Photooxidative Stability of Substituted Poly(Phenylene Vinylene) (PPV) and Poly(Phenylene Acetylene) (PPA)

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ABSTRACT: The addition of side groups to improve the photooxidative stability of polymers used in polymer-based light-emitting diodes (LEDs) is explored. Infrared spectroscopy and computational chemistry techniques are used to study the effects of chemical substitution of the reactive vinylene moiety in poly(phenylene vinylene) (PPV). The bond order of the vinylene group in small oligomers is calculated using semiempirical techniques to assess the improvement in stability toward oxidants such as singlet oxygen. We find that PPV dimers allow relative comparisons across a range of possible substitutions. Experimental results correlate well with these calculations. The addition of electron-withdrawing substituents, such as nitrile groups, to the vinylene moiety is found to be particularly effective in reducing the reactivity of alkoxy-substituted PPV toward singlet oxygen. The photooxidative stability of a poly(phenylene acetylene) (PPA) derivative is also studied. It appears that this family of polymers is more stable toward photooxidation than are its PPV analogs. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2451–2458, 1998

Key words: poly(phenylene vinylene); poly(phenylene acetylene); photooxidation; singlet oxygen; LED

INTRODUCTION

Two important classes of polymers for light-emitting diode (LED) applications are the derivatives of poly(*p*-phenylene vinylene) (PPV) and polythiophene (PT). PPV itself is an intractable polymer and is typically processed by spin coating a water-soluble precursor polymer salt followed by a thermal treatment, which converts the polymer into its fully conjugated form.[1,2] Side groups are added to both PPV and PT conjugated backbones to increase solubility and thus improve the ability to process the polymers by commercial dip- and spin-coating techniques. The addition of side groups further allows for small tuning of the emission color of the polymer.

Polymeric light-emitting devices are typically constructed in a layered structure with the thin polymer film sandwiched between two electrodes—a low work-function metal such as Ca for electron injection and a transparent, high work-function film such as indium tin oxide (ITO) for hole injection. The interface between the polymer and the low work-function metal electrode has been problematic because highly reactive metals such as Mg or Ca must be used to produce LEDs with high efficiencies. Interfacial interactions apparently lead to the formation of "dark spot" defects, areas of the LED that become nonemissive and increase the overall impedance of the device.[3] Electromigration has recently been addressed as a mechanism by which these dark spot defects form.[4] Researchers have addressed the interface problem by using less reactive metals[5] in con-
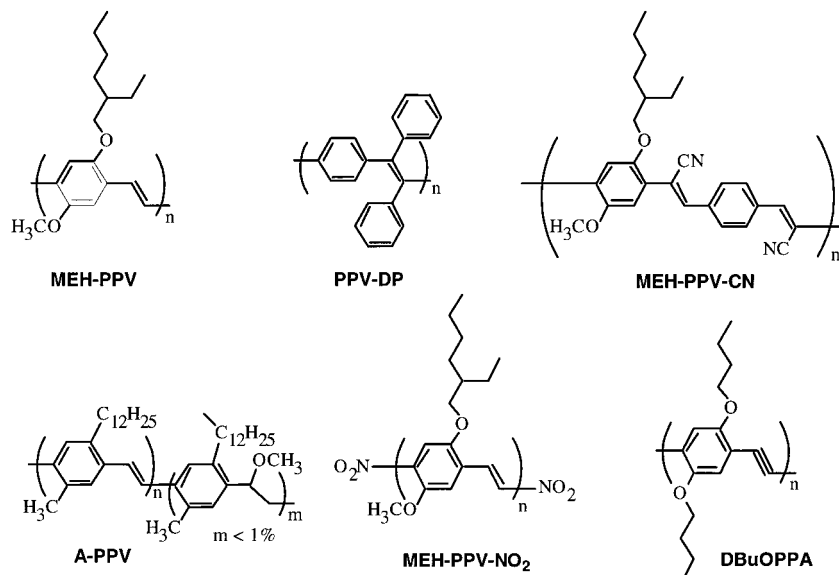
Figure 1   Idealized structures of PPV and PPA derivatives.

junction with charge-transporting layers[6] and through the development of electrochemical cells[7] that operate under lower applied voltages, use less reactive metal electrodes, and do not exhibit dark spot defect formation. Relatively little work has considered the degradation of the active polymer layer itself.[8]

EXPERIMENTAL

Idealized structures of the electroluminescent polymers studied are shown in Figure 1. Poly-(2,5-bis(5,6-cholestanoxy)-1,4-phenylene vinylene) (BCHA-PPV) (not pictured), poly(2-methoxy, 5-(2′-ethyl-hexoxy)-1,4-phenylene vinylene) (MEH-PPV), poly(2-methoxy,5-(2′-ethyl-hexoxy)-1,4-phenylene 7,8′-cyanovinylene) (MEH-PPV-CN), and poly(1,4-phenylene 7,8-diphenylvinylene) (PPV–DP) were supplied by Uniax Corp. (Santa Barbara, CA) and poly(2-methyl,5-dodecyl-1,4-phenylene vinylene) (A-PPV)[9] was supplied by Philips Research Labs, Eindhoven, The Netherlands. Poly(2,5-dibutoxy,1-4-phenylene acetylene) (DBuOPPA) was provided by Z. V. Vardeny of the University of Utah, Salt Lake City. Polymer solutions in tetrahydrofuran (THF) were spin-coated in a nitrogen drybox onto Al (3000-Å-thick) metallized Si wafers. All polymers have a film thickness of 300−400 Å as measured by profilometry.

Infrared reflection absorption spectroscopy (IRRAS) was used to probe both the bulk polymer and the polymer/metal interface. This is a single-reflection technique in which the incident IR beam strikes the sample at a grazing angle of about 10° from the surface. It is important to note that the IRRAS technique is only sensitive to chemical groups with dipoles perpendicular to the surface (parallel to the plane of incidence) due to the selection rule at metal surfaces.[10]

X-ray photoelectron spectroscopy (XPS), which is highly surface sensitive due to the shallow escape depth for electrons, was used *ex situ* to characterize the top 50−100 Å of the polymer film.[11] XPS was performed using monochromatic AlKα (1486.6 eV) radiation. The resolution of the spectrometer was about 0.8 eV, and a spot size of 600 μm was used. The detection angle for the hemispherical analyzer was 35°. XPS spectra were referenced to the aliphatic C1s peak at 285.0 eV and were fitted with 100% Gaussian peaks.

In situ photooxidation studies were performed using IRRAS. Films were UV-irradiated using an unfiltered low-pressure mercury lamp. The 254-nm line was the strongest with an irradiance of approximately 144 μW/cm^2. The irradiance of the second most intense line at 436 nm is about 15 μW/cm^2. Visible irradiation was performed using an Ar$^+$ laser or monochromatized output from a 300-W Xe lamp. During irradiation, samples were contained in a stainless-steel cell under flowing dry air.

The reactivity of PPV derivatives was also studied employing computational chemistry cal-

culations performed at the semiempirical level using MOPAC as supplied by MSI. The Austin Model 1 (AM1) technique, with a restricted Hamiltonian, was employed to minimize the geometry of dimeric segments of the polymers.[12] The use of semiempirical methods has been shown to be successful when calculating electronic properties, such as energy gaps, of conjugated polymers.[13] Mulliken overlap population analysis was used as a measure of electron densities for specific bonds.

RESULTS AND DISCUSSION

Several electroluminescent polymers were characterized in terms of their photooxidative stability in order to develop a degradation mechanism and to investigate the stabilization of these polymers. The idealized structures of the polymers studied are shown in Figure 1. The alkoxy derivatives of PPV (BCHA–PPV and, in particular, MEH–PPV) are the most used conjugated polymers for LED applications. They combine good luminescent properties with excellent solubility in common solvents.

The addition of side groups to the phenylene and/or vinylene segments of the PPV backbone provides both improved solubility and a method to tune the bandgap of the polymer and thus the wavelength of the emitted light. The width of the absorption peaks of these polymers tend to be large due to a distribution of conjugation lengths. A longer conjugation length leads to a lower bandgap, since a more extended electron delocalization leads to greater stabilization of the molecule. Emission from less conjugated segments can be absorbed by more highly conjugated segments within the film, resulting in self-destructive photooxidation.[8,14,15]

Photooxidation of Alkoxy PPV Derivatives

The major IR vibrational bands for MEH–PPV on Al (shown in Fig. 2) are CH_2 and CH_3 stretching (2850–2950 cm^{-1}), phenyl ring modes (1597, 1506, and 1415 cm^{-1}), asymmetric and symmetric CH_2 and CH_3 deformations (1465 and 1380 cm^{-1}), out-of-plane CH wag (860 cm^{-1}), ether C—O—C stretching (1350, 1255, 1208, and 1040 cm^{-1}), and *trans* double-bond CH wagging (969 cm^{-1}). The IR bands for BCHA are essentially the same.

When films of MEH–PPV or BCHA–PPV were exposed to dry air in the absence of light, no change was observed by IRRAS. Also, when films
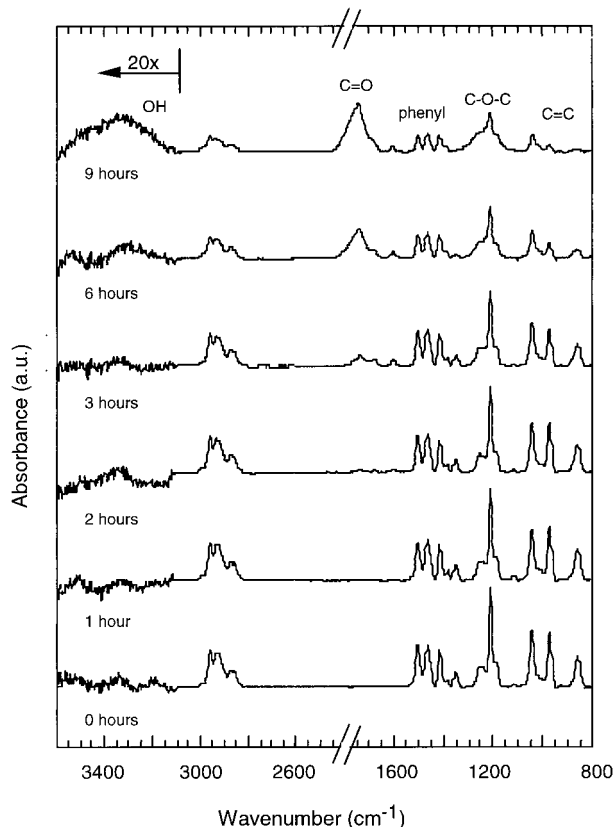
Figure 2 IRRAS spectra for the photooxidation of MEH–PPV on Al using 10-mW/cm^2 514-nm light from an Ar$^+$ laser. Spectra are shown for the as-coated film and after 1, 2, 3, 6, and 9 h of irradiation.

were exposed to 514-nm irradiation in a vacuum of less than 10^{-6} Torr, no change was observed up to 48 h after exposure. However, when films were simultaneously exposed to visible irradiation and dry air, the polymer oxidized. The evolution of the spectrum for a film of MEH–PPV cast onto Al and photooxidized by 514-nm irradiation is shown in Figure 2.

The spectra were taken at various times during the exposure to dry air and UV: as-coated, after 1, 2, 3, 6, and 9 h of exposure. The most obvious change is the growth of a broad carbonyl peak centered around 1740 cm^{-1} with a smaller shoulder at 1682 cm^{-1}. The peak at 1740 cm^{-1} is indicative of an ester, while the peak at 1682 cm^{-1} is indicative of an aromatic aldehyde. This aromatic aldehyde was reported previously for the oxidation of unsubstituted PPV.[16] The peak at 969 cm^{-1} associated with the vinyl double bond in the polymer backbone is attenuated but not fully destroyed during irradiation, indicating that the conjugation length of the polymer is shortened.

Further evidence for chain scission at the vinyl double bond is the growth of the phenyl ring band at 1597 cm^{-1}, which is normally IR inactive in symmetric molecules such as MEH–PPV and BCHA–PPV. There is a weak, broad band centered around 3400 cm^{-1} due to the formation of hydroxyl groups. These appear in very low concentration (the IR intensity in this region of the spectrum of Fig. 2 was multiplied by 20) and may further react to form an aromatic aldehyde; this is consistent with the observation of the shoulder at 1682 cm^{-1}. The results obtained for the photooxidation of BCHA–PPV are identical.

X-ray photoelectron C1s spectra of as-coated MEH–PPV on Al show peaks at 285.0 eV for aliphatic and aromatic carbons and at 286.3 eV for carbon atoms attached to ether oxygens linking the side groups to the conjugated backbone. After photooxidation, XPS results indicate the formation of ester groups. The presence of a strong peak at 289.0 eV for MEH–PPV on Al is clear evidence for a carbon atom bonded to two oxygens, as in an ester group. Again, the same changes are observed when BCHA–PPV is photooxidized.

The PL intensity decreases steadily with increasing concentration of carbonyl groups, which are known quenchers of PL,[17] and loss of conjugation. PL intensity rapidly decreases under visible light irradiation and the spectral position of the luminescence shifts to higher energies. These trends are shown in Figure 3 for the irradiation of MEH–PPV with 20-mW/cm^2 514-nm light. As carbonyl groups are formed, vinyl double bonds are broken, resulting in shortened conjugation lengths along the polymer chain and leading to PL that is blue-shifted relative to the as-coated film.

Based on the observations for both BCHA–PPV and MEH–PPV, a general mechanism was described for the photooxidation of alkoxy-substituted PPV derivatives.[8] In this mechanism, the initial oxidation occurs via a singlet oxygen reaction at the vinyl double bond in the polymer backbone.[8] Photooxidation of the double bond was also observed in poly(phenylene vinylene) (PPV), the backbone segment of BCHA–PPV and MEH–PPV.[14,18]

Other PPV Derivatives

To confirm the role of alkoxy oxygen in the formation of esters, photooxidation experiments were performed using the alkyl-substituted polymer A–PPV (see Fig. 1). The concentration of uncon-
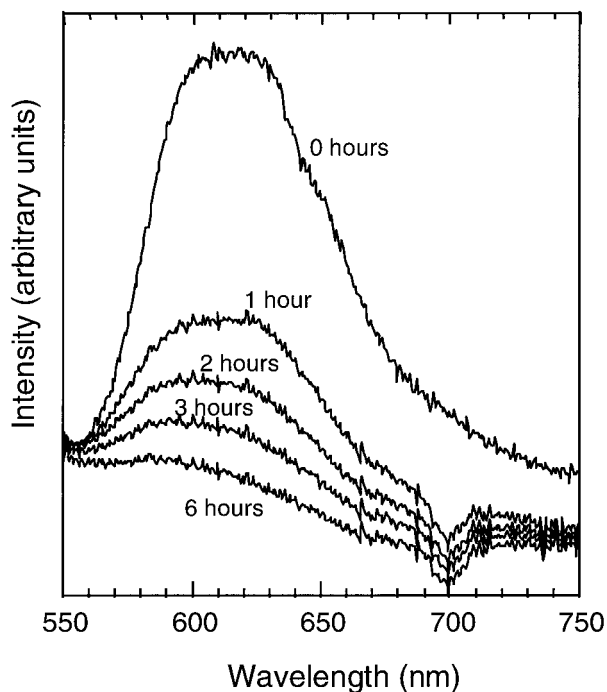

Figure 3 Relative intensities and spectral position of photoluminescence from MEH–PPV during irradiation in air with a 20-mW/cm^2 514-nm light from an Ar$^+$ laser.

jugated segments in this polymer is less than 1% and should not play a significant role in the oxidation mechanism. When irradiated using 514 nm light, substantial oxidation does occur, but the predominant carbonyl feature forms at 1685 cm^{-1}, indicating the presence of an aromatic aldehyde. There is no evidence of ester formation in the case of the alkyl-substituted PPV. This result implies that the ester that forms does so at the alkoxy group in MEH–PPV and not via oxidation of aldehyde or ketone groups.

The photooxidation mechanism for alkoxy derivatives of PPV clearly demonstrates that the vinyl double bond in these polymers is the most reactive segment in the chain.[8] The predominant mechanism for oxidation at this site is the cycloaddition of singlet oxygen. Because singlet oxygen is a highly electrophilic species, it is not surprising that the large electron density of the sterically exposed vinylene linkage is vulnerable. One possible method to make these polymers less reactive to singlet oxygen is to decrease the electron density at the vinylene segment. This can be achieved by the addition of atoms or groups with strong electron-withdrawing strengths. This chemical change will effectively decrease the elec-

tron density, but may also disrupt conjugation along the polymer backbone to the extent that luminescence efficiency is greatly reduced. Another means to protect the vinylene linkage is the addition of bulky groups to the double bond that will sterically protect the double bond from singlet oxygen attack.

The photooxidation of two "protected" derivatives was studied. MEH–PPV–CN and PPV–DP (see Fig. 1) were studied to evaluate the electron-withdrawing and steric protection of the vinylene segment. Of course, the phenyl substituents will also alter the electron density of the double bond, making it difficult to extract the effect of steric protection. The photooxidative stability of each polymer was evaluated relative to the degradation of MEH–PPV, which was irradiated in air using 514 nm light.

Upon examination of the UV/Vis absorption spectra for these derivatives, it is evident that the substituted polymers do not have equal absorbances at 514 nm. To correct for this discrepancy, the polymers were irradiated near their absorption maximum using 514-nm irradiation for MEH–PPV and monochromatized energy from a 300-W Xe lamp for MEH–PPV–CN and PPV–DP. An interference filter with a center wavelength of 340 nm and a bandwidth of 10 nm was used. The irradiance was adjusted so that in every case the total energy dose received after 10 h of exposure was 380 J. Assuming Beer's law dependence for absorption, the absorbance values from the UV/vis spectra and the film thicknesses, measured with a profilometer, were used to calculate the molar absorptivity of each polymer at its irradiation wavelength.

For easy comparison, a reactivity, R, relative to that of MEH–PPV is defined as follows:

$$R = \frac{(A_{C=C}/A_\phi)_{MEH,ox}/(A_{C=C}/A_\phi)_{MEH,0}}{(A_{C=C}/A_\phi)_{ox}/(A_{C=C}/A_\phi)_O} \times \left(\frac{\varepsilon_{MEH,514}}{\varepsilon_\nu}\right) \quad (1)$$

where $A_{C=C}$ and A_ϕ are the IR absorbances of the C=C vinyl bond and the 1500 cm^{-1} phenyl band, respectively, and the subscripts ox and O refer to the oxidized film after a total irradiation dose of 380 J and the as-coated film (an irradiation time equal to zero), respectively. ε_ν is the molar absorptivity of the derivative under study at its irradiation wavelength (e.g., MEH–PPV–CN and

PPV–DP at 340 nm) and $\varepsilon_{MEH,514}$ is the absorptivity of MEH–PPV at 514 nm. Again, the total energy absorbed by the polymer per unit thickness is constant, defined by the experimental conditions of power and irradiation time. The numerator is defined for MEH–PPV and the denominator is defined for either MEH–PPV–CN or PPV–DP.

Using the ratio of the absorptivities of the polymers as a correction factor in eq. (1), we can directly compare the polymers' reactivity to singlet oxygen after receiving an identical energy dose per unit thickness. Using eq. (1), $R_{MEH–PPV–CN}$ = 0.24 and $R_{PPV–DP}$ = 0.55. So MEH–PPV–CN is 76% less reactive and PPV–DP is 45% less reactive than is MEH–PPV in terms of photooxidative stability. Therefore, the addition of electron-withdrawing and/or bulky groups to protect the vinylene linkage appears to be quite effective, even after accounting for absorption differences in the polymer. The electron-withdrawing nitrile groups appear particularly effective.

Semiempirical Calculations of Polymer Reactivity

To investigate more fully the role of side groups on the reactivity of the vinyl double bond, AM1 semiempirical geometry optimizations were performed. These methods are not as rigorous as are *ab initio* or density functional methods, but they are computationally tractable for polymer segments. While not quantitatively accurate, they provide a relative basis for comparison between polymers. AM1 was used to optimize the geometry of dimeric segments of the polymers discussed above. After the geometry was optimized, the bond order of the double bond was calculated using Mulliken overlap population analysis. The bond order is a way of viewing the electron density of the bond; that is, the higher the bond order, the greater the density of electrons between the two atoms. For localized double and single bonds, the bond orders are two and one, respectively. In a delocalized π-electron system, as in these conjugated polymers, the bond order is between one and two.

The results of the AM1 calculations are summarized in Table I, wherein R refers to phenylene substituents and R′ refers to vinylene substituents. Dimer #1, the unsubstituted PPV dimer, is shown for comparison in the top row of the table. As one might expect, substitution on the ring structure is not as effective as direct substitution on the double bond for decreasing the reactivity of the molecule. For example, dimer #8 is much

Table I   AM1 Results for Substituted PPV Dimers with the Following Structure:
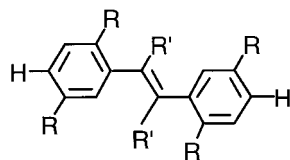
#	R	R′	Bond Order
1	H	H	1.83
2	H	Phenyl (×2)	1.87
3	CH$_3$	H	1.86
4	OCH$_3$	H	1.85
5	H	CH$_3$	1.84
6	OCH$_3$	CN	1.83
7	H	CN	1.77
8	H	OCH$_3$	1.77
9	H	OCH$_3$ (×2)	1.75

more effective than is dimer #4 (representative of MEH–PPV) in decreasing the bond order. MEH–PPV–CN can be represented as a combination of dimers #6 and #7. In either case, the electron density is lowered relative to MEH–PPV (represented by dimer #4), which is consistent with experimental observations. Interestingly, the methoxy substituent, which is a weak electron donor, still reduces the bond order of the vinylene group. The improvement upon substitution with methoxy groups is not fully understood. One explanation of this effect is that hydrogen bonding between the methoxy group and a neighboring phenyl ring may increase the planarity of the molecule, leading to greater π-orbital overlap. This would result in greater electron delocalization and a reduction of the bond order of the vinylene segment. The best results can be achieved by substituting both vinyl carbons with strong electron-withdrawing groups such as nitrile moieties.

Dimer #2 (representative of PPV–DP) is interesting because the substitution of two phenyl rings in a *trans* configuration across the double bond increases the bond order relative to the unsubstituted PPV. This may be related to the high degree of nonplanarity in this structure caused by the bulky phenyl substitutions, resulting in less electron delocalization and, therefore, a higher bond order. The fact that PPV–DP performs so well when irradiated with visible light is probably related more to steric protection of the double bond from singlet oxygen than to electronic protection.

PPA Derivatives

Poly(phenylene acetylene) (PPA) and its derivatives present an interesting comparison to PPV derivatives due to the presence of a triple bond instead of a double-bond linkage between phenyl rings. The reactivity of singlet oxygen with double bonds is high, and the mechanisms for these reactions are well understood.[19] However, there are very few literature reports of singlet oxygen reactions with triple bonds.[20] In fact, the only known reaction involves highly strained, cyclic acetylenes heated to greater than 90°C in an oxygen-saturated solution.[20] There are, however, many known thermal oxidation mechanisms for acetylenic compounds.[21] Thermal oxidation of phenyl-substituted acetylenes results in the formation of aldehydes, acids, anhydrides, and ketones. It should be noted that LEDs have been fabricated using soluble derivatives of PPA and have demonstrated excellent stability.[22–24]

To compare the photooxidation of PPA derivatives with PPV derivatives, spin-coated films of the soluble polymer poly(2,5-dibutoxy,1-4-phenylene acetylene) (DBuOPPA) (see Fig. 1) were irradiated in air using the 457 nm line from an Ar$^+$ laser. The 457-nm line is near the absorption maximum for DBuOPPA.

The results of IRRAS characterization of the photooxidation of DBuOPPA using 457-nm light are shown in Figure 4. This experiment was started 3 days after a solution of DBuOPPA was prepared in 99+% THF. It was evident from the spectrum for the as-coated film that some carbonyl impurity had formed while in solution, even though the solution was prepared and stored in a nitrogen glovebox and protected from light. This impurity was not seen in films cast from freshly prepared solutions. Figure 4 shows that no further oxidation occurred during the irradiation process, with a total energy dose of 380 J over 10 h.

That DBuOPPA appears stable when irradiated at 457 nm is encouraging because it suggests that this polymer will not exhibit the self-destructive behavior previously reported for MEH–PPV.[14,15] The photoluminescence of DBuOPPA displays a broad tail, blue-shifted from the PL maximum, which will be reabsorbed by the polymer; therefore, it is very important that the polymer be photooxidatively stable. Thus, it appears that DBuOPPA is much more stable than is
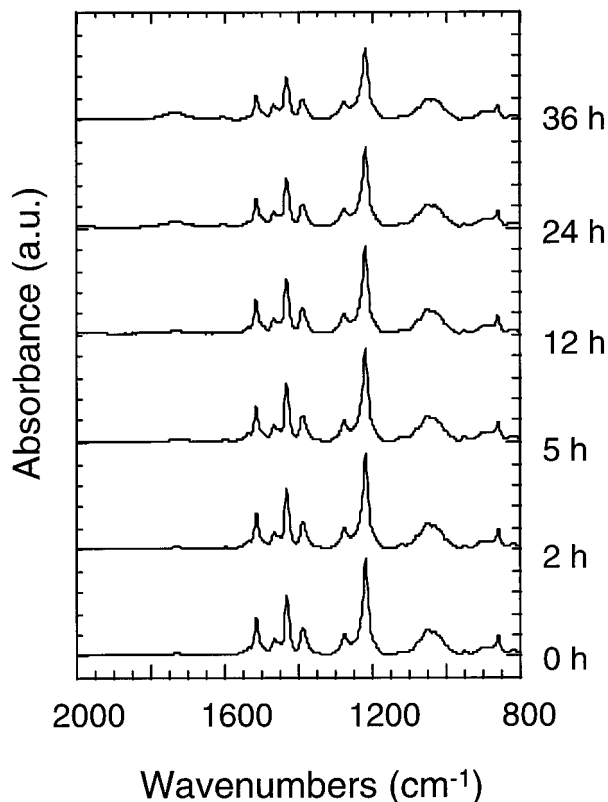
Figure 4 IRRAS spectra of the photooxidation of DBuOPPA using a 10-mW/cm² 457-nm light from an Ar⁺ laser.

MEH–PPV, showing no oxidation when irradiated at its absorption maximum.

CONCLUSIONS

The addition of electron-withdrawing groups to PPV-like backbones was shown to decrease the overall reactivity of alkoxy-substituted PPV derivatives. PPV–DP and MEH–PPV–CN both exhibited higher stability than that of MEH–PPV. These observations were supported by AM1 semiempirical calculations, demonstrating that the substitution of highly electronegative groups directly onto the vinyl double bond could prove to be very effective in improving the oxidative stability of these polymers. The two substitutions studied that had the largest effect were the nitrile and methoxy groups. The calculated performance of the methoxy substitution is unexpected since alkoxy groups are considered weak electron donors. The methoxy substitution may have more of an effect on the geometry of the polymer than

on its electronic characteristics. Functionalization with phenyl groups appears to protect the double bond of the polymer by steric interactions but bulky alkoxy segments may be a more attractive alternative to aryl substitution in terms of both stability and solubility. The PPA derivative investigated performed better than did all of the PPV derivatives studied. The improved stability is attributed to a lower reactivity between singlet oxygen and the triple bonds of PPA than with the double bonds of PPV.

These results only take into account stability and do not consider the ease of synthesis or efficiency of light emission. Nor is the efficiency of singlet oxygen production taken into account. It is clear from the computational chemistry results that the addition of electron-withdrawing groups can dramatically decrease the reactivity of double bonds in conjugated polymers. It is unknown, though, how these substitutions may effect the quantum yield for the production of singlet oxygen. Both MEH–PPV–CN and PPV–DP have higher bandgaps than those of MEH–PPV so both polymers probably have sufficiently energetic triplet states to produce singlet oxygen. However, the population of these triplet states may be lower than that of MEH–PPV due to shorter triplet lifetimes or lower rates of intersystem crossing. In any event, it is clear both from the experimental and theoretical results presented in this article that chemical substitution makes these polymers more photooxidatively stable than is MEH–PPV.

Electroluminescent polymers show outstanding potential to replace inorganic light-emitting materials, particularly in novel applications including lightweight, large-area, flexible displays. However, the stability of these devices remains an issue. Currently, there is interest in developing encapsulation materials to protect polymeric LEDs from oxygen and moisture without absorbing emitted light. Because encapsulation materials could fail, dramatically increase fabrication costs, and reduce external quantum efficiencies, it is preferable to strive to design polymers that have inherent environmental stability.

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