Rapid Formation and Spectroscopic Observation of Polystyrene Conjugation in Individual Micron-Diameter Particles with Visible Radiation

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Received: July 10, 1996; In Final Form: September 24, 1996[⊗]

Rapid generation of polystyrene conjugation in individual micron-diameter particles isolated in a visible wavelength radiation trap is reported. Double-bond formation, as a result of radical recombination and hydrogen abstraction, in the backbone of the polymer chain is monitored by observing the magnitude and duration of emission from the polymeric particles. These processes, which ultimately lead to polymer degradation, are observed to be strongly dependent upon the thermal conductivity and polarity of the solvent used to suspend the particles. Doping the polymer with chemical modifiers containing chromophores in order to reduce photodegradation is demonstrated to be counterproductive.

Introduction

A polymer is said to degrade when a change in the molecular weight of the polymer occurs, resulting in changes in the physical properties of the polymer. Understanding the degradation of polystyrene and related polymers is critical for device fabrication, long-duration device employment, and design of improved polymeric materials. This knowledge is also beneficial in developing recycling and refabrication processes for these materials. Although there has been significant investigation of polystyrene photoinduced degradation, many reported studies only consider exposure to ultraviolet radiation.

Investigations of both thermal and photodegradation of polystyrene[1−7] have resulted in various conclusions about the mechanism of polymer breakdown. There are three main pathways of degradation as shown in Figure 1. The polymer can undergo cross-linking, double-bond formation in the backbone, or chain scission (with or without oxygen incorporation). These previous studies have examined both solution and solid states with the latter in the form of thin films. The photodegradation of polystyrene has been investigated under many conditions, but typically it is investigated with $\lambda < 360$ nm. In these photochemical experiments polystyrene radicals were observed, Figure 2, by ESR, when the polymer was exposed to radiation below 440 nm. Polymer degradation however was only observed with UV radiation (<360 nm).[1] These same reports have also concluded that radical formation does not occur with exposure to wavelengths greater than 440 nm since these species were not detected by ESR.

It is well-known that polystyrene exposed to sunlight for extended periods of time develops a yellow color. This must be due to the formation of polyene-type structures in the polymer backbone[2] as shown in the reaction of Figure 1. Irradiation with wavelengths between 40[8] and 360[1] nm produces polystyrene radicals which lead to the decomposition of the polymer chains by either chain scission or polyene formation. The presence of solvent, oxygen, or impurities such as peroxides can significantly affect the rate and pathway of the degradative reactions.

Ultraviolet radiation, however, is a low-intensity component of solar radiation at the earth's surface relative to visible wavelengths due to attenuation by the atmosphere.[6] The effects of visible radiation on polymer degradation should be considered, since minor impurities in polystyrene such as peroxides

can serve as the source of the initial radical, forming the first double bond and facilitating further conjugation.

Significant thermal degradation of polystyrene has been observed at high temperature (>80 °C in benzene[4] and >300 °C for solid films[3]). Thin films have been studied in vacuum, air, and pure gases.[3] The main degradation products identified were styrene (in vacuum), carbonyl-terminated species (in the presence of O_2), styrene monomer, and some oligomers (in solution). Cross-linking occurs to some extent under most conditions investigated. The oxygen incorporated into the polymer backbone during polymerization (peroxides) has been shown to affect the rate and extent of degradation. The rate of generation of conjugated regions in the polystyrene backbone (polyenes) as a result of thermal processes has not been thoroughly investigated, but it is known that temperature has an effect on the photodegradation processes.[9] The combined role of thermal processes and photon absorption in the breakdown of polystyrene has yet to be fully elucidated.

We report, for the first time, that polystyrene radicals can be rapidly formed with continuous radiation utilizing wavelengths greater than 440 nm and that the resulting conjugation of the polystyrene backbone may be easily observed by emission spectroscopy. The effects of solvent thermal conductivity and polarity on the formation of polystyrene radicals provide evidence that the mechanisms previously proposed for UV radiation exposure also adequately describe polystyrene degradation during exposure to visible (488.0 nm) radiation.

In addition, due to the poor thermal conductivity of polystyrene it has been possible to spatially control the generation of radicals and location of backbone conjugation in the 6 μm diameter particles investigated. We demonstrate that the extent of polymer degradation can be manipulated by controlling the heat dissipation characteristics of the system. Solvents with good thermal conductivities reduce the extent of the reaction, while solvents with poor thermal conductivities serve to increase the magnitude and extent of the reaction (duration). Likewise, solvents with easily abstracted hydrogens serve to increase the extent of reaction.

In the search for a means to reduce or eliminate the conjugation, cross-linking, and chain scission reactions that occur when polystyrene is illuminated with solar radiation, it has been suggested that doping the polymer could be beneficial. Commercially available "protective" compounds can be grouped according to their mechanism of protection. These include compounds which have large absorption coefficients, those

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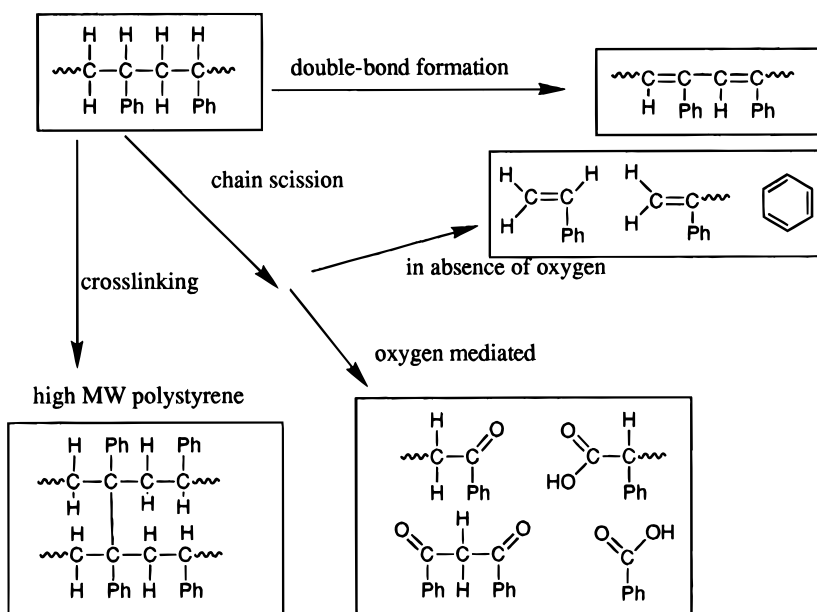*J. Phys. Chem. B, Vol. 101, No. 6, 1997* **865**

Polystyrene

Figure 1. Examples of reaction products formed during the thermal degradation or photodegradation of polystyrene.
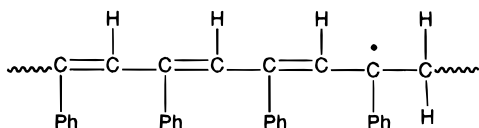

Figure 2. Proposed visible excitation generated polystyrene radical.

which act as antioxidants by scavenging low molecular weight radicals or decomposing peroxide linkages, or those which are capable of quenching a physically excited state of the polymer.[10] Our results on individual latex particles doped with fluorescent dyes indicate that compounds that simply address absorption mechanisms serve to increase the rate of polymer conjugation. Thus they do not protect the polymer but actually enhance the degradative reactions.

Experimental Section

Polystyrene particles were obtained as aqueous suspensions (Polysciences). Particles investigated were surface functionalized with amine groups and carboxylate groups, as well as nonfunctionalized. Identical results were obtained regardless of the surface functionality. The following diameters were used: 0.513 ± 0.011, 0.773 ± 0.014, 3.285 ± 0.146, and 6.326 ± 0.411 μm undyed particles, 0.933 ± 0.01 μm fluorescein-doped particles, and 1.09 ± 0.01 μm nile red particles. Methanol (Fisher), ethanol (90%, 5% methanol, 5% isopropanol, Aldrich), 1-butanol (Baker), isopropanol (Fisher), and DMSO (Fisher) were used as purchased. Nanopure water (Barnstead) was used for all dilutions.

Optical Trap and Microscope. An Olympus IMT-2 inverted microscope and Olympus 100× SPlan oil objective (NA = 1.40) were used for all experiments. Fluorescence images were collected using a TV-rate CCD camera model JE-7442 (Javelin, 0.4 lux sensitivity) and IPLab image-capturing software running on a Macintosh IIci computer. Emission spectra were obtained using a cooled CCD camera model LN/CCD-1152 (Princeton Instruments) and a single-stage spectrometer (Spex, model CP200). Excitation and optical trapping were conducted using an argon-ion laser (Coherent) at 488.0 nm. A simplified diagram of the setup used is shown in Figure 3.

Optical Trapping. In order to investigate the photodegradation of the polymer particles, they are first suspended in the
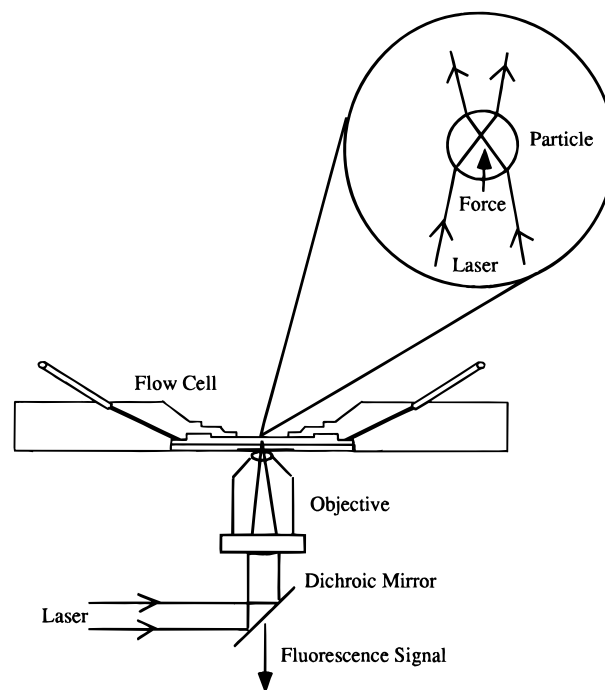

Figure 3. Diagram of setup for the observation and optical trapping of polystyrene microspheres. The inset shows a particle below the optical trap focus and the direction of the net force on it due to the refraction of laser radiation.

chosen solvent. This suspension of particles is then pumped into a flow cell for observation through the microscope. A laser source is focused into the flow cell through the microscope objective in an epifluorescence geometry. Refraction of the radiation through the particle results in opposing forces which balance in three dimensions to hold the particle in place (inset of Figure 3). This phenomenon is known as optical trapping, and thus the laser radiation is used in this paper as both the excitation radiation and the means for immobilizing the particle. The optical trap described has a single requirement, that the refractive index of the particle is larger than that of the suspending solvent. Additional descriptions of this phenomena have been presented in the literature.[11–14] Using a power of
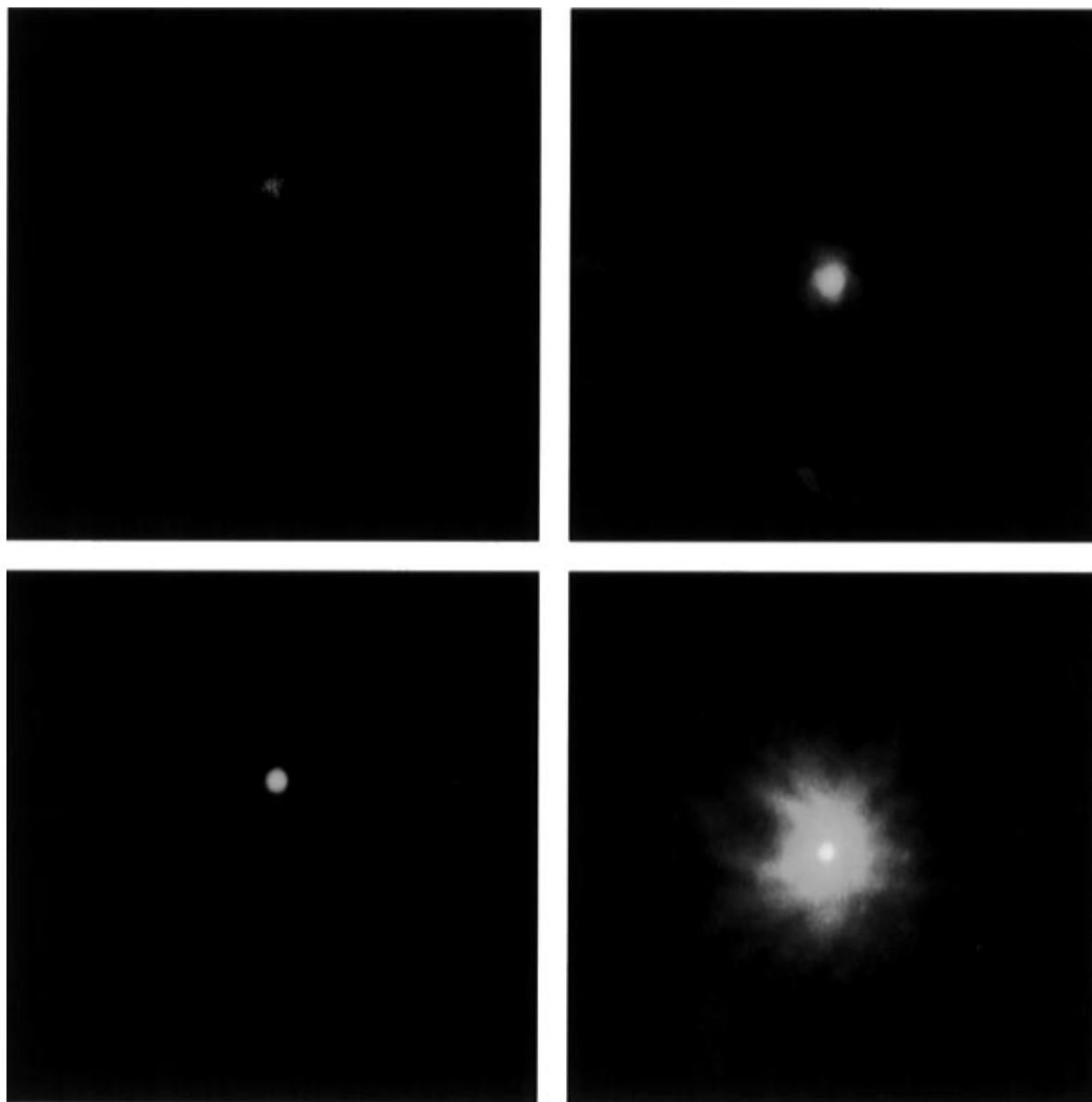
Figure 4. (a (top left), b (bottom left), c (top right), d (bottom right)) Sequence of pictures revealing the appearance of fluorescence from an optically (488.0 nm) trapped 0.773 μm polystyrene particle suspended in ethanol. An Olympus 100× (1.4 NA) objective lens was used along with 4× photographic magnification.

1.4 mW of 488.0 nm radiation, a 30 s exposure time in the trap is equivalent to approximately 3.4 years of 12 h sunlight days of 488.0 nm radiation at the earth's surface.[6]
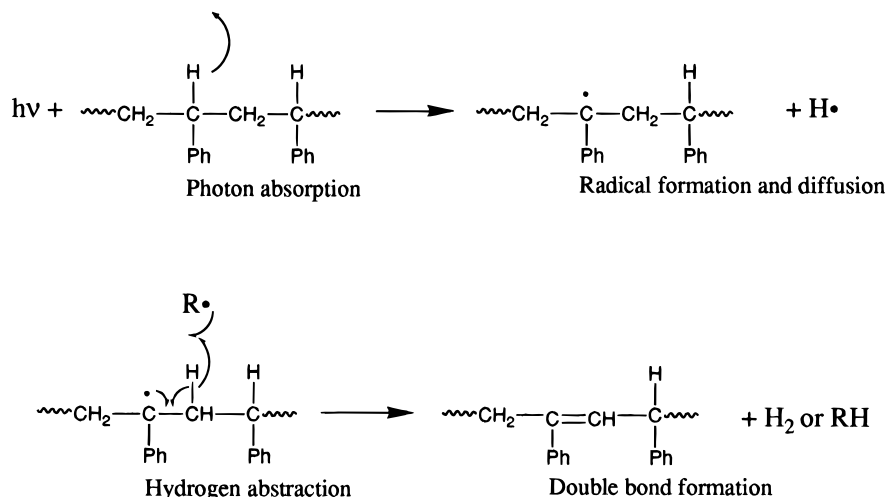
Results and Discussion

Polystyrene particles suspended in solution were optically trapped with 1.4 mW of 488.0 nm radiation generated with an argon-ion laser. In this particular optical trap, the diameter of the focused radiation is approximately 1 μm, and the particle is immobilized very close to this focal point.

Initially no emission is observed when the particle is pulled into the trap. If the particle is retained in the optical trap for longer than a few seconds, a green emission slowly develops. Four sequential photographs are shown in Figure 4a−d and depict the temporal characteristics of a typical particle emission. Once in the trap, emission from the particle steadily increases to a maximum and then quickly fades to a point where no emission can be observed. The spectral profile of the particle was measured with 2 nm resolution, Figure 5, and is observed to be quite broad with maximum emission near 530 nm. At least six double bonds in the polymer backbone are required to
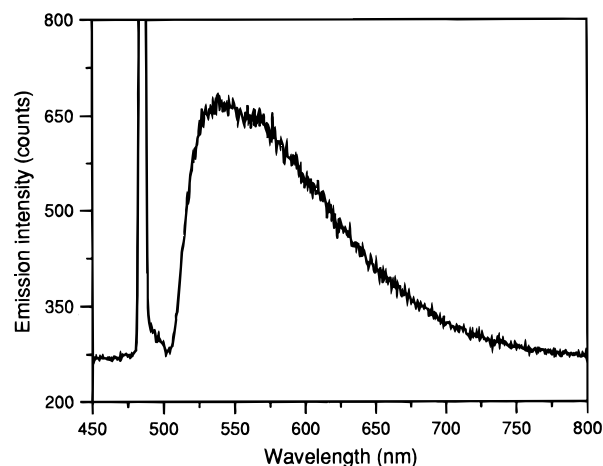
Figure 5. Green fluorescence emission from a 0.773 μm polystyrene particle in a 488.0 nm optical trap. The excitation line is included along with the effects of a 515-nm long-pass filter.

produce a polyene chromophore with emission greater than 500 nm.[8] The emission spectrum in Figure 5 provides evidence that

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hν + ~~~CH₂—C—CH₂—C~~~   →   ~~~CH₂—C—CH₂—C~~~   + H•

Photon absorption   Radical formation and diffusion

~~~CH₂—C—CH—C~~~   →   ~~~CH₂—C=CH—C~~~   + H₂ or RH

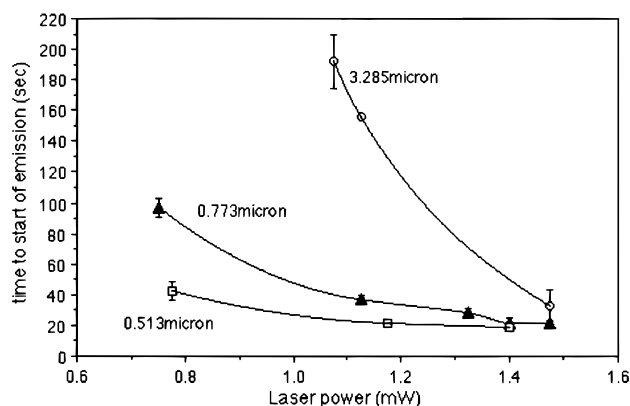Hydrogen abstraction   Double bond formation

Figure 6. Reaction scheme for the production of polyene regions in polystyrene particles held in an optical trap (visible radiation).

conjugation even more extensive than this is present. Emission spectra with a wavelength maximum greater than 500 nm corresponding to polyene chromophores have only been observed previously in films irradiated with radiation of wavelengths less than 220 nm.[8]

In order for intense emission to occur in the visible region, an extensive system of backbone conjugation must be developed, and this will require a finite amount of time under constant illumination. This time period is observed to be dependent on the nature of the solvent, excitation power, and particle size and is referred to as the initiation time or time to emission.

The first step in this process is the formation of a carbon radical on the polystyrene backbone and a free hydrogen radical due to the absorption of a photon. The threshold energy required to break the αC$-$H bond is 71 kcal/mol (before considering resonance stabilization of the radical[15]). Previous investigations have focused on ultraviolet radiation because it is energetic enough to break the αC$-$H bond on the polystyrene backbone through energy transfer from phenyl absorption. Breaking of the αC$-$H bond results in radical formation and ultimately the formation of a double bond with the evolution of hydrogen gas (Figure 1). Previous work[16] has demonstrated that hydrogen, as well as benzene and other styrene oligomers, are evolved from polystyrene films exposed to short-wavelength ultraviolet light in vacuum. Several possibilities exist for the absorption of a photon at 488 nm. The stabilization of the αC$-$H radical species by a nearby double bond in the polystyrene backbone can significantly lower the activation energy[15] for production of the radical. The presence of isolated double bonds in high molecular weight polystyrene molecules is documented,[1] as is the presence of peroxide impurities which have lower bond dissociation energies. The energy of 488.0 nm radiation is 59 kcal/mol, thus providing the possibility that an αC$-$H bond near a double bond on the chain backbone could be broken with 488.0 nm radiation. Although there is a low probability of photon absorption by the phenyl group at 488 nm, the high photon flux of the focused laser can provide the possibility that this event could occur with the phenyl group directly or with impurities such as peroxides or regions of conjugation in the polymer. Thus, bond stabilization in combination with high photon fluxes provides a means for generating polystyrene radicals.

The hydrogen radical formed in the first step is then free to move down the polymer backbone to abstract a hydrogen from a second carbon atom on the chain backbone or from a solvent molecule. A lower energy state for hydrogen abstraction can

Figure 7. Effect of particle size and laser power on initiation time from optically trapped polystyrene particles (488.0 nm, 22.4 °C room temperature).

be found in the vicinity of a double bond or conjugated region of the backbone since radicals are stabilized by resonance. Finally, radical recombination in the polymer backbone results in the formation of a double bond. This series of events leads to the formation of large polyenes which can be observed by emission spectroscopy. In our experiments this region of the polymer structure is subsequently oxidized by further illumination, and the emission stops. It should be noted that a major competing pathway to conjugation is chain scission in the polymer backbone yielding the monomer or carbonyl species as shown in Figure 1.

Figure 6 illustrates the key steps for polymer conjugation formation: the initial formation of radicals, thermal diffusion of the free radicals, and formation of double bonds. These three steps were addressed experimentally. Our results demonstrate that generation of polyene structures can be controlled by manipulating the rate of initial radical formation, thermal diffusion, and through control of hydrogen abstraction, which propagates the reaction through the polystyrene backbone.

The length of time before emission is observed from the optically trapped particle (initiation time) is dependent on the average power and wavelength of the visible radiation used to create the optical trap, the size of the particle, and solvent characteristics. A plot of initiation time versus optical power is presented in Figure 7 for several particle sizes. As the average power of the exciting radiation increases, there is a decrease in the time required to observe emission from the particle. There is a greater decrease in initiation time with increases in power for larger particles. This effect is related to the heat transfer
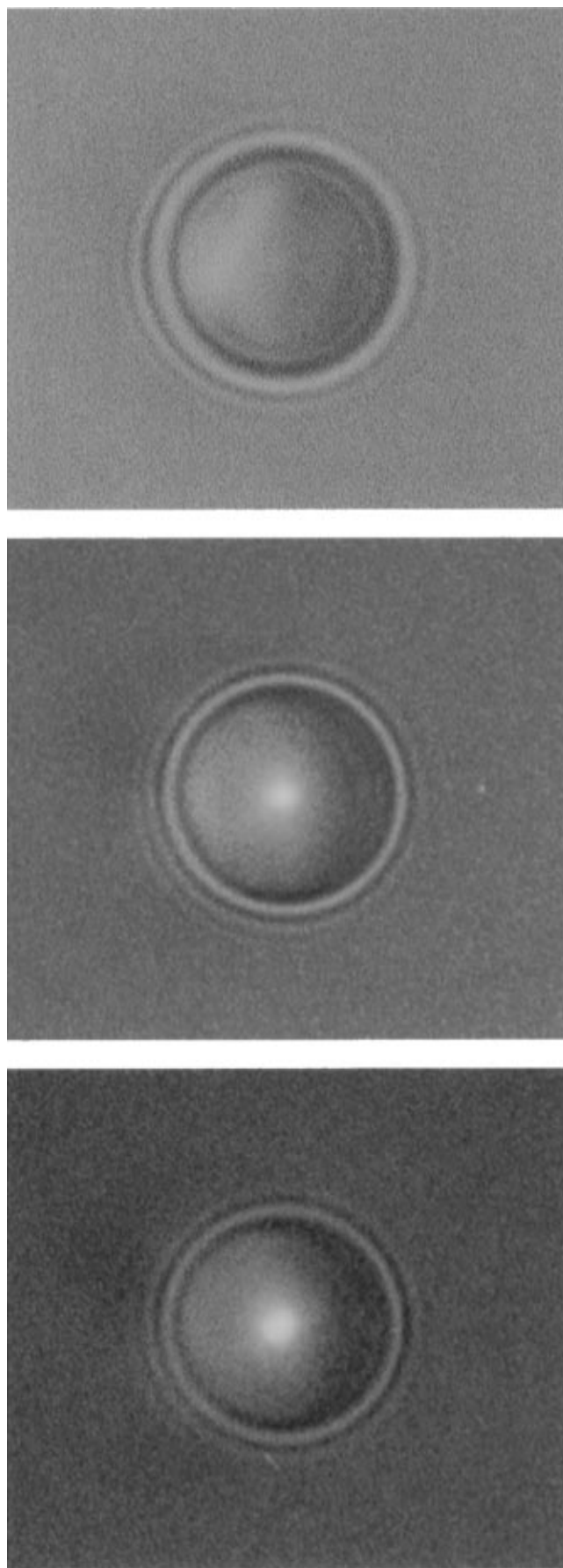
properties of the system and the focal spot diameter of the radiation and will be discussed vide infra. Figure 8 clearly shows the spot size of the focused radiation in an optically trapped 6 μm diameter particle. This image demonstrates the capability of localizing the degradative reactions.

The results presented in Tables 1−3 provide clear evidence that the formation of polymer conjugation is a complicated process controlled by both thermal and photon mediated processes. The results provided in these tables indicate that emission results from a multistep process, similar to that which is reported for UV illumination.[17] Table 1 compares the thermal conductivity of a homologous series of solvents with the emission initiation time (time resolution approximately 0.5 s) in particles of 0.773 μm diameter (1.4 mW excitation at 488.0 nm). This relationship is linear ($r = 0.994$) and clearly demonstrates that solvents/matrices with poor thermal conductivity characteristics decrease the initiation time for the particles. The much larger thermal conductivity of water provides the greatest increase in initiation time. In addition, ambient room temperature has a large effect on the initiation time. This is evident from the initiation times for polystyrene particles suspended in water as shown in Tables 1 and 3. Higher room temperatures result in much shorter initiation times.

The particle temperature and rate of initial radical formation are dependent on the power of the laser. Figure 7 shows the dependence of initiation time on particle size and laser trap power. At lower powers, the temperature of the particle increases more slowly. Since radicals are quickly formed through photon absorption when the particle enters the optical trap, the initiation time is only weakly dependent on the first step. The strong dependence of initiation time on laser power must be due to temperature increases in the particle. Poor thermal conductivity of polystyrene results in increased temperatures of larger particles, and the rapid initiation time observed is a demonstration of this fact. Small particles show a weaker dependence (rate of decrease in initiation time) on the power of the laser. The actual initiation time for smaller particles is shorter, however, due to their reduced mass. As the number of radicals increase and double bonds are formed in the smaller particles, it becomes more probable that a region of extended conjugation will develop.

The linear relationship between the initiation time and thermal conductivity of the solvent, Table 1, is further evidence that the temperature of the particle increases as a result of the absorption of light and plays a major role in generating conjugation. In a solvent of higher thermal conductivity, such as methanol, the heat generated due to absorption of photons is transferred away from the particle into the surrounding solvent. When the transfer of heat away from the particle is inefficient, as with 1-butanol or isopropanol, the temperature of the particle increases quickly. The temperature increase causes an increase in the rate of reaction propagation through quicker diffusion of the free radical away from the formation site as well as an increase in the rate of radical recombination and hydrogen abstraction. A significant difference between the initiation time for a 0.773 μm diameter particle in water (Tables 1 and 3) at 22 and 30 °C is also observed.

Thermal conductivity, however, does not fully describe the emission characteristics of this system, as Table 2 demonstrates. In Table 2, the maximum emission intensity for a 0.773 μm diameter particle (1.4 mW excitation at 488.0 nm) is demonstrated to be related to the polarity and the ease of hydrogen abstraction of the solvent. As the polarity of the solvent decreases, the intensity of the particle emission increases.

Figure 8. (a (top), b (middle), c (bottom)) Sequence of pictures showing optical trap focal spot size in a 6 μm diameter polystyrene particle suspended in water. An Olympus 100× (1.4 NA) objective lens was used along with 4× photographic magnification.

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TABLE 1: Effect of Solvent on Initiation Time (Time to Emission) from a 0.773 μm Polystyrene Particle in a 1.4 mW 488.0 nm Optical Trap[a]

solvent	n[b]	thermal conductivity (cal/(s cm K))[22]	initiation time (s)	total time (s)
isopropanol	3	0.0003362	15.0 ± 0.5	8.3 ± 1.0
butanol	3	0.0003663	16.0 ± 0.5	18.3 ± 3.0
DMSO[c]	6	0.000375	9.5 ± 0.5	2.0 ± 0.5
ethanol[d]	4	0.0003995	18.25 ± 0.5	6.0 ± 1.5
methanol	4	0.0004832	20.75 ± 0.96	18.8 ± 3.6
water[c]	4	0.001456	25 ± 2.5	13.5 ± 1.9

[a] Solution temperature was 22.4 °C. The homologous series of alcohols shows a linear relationship between initiation time and thermal conductivity. [b] n = number of particles. $Y = 1.673 + (4.025 \times 10^4)X$, $R^2 = 0.994$. [c] Not included in linear regression [d] Thermal conductivity given for 100% ethanol.

TABLE 2: Effect of Solvent on Maximum Fluorescence Intensity Observed from a 0.773 μm Polystyrene Particle in a 1.4 mW 488.0 nm Optical Trap[a]

solvent	n	polarity index[23]	intensity observed	ΔH_f° (R$^\bullet$) (kcal/mol)[24]
water	4	10.2	25.0 ± 2.4	9.2 ± 1 (OH$^\bullet$)
DMSO	6	7.2	39.8 ± 8.6	not available
methanol	4	5.1	37.2 ± 10.5	3.8 ± 0.2 (CH$_3$O$^\bullet$)
ethanol	4	4.3	211.9 ± 17.8	−4.1 (C$_2$H$_5$O$^\bullet$)
isopropanol	3	3.9	223.9 ± 24.9	−12.5 (i-C$_3$H$_7$O$^\bullet$)
butanol	3	3.9	226.3 ± 25.1	−14.7 (n-C$_4$H$_9$O$^\bullet$)

[a] Solution temperature was 22.4 °C.

TABLE 3: Effect of Doped Fluorescent Dye on Polystyrene Particle Fluorescence Characteristics Using a 1.4 mW 488.0 nm Optical Trap[a]

dye type	n	initiation time (s)	total time (s)	max intensity
plain	7	14.3 ± 2	9.3 ± 2	28.7 ± 3
fluorescein	6	10.0 ± 0.9	12.7 ± 4	66.1 ± 6
nile red	5	5.8 ± 0.8	25.5 ± 7	62.8 ± 6

[a] Water temperature was 30.3 °C.

Previous work[15] has shown that the rate of increase in optical density at 440 nm (yellowing of the film) is much greater in the presence of oxygen gas or nitrogen gas compared to the film in vacuum. The oxygen and nitrogen were assumed to be unreactive to the polymer, and the rate increase was hypothesized to be related to localization of the hydrogen radical near the polymer backbone. In vacuum, the radical diffuses away from the polymer backbone quickly, so further reaction with the polymer to produce H$_2$ gas and a double bond is reduced. When nitrogen or oxygen is present, collisions with these species keep the initial radical in the vicinity of the polymer chain for a longer time, permitting the formation of the polymer radical, hydrogen gas, and ultimately additional double bonds. Another work[18] showed that solvents which produce highly reactive radicals cause an increased rate of polyene formation in the dissolved polymer. In our work all particles are suspended in solution; thus, rapid movement of the radical out of the interstitial space will be limited. Table 2 details significant solvent effects on the maximum emission that could be rationalized with a simple "filling" of polymer void volume. Ethanol, isopropanol, and butanol generate a significant increase in particle emission compared to water, DMSO, and methanol. Radicals of water and DMSO are less stable than the alcohols and more difficult to generate. Solvents with easily abstracted hydrogens serve to increase the duration and magnitude (maximum emission) of reaction as shown in Table 2. Methanol, however, does not show a large increase in emission intensity although it is capable of forming stable radicals. This result could be explained by the lack of swelling and penetration

of the polymer particle.[19] If more polymer is accessible to the solvent, increased reaction duration and emission would be expected. As solvent interaction with the polymer is decreased (more polar solvents), hydrogen abstraction must be obtained from the polymer itself; thus, the reaction proceeds more slowly. The polymer in ethanol shows a maximum emission five times greater than that from a particle in DMSO or methanol. The increased emission with ethanol cannot be due to increased temperature in the particle as ethanol has a higher thermal conductivity than DMSO (Table 1), and as expected, the initiation time is nearly twice that for a particle suspended in DMSO. Both DMSO and methanol are more polar solvents (Table 2) than ethanol, indicating that swelling of the polymer particle is greater in the presence of ethanol compared to methanol or DMSO. The emission maxima for polymer particles in methanol and DMSO are nearly identical, indicating a threshold for significant penetration of the solvent into the polymer particle.

Emission from the optically trapped particle ceases quickly after reaching its maximum emission, but the particle remains in the optical trap in most cases. The particle itself is not completely reduced to small molecular weight compounds, thus the species responsible for the initial radical formation must be depleted during the generation of the polyene structures. This is strong evidence for the presence of impurities which absorb the 488 nm radiation, as opposed to energy transfer from the phenyl rings of pure polystyrene. Stable optical trapping of a particle depends on a difference in refractive indices; this observation implies that chain scission does not play a significant role since this would decrease the refractive index of the particle and therefore our ability to trap the particle. In the instances where the particle can no longer be retained in the optical trap, we observe that the particle is deformed and appears to have fractured regions. These abnormalities would result in the loss of the ability to trap it. Spectroscopic investigation of this cross-linking process is underway.

Minimizing the degradation of polystyrene involves addressing one of the three steps in the process. This typically involves adding a compound to the polymer matrix which physically or chemically prevents one step in the process from occurring. "Screening" compounds attempt to prevent the formation of the radicals in the first step due to extensive absorption of light by the compound instead of the polymer. Initial attempts in this area[6] using "phthalo-type" compounds resulted in an increase in cross-linking of the polystyrene chains but reduced chain scission, with no observed effect on the production of conjugated polyene structures.

In order to observe the effect of a compound with a strong absorption at 488 nm on the degradation of the particle, two different polystyrene particles impregnated with fluorescent dyes were optically trapped, and the time profile of the polystyrene emission was characterized. The results are shown in Table 3 and indicate that the presence of the fluorescent dye actually increases the rate at which conjugation is produced in the polymer backbone. This results in increased emission from the particle due to polystyrene conjugation. The data shown in Table 3 provides evidence that the rate and magnitude of polystyrene conjugation and ultimately polymer degradation are highly dependent upon the compound doped into the polymer particle. Excitation of particles containing fluorescein and nile red fluorophores was conducted with 488.0 nm radiation in aqueous solution, and the magnitude and extent of reaction were quantified as discussed previously. With the excitation power

at 1.4 mW, the size difference between the types of particles has a negligible effect by itself on the initiation time for emission (Figure 7).

The rate of polyene formation is observed to be greater in the nile red system than in either the fluorescein or undoped system even though the excitation is approximately 50 nm away from the absorption maximum for this dye. Fluorescein-doped particles still have a greater degree of conjugation than the undoped polymer. Explanations for these observations are complicated by the small scale of the polymer systems under investigation and the need to address the absorptivity, fluorescence quantum yield, and number density of the fluorophores. With respect to absorptivity, it is quite reasonable to believe that the fluorophores in each particle are completely saturated due to the large photon flux of the optical trap, and thus absorption mechanisms are eliminated from further consideration. Separating the contributions of number density and quantum yield is more difficult since these numbers are not easily attainable for the individual particles investigated. If we assume the quantum yields for nile red (0.7 in dioxane)[20] and fluorescein (0.92 in water)[21] are not significantly altered in the particles (spectral characteristics are unchanged), then equivalent number densities of fluorophores would yield a difference in initiation time of a factor of 4, as less heat would be generated in the fluorescein-doped system since the radiation absorbed is re-emitted, while in the nile red case more absorbed radiation is transferred to heat and thus a larger degradation of polystyrene (formation of double bonds) is observed. The observed initiation time difference is approximately a factor of 2, providing the possibility that the fluorescein concentration is twice that of the nile red. Experiments to determine fluorophore number densities in individual particles are underway. Although accurate determination of the contributions from each of these variables is not possible at this time, clearly compounds proposed for "protective" measures should address step two or three in the degradative process—the diffusion of the radical and formation of the double bond.

Conclusions

The results from these experiments show that polystyrene does form conjugated polyene regions in the polymer backbone when illuminated with visible radiation. Using the optical laser trap, it is possible to generate the radicals which form the conjugated polyenes in a very short time, leading to a greater length of conjugation than previously reported. The degradation of polystyrene in the optical trap is dependent on both the power of the trap and the temperature of the system. Solvent also plays a major role in the rate of formation of the polyene systems. There is evidence for the dependence of the initiation time on the polarity of the solvent, as the intensity of polystyrene emission is greatly increased in less polar solvents. Finally, routine analyses of the degradation of polystyrene under these conditions can be conducted with inexpensive imaging equipment.

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