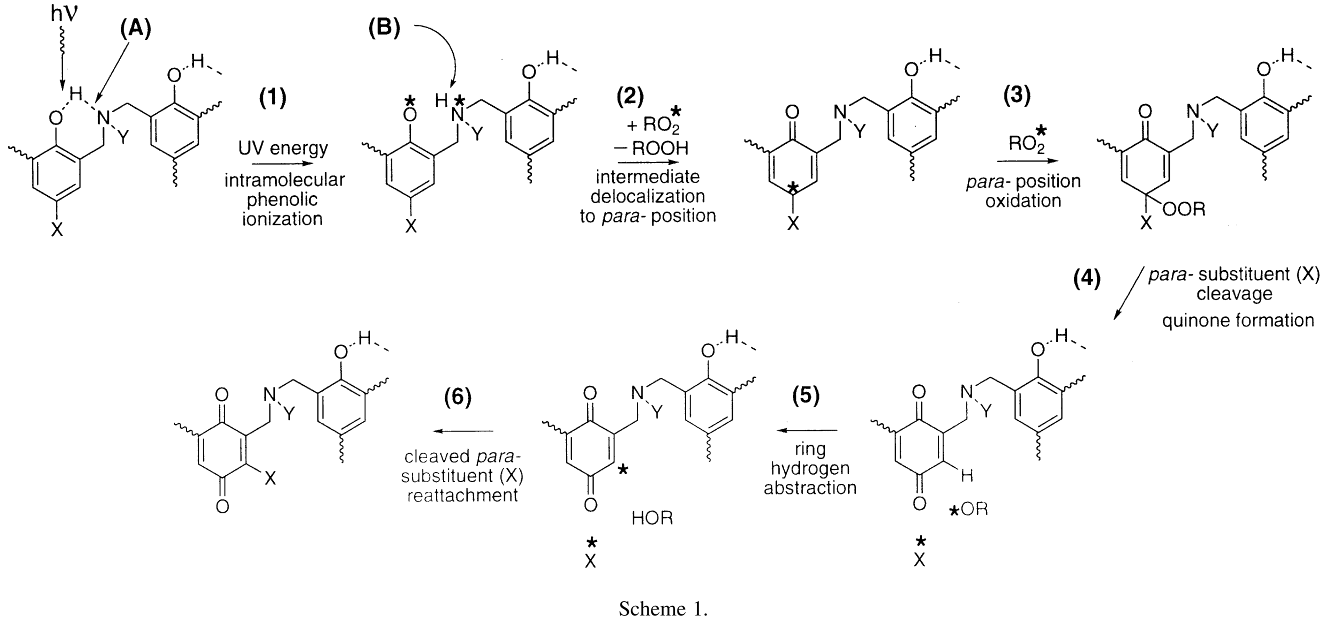
Fig. 3. Various structures evaluated in the study of the effects of UV radiation on BA-m polybenzoxazine.

in the difference spectra of the present samples were also similar to the previous samples, so these polymers could, likewise, be directly compared with one another. As a result, the formation of the SB carbonyl peaks in each sample was used as benchmarks for measuring the comparative extents of photooxidation.

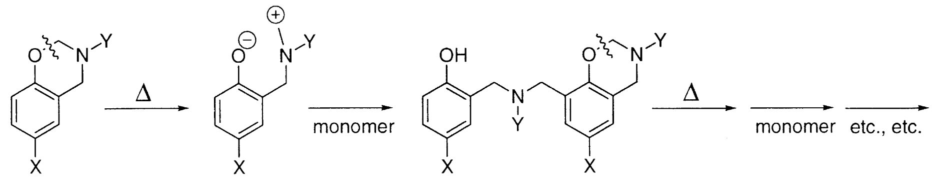
Therefore, in an effort to complement the study on the effect of phenols on the polybenzoxazine photooxidation process, the present study was undertaken to assess the degree to which the amine functionality in polybenzoxazines affects the photooxidation mechanism. Each component incorporated into a polybenzoxazine may have an effect on the photooxidation mechanism, either individually or in conjunction with other functionalities in the polymer system. As a result, the present work compares the responses of a number of polybenzoxazines to UV radiation, each of which contained different amines with the same phenolic unit (bisphenol-A). The prior UV exposure studies determined that polybenzoxazines based upon bisphenol-A have the least tolerance to UV radiation with the greatest degree of SB formation. As a result, bisphenol-A was again chosen as the phenolic component in order to make the characterization of the changes due to UV-induced molecular modification more profound, and thus, easier to characterize.

2. Experimental

Chemicals purchased from Aldrich Chemical Company included formaldehyde (37% in water), methylamine (40% in water), ethylamine (99%), propylamine (99+%), cyclohexylamine (99+%), aniline (99.5+), *meta*-toluidene (99%), and 2,4-dimethylphenol (98%). Polycarbonate grade 4,4′-isopropylidenediphenol (bisphenol-A) was obtained from Shell Chemical Company. Novolac resin was obtained from Advanced Ceramics Corporation. All chemicals were used as received. Benzoxazine monomers were synthesized using bisphenol-A and the following amines: methylamine, ethylamine, propylamine, cyclohexylamine, aniline, and *meta*-toluidene. All benzoxazine monomers were synthesized in dioxane from bisphenol-A, formaldehyde, and the



Scheme 1.



Scheme 2.

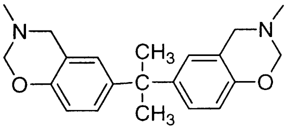
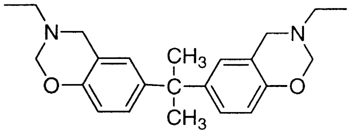
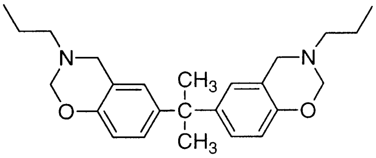
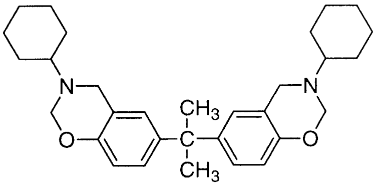
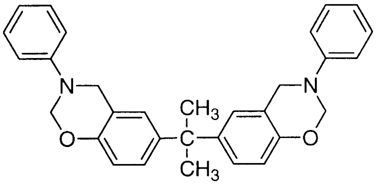
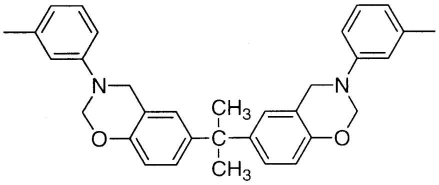
particular amine in a 1:4:2 mole ratio as described in previous studies [8,9]. Model compound dimer molecules were synthesized from 2,4-dimethylphenol, formaldehyde, and methylamine or ethylamine in a 2:2:1 mole ratio as described in a previous study [10]. The asymmetric methyl dimer was synthesized as described in a previous study [11]. Oligomeric polybenzoxazine was also synthesized according to a previous method [2]. 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 infrared (FTIR) spectrometer was used to monitor the changes which 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 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 permanently affixed in a special FTIR mount which 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. It was not possible to cure each of the thermosetting polymer films to exactly the same thicknesses so that the 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 which 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 absorbances which did not change due to UV irradiation subtracted to the baseline in the difference spectra while absorbances of newly appearing species grew upwards and the absorbances of disappearing species grew downwards. The actual concentrations of the characterized oxidation product which 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

The benzoxazine monomer precursors to the presently tested polymer samples were thermally cured to produce thermosetting polymer resins by the ring-opening reaction shown in Scheme 2. The monomeric structures of the polybenzoxazines tested, the abbreviations used for the polymeric samples, and the curing conditions employed, are listed in Table 1. The growth profiles of the SB product carbonyl stretching absorbance at approximately 1655 cm^{-1} in the different polymer samples are shown in Fig. 4. As can be seen, there is a marked difference between BA-m polymer and all the other polybenzoxazines. While BA-m polymer achieved a high relative degree of SB formation, BA-e, BA-p, BA-ch, BA-a, and BA-mt polymers, each reached surprisingly similar degrees of SB formation which were approximately six times lower than that in BA-m by the end of the experiment at 500 h. These results suggested that there is some condition, or combination of conditions, which are unique to BA-m polymer which allowed a substantial degree of photooxidation to occur. In addition, the amine functionality initially appears to have an impact upon the degrees of photooxidation.

Polybenzoxazines have been shown to undergo a high degree of intermolecular and intramolecular hydrogen bonding interactions [10]. Solid state NMR studies of

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	
		Temp (°C), Time (h)	Temp (°C), Time (h)
	BA-m	195, 2	210, 2
	BA-e	195, 2	210, 2
	BA-p	175, 2	210, 2
	BA-ch	175, 2	210, 2
	BA-a	175, 2	190, 2
	BA-mt	175, 2	190, 2

cured polybenzoxazine resins have confirmed that the hydrogen bonding architecture present in a methyl dimer model compound for polybenzoxazines (shown in Fig. 5) is similar to that occurring within the polymer samples [12]. As can be seen, for the two hydroxyl groups on one dimer molecule, one has an intermolecular hydrogen bond to the hydroxyl group of another dimer molecule (A) while the other hydroxyl group shares both an intermolecular bond with an oxygen from another dimer molecule and an intramolecular bond with the Mannich bridge nitrogen functionality in its own molecular backbone (B). Therefore, because the nitrogen is involved in intramolecular bonding interactions in the polymer prior to UV irradiation, it is theorized that the intramolecular hydrogen bonding interaction may contribute to the initiation of the photooxidation process by assisting in permanently removing the hydroxyl proton from the phenolic unit in accordance with Scheme 1, step 1. As can be seen in this step, the hydrogen of the hydroxyl group, which is primed for separation from the phenolic oxygen by the existing intramolecular hydrogen bond (A), is physically dissociated from the oxygen and ends up on the nitrogen (B) upon absorption of UV radiation. This process is similar to that of another intramolecular photochemical reaction in which an *ortho*-quinone methide was demonstrated to form from a 4-phenyl-substituted phenol derivative with an *ortho*-substituted Mannich base (upon exposure to UV radiation $\lambda > 300$ nm), involving an intramolecular hydrogen bond to the Mannich base nitrogen [13]. The reaction was performed in solution and was shown to be highly accelerated in aqueous solvents rather than aprotic solvents. The photochemical reaction, therefore, appeared to proceed via ionic means resulting in the formation of a phenolate

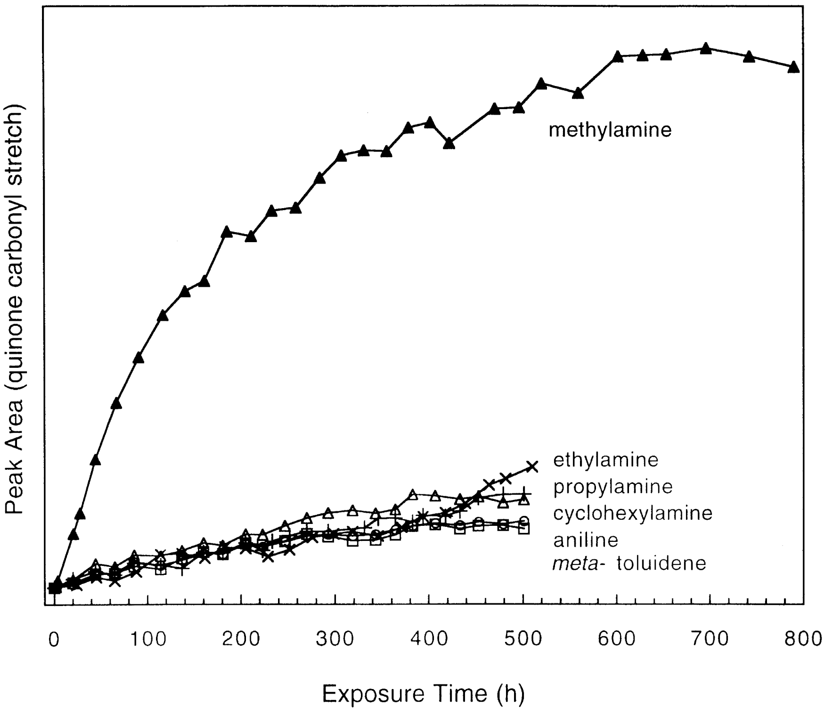


Fig. 4. Photooxidation profiles of irradiated polybenzoxazine samples: growth of substituted benzoquinone carbonyl peak.

anion. In other UV irradiation studies, absorption of UV energy has been shown to produce high concentrations of radical species within the polymers resulting from various high energy cleavage and abstraction reactions [14,15]. Nevertheless, it is suspected that ionic intermediate species are preferentially created in the photooxidation process in polybenzoxazines. However, since the actual nature of the reactive intermediate species leading to the formation of SB in polybenzoxazines are unknown (ESR experiments are beyond the scope of this study), the pre-SB intermediates are designated as anion/radicals and denoted with stars in the reaction schemes. In the case of bisphenol A-based polybenzoxazines, the possibility of ortho-quinone formation is less likely than para-quinone as it requires bond cleavage of the Mannich base.

In an effort to deduce the actual role Mannich base nitrogen plays in the polybenzoxazine photooxidation

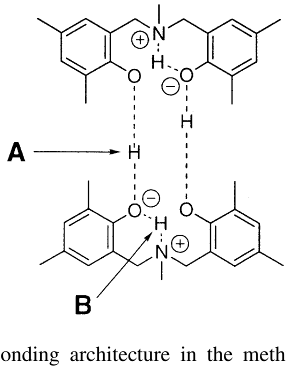


Fig. 5. Hydrogen bonding architecture in the methyl dimer: (A) intermolecular; (B) intramolecular.

process, two dimer model compounds (methyl dimer and asymmetric methyl dimer) were irradiated and their responses to UV radiation compared to that of BA-m polymer. Each of these three amorphous materials are identical with regards to the Mannich base bridging structures, but differ in their relative degrees of hydrogen bonding characteristics. The structures and spectra of the unirradiated materials are compared to one another in Fig. 6, and as can be seen in the spectrum of the methyl dimer (A), there is a large, broad peak centered at 3390 cm^{-1} (indicated by an asterisk) which has been attributed to intermolecular hydrogen bonding [10]. Additionally, there is a smaller, much wider absorbance between 3100 and 2250 cm^{-1} which has been assigned to intramolecular hydrogen bonding. As for the asymmetric methyl dimer (B) and BA-m polymer (C), the same intermolecular hydrogen bonding regions are vastly decreased and the intramolecular hydrogen bonding regions are nearly double in intensity. The difference spectrum of the irradiated asymmetric methyl dimer, obtained after 250 h of UV exposure, is presented along with the difference spectra of the methyl dimer and BA-m polymer, obtained after 527 and 500 h of UV exposure, respectively, in Fig. 7. As can be seen for the methyl dimer (A), there was no apparent degree of SB formation, as the presence of this product would have resulted in a new SB carbonyl stretching peak in the difference spectrum at ~1655 cm^{-1} (indicated by an arrow). As for the asymmetric methyl dimer (B), a new 1655 cm^{-1} peak did appear in the irradiated material which matched the 1655 cm^{-1} peak in BA-m polymer (Fig. 7C). As the only structural difference between the

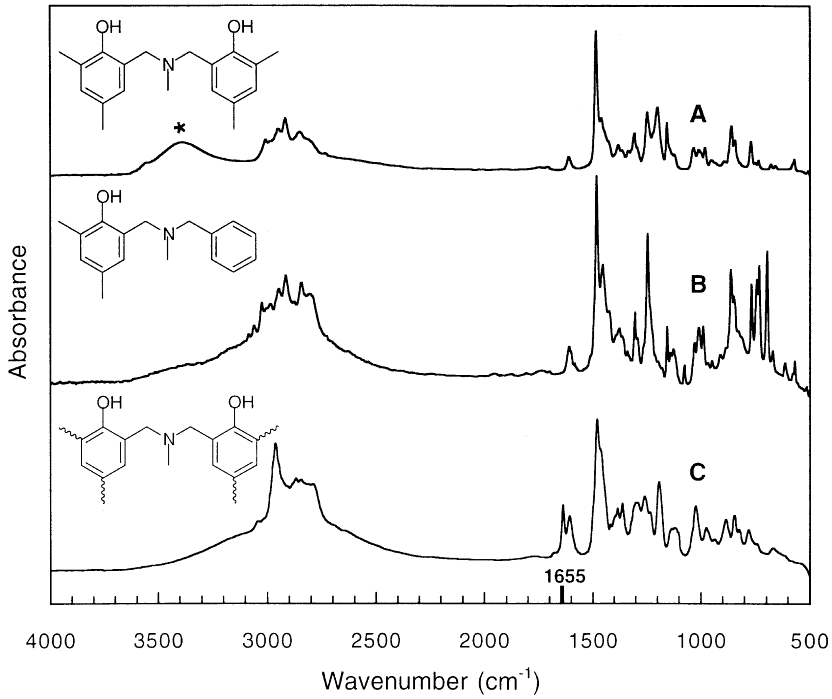


Fig. 6. Structures and FTIR spectra of unirradiated materials: (A) methyl dimer; (B) asymmetric methyl dimer; and (C) BA-m polymer.

unoxidized methyl dimer and the oxidized asymmetric methyl dimer was the hydrogen bonding architecture, the relatively high degree of intermolecular hydrogen bonding in the methyl dimer may have, therefore, been responsible for stabilizing this model compound towards photooxidation.

It was not possible to characterize the photooxidation products resulting from the oxidation of the asymmetric methyl dimer by gas chromatography/mass spectroscopy as the raw material did not remain intact upon analysis, but fragmented into various species. Nevertheless, sufficient

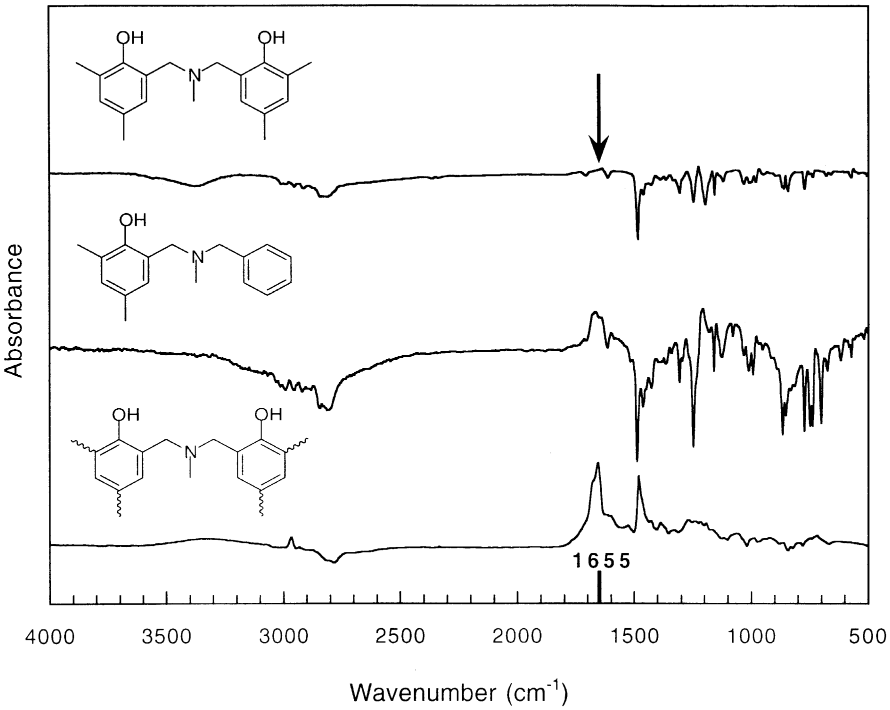


Fig. 7. FTIR spectra and structures: (A) difference spectrum of methyl dimer irradiated for 527 h; (B) difference spectrum of asymmetric methyl dimer irradiated for 250 h; and (C) difference spectrum of BA-m polymer irradiated for 500 h.

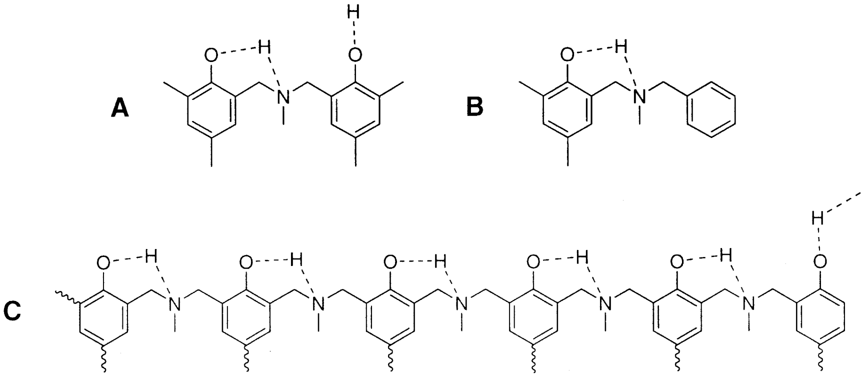
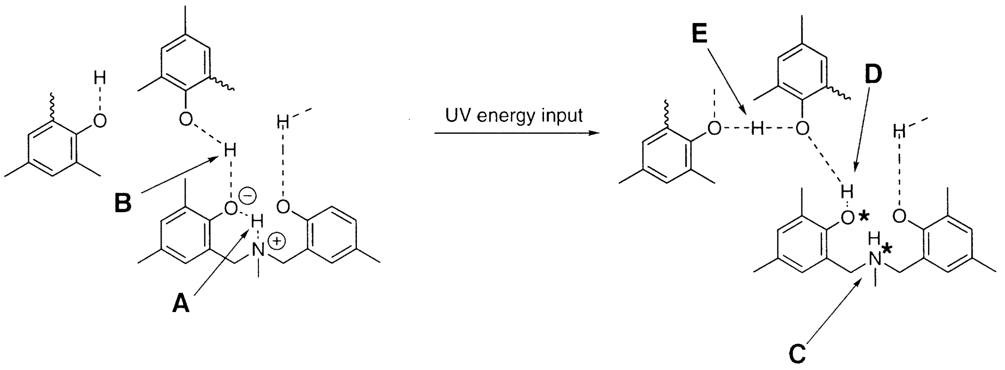


Fig. 8. Hydrogen bonding architecture comparison: (A) methyl dimer; (B) asymmetric methyl dimer; and (C) BA-m polymer.

data obtained from the previous analysis of BA-m polymer demonstrated that the carbonyl stretching absorbance of the SB oxidation product was responsible for the 1655 cm^{-1} peak appearing in the spectrum upon UV exposure in air.

It has been demonstrated that phenolic oligomers, based upon phenol and formaldehyde, undergo strong intramolecular hydrogen bonding interactions between the hydroxyl groups in a highly stable molecular arrangement in which all the hydroxyl groups act as both hydrogen donors and acceptors (isodromic) [16]. In the FTIR spectrum of unirradiated methyl dimer (Fig. 6A), it can be seen that the intermolecular hydrogen bonding interactions at 2290 cm^{-1} (asterisk) is comparitively substantial. Rather than isodromic hydrogen bonding only between oxygens, the Mannich base-containing methyl dimer with two hydroxyl groups per molecule has the ability to form both oxygen/hydrogen intermolecular and nitrogen/hydrogen intramolecular hydrogen bonds as shown in Fig. 8A. In this dimer, only 50% of the hydroxyl groups are able to undergo intramolecular hydrogen bonding to nitrogen, while at least 50% of the hydroxyl oxygens are able to act more as both hydrogen donors and acceptors in intermolecular oxygen/hydrogen interactions. In the asymmetric methyl dimer, however (Fig. 8B), 100% of the hydrogen bonding interactions are intramolecular as the single hydroxyl group per molecule is shared exclusively with the Mannich bridge nitrogen. The absence of intermolecular interactions in the asymmetric dimer (and thus, the absence of hydrogen sharing between oxygens) may allow the single phenolic oxygen to be permanently ionized in a manner similar to Scheme 1, step 1. In the methyl dimer, however, it is possible that the permanent ionization quenching reaction shown in Scheme 3 occurs. As can be seen in this mechanism, the intramolecularly bound phenolic hydrogen (A) moves to the nitrogen upon UV absorption (C). When the phenolic oxygen loses this proton, the existing intermolecularly bound hydrogen which weakly interacts with the ionizable oxygen prior to UV irradiation (B) briefly becomes strongly associated with the oxygen following UV irradiation (D), while hydrogen sharing from the other molecules (E) compensates for the original loss of the hydrogen which is now associated with the Mannich base nitrogen. Therefore, it is concluded that an intramolecular hydrogen bonding-like interaction to a Mannich base nitrogen is responsible for ionizing the phenolic oxygen in the asymmetric methyl dimer, thereby initiating the photooxidation process, but only when intermolecular hydrogen bonding is minimal.

Due to the similarity of the BA-m polymer structure to the non-oxidizing methyl dimer (with hydroxyl units on each phenyl ring), the potential for a 50/50 intermolecular/intramolecular methyl dimer-style hydrogen bonding arrangement exists for the repeating units of the polymer.



Scheme 3.

Table 2
pK_b values of the various amine constituents used in the presently evaluated polybenzoxazines

Amine	pK_b
Methylamine	3.36
Ethylamine	3.25
Propylamine	3.33
t-butylamine	3.55
Cyclohexylamine	3.36
Aniline	9.42
meta-Toluidene	9.29

However, the BA-m polymeric structure is responsible for causing more than 90% of the hydroxyl groups to undergo nitrogen/hydrogen intramolecular bonding as is shown by the FTIR spectrum of the unirradiated polymer in Fig. 6 and illustrated in Fig. 8C. As a result, even though BA-m polymer and the methyl dimer are structurally more similar to one another, the photooxidative behavior of BA-m is more like that of the photooxidizable asymmetric methyl dimer having ~100% intramolecular hydrogen bonding. The same intramolecular ionization reaction occurring in the asymmetric methyl dimer is, therefore, concluded to occur in BA-m polybenzoxazine. Consequently, it may be possible that an increase in intermolecular hydrogen bonding in the polymer could hinder the photooxidation process, as was seen for the methyl dimer.

It has been demonstrated that a change in the electronic environment at one end of a molecule can have an effect on another part of the molecule through an intramolecular hydrogen bond [17]. With the amine of the Mannich bridge apparently playing such an intimate role in the present photooxidation process, through an intramolecular hydrogen bonding-like interaction, it is logical to theorize that the more basic the amine, the easier and more facile an intramolecular phenolic ionization reaction would be (Scheme 1, step 1), as long as intermolecular hydrogen bonding remains low. The amines used for the polybenzoxazines in the present study were of differing basicities, the pK_b values of which are listed in Table 2 [18,19]. If the above theory holds, and a more basic amine leads to a stronger intramolecular hydrogen bond, and thus a higher degree of SB formation, then those polymers derived from methylamine (BA-m), ethylamine (BA-e), propylamine (BA-p), and cyclohexylamine (BA-ch) should have photooxidized significantly more than those polymers derived from aniline (BA-a) and *meta*-toluidene (BA-mt). However, as Fig. 4 shows, BA-m polymer alone achieved a high degree of oxidation which was approximately six times more severe than that of all the other samples. In addition, the response of the other non-BA-m polymers to UV radiation, some of which were of vastly differing basicities, were strikingly similar. Taking the polymer oxidation profiles and the corresponding amine pK_b values into consideration, it is now apparent that the combination of a highly basic amine and a lack of intermolecular hydrogen bonding will not guarantee the production of a high degree of ionized phenoxy species in polybenzoxazines, even though the strong deprotonating capability of a highly basic amine may significantly assist in the permanent hydrogen removal process. There is another critical factor present which does not allow the other highly basic amine-containing polymers to photooxidize like BA-m.

In a previous study on hydrogen bonding in polybenzoxazines [10], two specific model compounds were analyzed and compared. These compounds were the previously discussed methyl dimer and another dimer molecule, identical in structure, but made with *t*-butylamine (referred to as *t*-butyl dimer). Both methylamine and *t*-butylamine are very basic (Table 2) with similar pK_b values, yet the hydrogen bonding properties of the dimer molecules derived from these compounds are significantly different. By solution FTIR spectroscopy, it was demonstrated that the intramolecular hydrogen bonding interaction in the *t*-butyl dimer was lower than that in the methyl dimer. In order to clarify this disparity between the intramolecular hydrogen bonding behaviors, molecular modeling was conducted in the previous study on these two dimer molecules and the results compared. It was speculated that the bulkiness of the amine functional group could have an influence on the torsional angle in the Mannich bridge backbone, which could thereby compromise the intramolecular hydrogen bonding capability of the molecule [10,20]. The conclusions from the modeling results were that the OH···N intramolecular hydrogen bonding distance in the *t*-butyl dimer was slightly longer than that in the methyl dimer (due to the bulkier amine), which thereby weakened the interaction. In addition, the OH···O intramolecular hydrogen bonding distance was found to be significantly shorter, which thereby caused the sharing of hydrogens between the oxygens of other dimer molecules to be even more extensive in the *t*-butyl dimer compared to the methyl dimer (resulting in the decreased photooxidizability of the methyl dimer as has been shown). Due to this result, it is highly probable that the difference in the sizes of the amines in the present polymer samples is a more important factor in influencing the intramolecular hydrogen interaction capabilities than the differences in the basicities.

In Fig. 4, it can be seen that there was a dramatic drop in the degree of photooxidation in the present polymer samples when the amine functionalities were substituted for substituents larger than methylamine. The smallest structural change between BA-m and any of the other polymer samples is the addition of a CH_2 in the amine functionality (for BA-e polymer). This small structural change is, therefore, the minimum change that is necessary in order to get the significantly different photooxidation behaviors observed for these two samples. Confirmation of the effect, which the slightly larger amine can have on the degree of intramolecular hydrogen bonding (due to changes in interatomic bonding distances) was sought by the use of an ethylamine-based dimer model compound for BA-e polymer

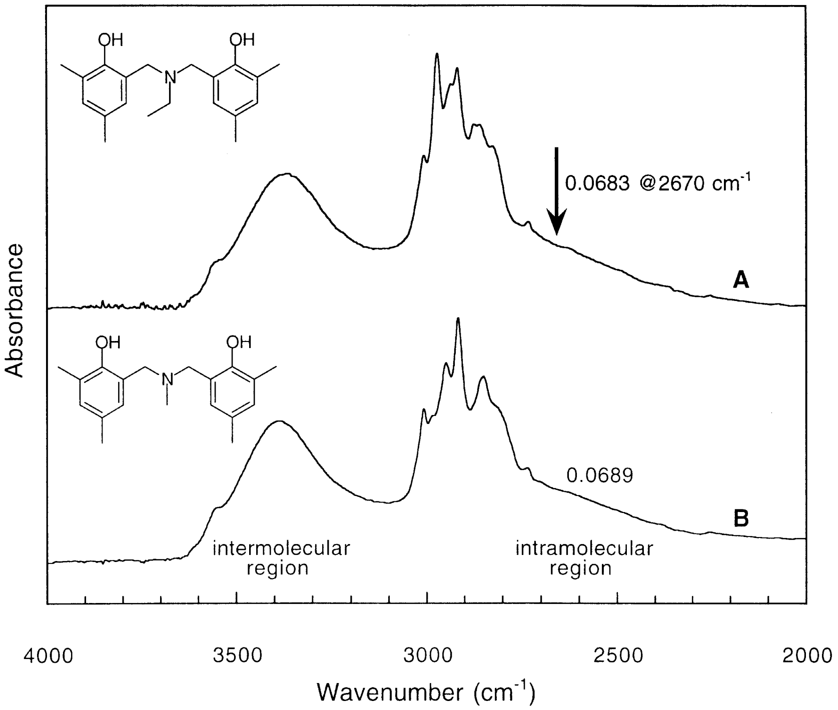


Fig. 9. FTIR spectra and structures: (A) hydrogen bonding regions of unirradiated ethyl dimer and (B) unirradiated methyl dimer, each with curve intensities at 2670 cm^{-1}.

(referred to as ethyl dimer), the FTIR spectrum of which was compared to the methyl dimer model compound for BA-m polymer. The structure and FTIR spectrum of the unirradiated amorphous ethyl dimer are presented with those of the methyl dimer in Fig. 9. The intramolecular hydrogen bonding region between 3100 and 2800 cm^{-1} in the spectrum of the ethyl dimer is, however, almost identical to the same region of the methyl dimer spectrum, as is shown by the representative intensity values for the normalized values for intramolecular hydrogen bonding at 2670 cm^{-1}. These model compounds, therefore, fail to clarify the possible reasons why the polymers corresponding with these dimers photooxidize so differently (the torsional effect of large amines in the dimers is apparently only observable with very large amine-containing dimers). If attention is then turned to the polymers themselves, then a clearer picture begins to form. In the polymers corresponding to these model compounds, as with the polymers containing the larger amine functionalities, there appears to be a trend of decreased intramolecular hydrogen bonding as the amine functionalities are increased in size over methylamine. The FTIR spectra of all of the present unirradiated aliphatic amine-containing polymer samples are compared to BA-m polymer in Fig. 10. It appears that amine functionalities greater than methylamine lead to a degree of intramolecular hydrogen bonding lower than that for methylamine-containing BA-m, as is indicated by the representative normalized values for intramolecular hydrogen bonding at 2670 cm^{-1}. Even though each amine is highly basic and should have a level of intramolecular hydrogen bonding commensurate with that of BA-m polymer, BA-m has the highest amount of intramolecular hydrogen bonding. In keeping with the relationship of backbone tortional angle to amine size which was set forth in the previous evaluation of the *t*-butyl dimer, the small size of the methylamine functionality in BA-m polymer may allow the Mannich bridge backbone linkage to rotate to such an extent as to arrange into a strongest and most stable "ideal" intramolecular hydrogen bonding conformation with the phenolic hydroxyl unit (Scheme 1–, step 1). The resulting conformational arrangement may have been particularly advantageous for the facile UV-induced removal of the phenolic hydrogen from the hydroxyl group. Therefore, it is likely that the backbone tortional angles of the larger aliphatic amine polymer chains are perturbed from the "ideal" BA-m polymer intramolecular hydrogen bonding electronic angle to different conformations by their larger amines. Such an angle adjustment likely leads to increases in the interatomic intramolecular bonding distances and thereby lowers the degree of intramolecular hydrogen bonding interactions, in keeping with the FTIR data. The reduced intramolecular interactions in these larger amine-containing polymers, while not dramatically manifested in the FTIR spectra, nevertheless appear sufficient to dramatically lower the ability for these larger aliphatic amine-containing polybenzoxazines to assist in the formation of ionized oxygen, and as a result, severely inhibit photooxidation.

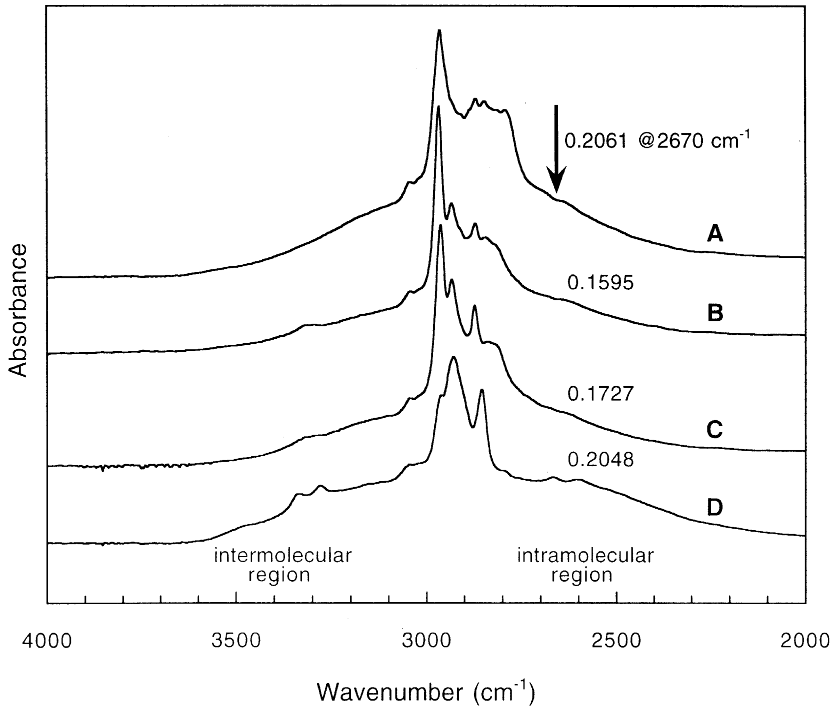


Fig. 10. FTIR spectra of hydrogen bonding regions: (A) unirradiated BA-m polymer; (B) unirradiated BA-e polymer; (C) unirradiated BA-p polymer; and (D) unirradiated BA-ch polymer, each with curve intensities at 2670 cm^{-1}.

The larger aliphatic amine-containing polymers were not the only samples to photooxidize to a lesser degree than BA-m polymer. Those polymers derived from aromatic amines, BA-a (aniline) and BA-mt (*meta*-toluidene), also showed a natural resistance to UV radiation-induced oxidation. The FTIR hydrogen bonding regions of these materials are compared to those of BA-m in Fig. 11. Neither one of these materials had a degree of intramolecular

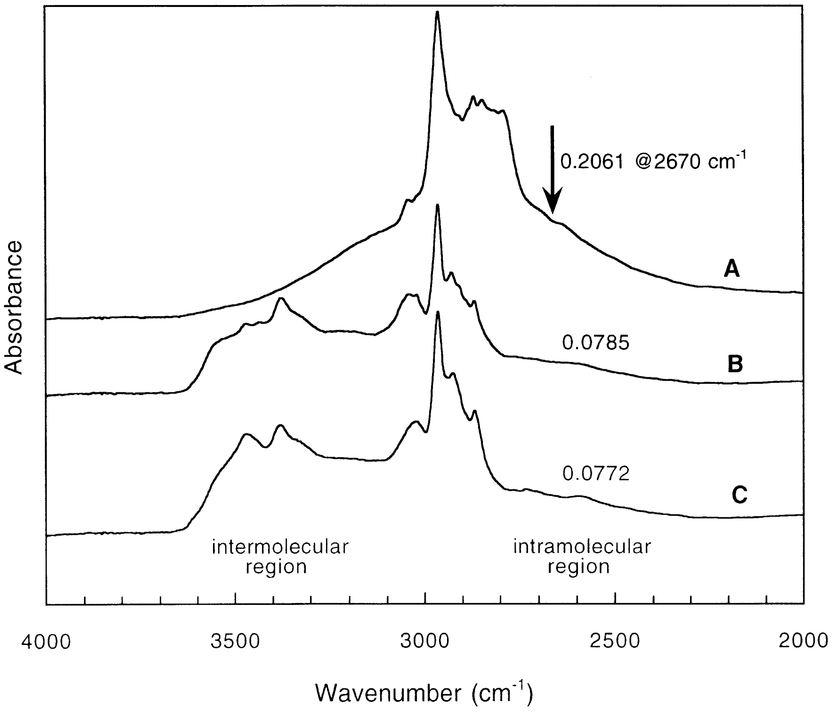


Fig. 11. FTIR spectra of hydrogen bonding regions: (A) unirradiated BA-m polymer; (B) unirradiated BA-a polymer; and (C) unirradiated BA-mt polymer, each with curve intensities at 2670 cm^{-1}.

hydrogen bonding approaching that of BA-m polymer (as indicated by the normalized values for intramolecular hydrogen bonding at 2670 cm^{-1}), nor those of the other larger aliphatic amine-containing polybenzoxazines. These samples did, however, have significantly higher degrees of intermolecular hydrogen bonding with peaks in the region of 3390 cm^{-1}, just as in the non-oxidizing methyl dimer. However, the larger aliphatic amine-containing polymers and the aromatic amine polymer samples photooxidized to the same extent and in the same manner. It is likely that these large aromatic amines have the same perturbation effect on the Mannich bridge backbone torsional angle as the larger aliphatic amine-containing polybenzoxazines. However, if the effects from both the high degrees of intermolecular hydrogen bonding interactions and the sizable amines were additive in BA-a and BA-mt, then these samples would have been expected to oxidize to the absolute lowest degrees of any of the polybenzoxazines tested, yet this was not the case. It is apparent, therefore, that the UV photooxidation stability gained from the larger physical size of all the amines tested (excluding methylamine) outweighs the effects on the intramolecular hydrogen bonding interactions from the varying basicities of the amines. However, if the intermolecular hydrogen bonding interaction could be boosted in BA-m polymer, the degree of photooxidation might be dramatically reduced in a manner similar to that of the methyl dimer. In the end, though, it is apparent that the sizes of the amines, while variable in each of the polybenzoxazines presently tested, are not such as to completely prevent a base minimum degree of oxidation from occurring within each of the non-methylamine-containing samples.

4. Conclusions

It has been shown that the structures of the amines in polybenzoxazines have a significant impact on the photooxidation process. BA-m polybenzoxazine, made with methylamine, had a degree of oxidation approximately six times higher than that of those polymer samples made with the same phenolic unit (bisphenol-A), but with ethylamine, propylamine, cyclohexylamine, aniline, and *meta*-toluidene. From the present work, it is apparent that the ability to permanently remove a critical amount of hydrogen density from the hydroxyl oxygen of the phenolic unit, by a strong intramolecular hydrogen bonding interaction between the phenolic hydroxyl group and the amine functionality (a highly basic amine), is the first factor necessary in order for photooxidation to be extensive. The presently proposed intramolecular initiation reaction is very similar to that proposed in a previous study [13], which indicated that phenolic anions were likely to be responsible for propagating the photochemical reaction. The methyl dimer was unable to efficiently remove hydrogen density permanently from the phenolic component, due to the presence of a large amount of non-intramolecularly bound and shareable hydrogens (involved in intermolecular hydrogen bonding interactions). The asymmetric methyl dimer, with pure intramolecular hydrogen bonding, photooxidized extensively like BA-m polymer (itself having a high degree of intramolecular hydrogen bonding and a much smaller fraction of the intermolecular interactions), leading to the conclusion that the intramolecular hydrogen ionization reaction is initiating the photooxidation process. Those aliphatic amine-containing polymers derived from ethylamine (BA-e), propylamine (BA-p), and cyclohexylamine (BA-ch), the amines of which are similarly basic to methylamine (similar potential for a strong intramolecular hydrogen bond), photooxidized to the same extent as the weakly basic aromatic amine-containing polymers derived from aniline (BA-a) and *meta*-toluidene (BA-mt), each containing high degrees of intermolecular hydrogen bonding. The Mannich bridge backbone torsional angle formed in these larger amine-containing polybenzoxazines may have been perturbed away from an “ideal”, lowest energy configuration present only in BA-m polymer. This angle change may have, therefore, lowered the potential for these samples to form strong intramolecular hydrogen bonding-like interactions upon absorption of UV energy by increasing the interatomic hydrogen bonding distances to values greater than those necessary for such an interaction. There was apparently no addition to the photo-stability of the aromatic amine polymers from the intermolecular hydrogen bonds, as these polymers were not uniquely stable compared to their aliphatic amine polymer counterparts. This result indicated that amine size is more important than the hydrogen bonding characteristics. By considering all of the amine data thus collected, it is apparent that methylamine-containing polymers (specifically BA-m polymer) satisfy all the necessary criteria for a disproportionately high degree of photooxidative damage (small amine, highly basic amine, strong intramolecular hydrogen bonding-like interaction due to close proximity to Mannich nitrogen, absence of high degree of non-intermolecularly bound hydrogens), and therefore appear to be more of an exception to the general behavior of the polybenzoxazine class of phenolic resin upon exposure to UV radiation than the rule. It is also apparent that by not fully satisfying this set of criteria, a minimum level of photooxidation will, nevertheless, occur in other polybenzoxazines.

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