

Photodegradation of Polyfluorene and Fluorene Oligomers with Alkyl and Aromatic Disubstitutions

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Received: April 28, 2006; In Final Form: May 26, 2006

The stability of fluorene-based compounds and polymers, especially at the bridged C-9 position under photoirradiation and thermal treatment, has claimed wide attention. We report the electronic, vibrational, and MALDI-TOF mass spectral combined studies for the fluorene oligomers with alkyl and aromatic substitutions under UV-light irradiation. The low-energy emission and the formation of ketonic defects after degradation highly depend on the proportion of alkyl substitution. The oligomer with fully aromatic substitution shows good stability, but when the proportion of alkyl substitution increases, their photostability rapidly decreases. The mass spectra show not only the mass of the fluorenone–fluorene trimer but also another new degradation product with a large mass (pristine oligomer plus 14) from alkyl oxidation, which testify to the assistance of alkyl side chain during degradation. We propose that the degradation of fluorene is a radical chain process propagated by alkyl side chains, and then the different stability between alkyl and aromatic substitution can be well explained.

Introduction

Bridged poly(*p*-phenylene) polymers (PPP) have been extensively studied over the past few decades. In these polymers, the adjacent phenylenes are bridged by a methylene, which is substituted by alkyls, to increase the solubility. The most typical materials are polyfluorene (PF) and ladder PPP (LPPP) (Chart 1). High quantum efficiency of fluorescence and blue emission make this class of materials promising candidates for high-efficiency polymer-based electroluminescent (EL) devices.¹

However, one of the difficulties often encountered is that the light emitting diodes (LED) are unstable during operation, with a low-energy emission band gradually appearing in the range between 2.0 and 2.5 eV. This turns the desired blue color of EL into a green emission.¹ Thus, efforts are focused to find the origin of the green emission. Earlier, the long wavelength emission was considered as the emission from molecular aggregation induced by the heat treatment, especially the Joule heat generated during the operation of LEDs.² Thus the main method to remove the low-energy emission was proposed to decrease the tendency toward interaction of the polymer chains and increase the glass transition temperature by introducing big substituents. However, this interpretation was challenged first because of the failure of many attempts to remove the low-energy band by adjusting molecular structure that can restrain the excimer or aggregate formation, second because the reports that PF show spectral stability when annealed in a vacuum and LPPP showed low energy emission in dilute solution,³ and third because of the absence of π – π interactions in the single-crystal structures of fluorene polymer and oligomers.⁴

More powerful evidence confirmed that the low-energy emission bands are due to the formation of fluorenone in the polymer backbone.⁵ It was proposed that these fluorenone

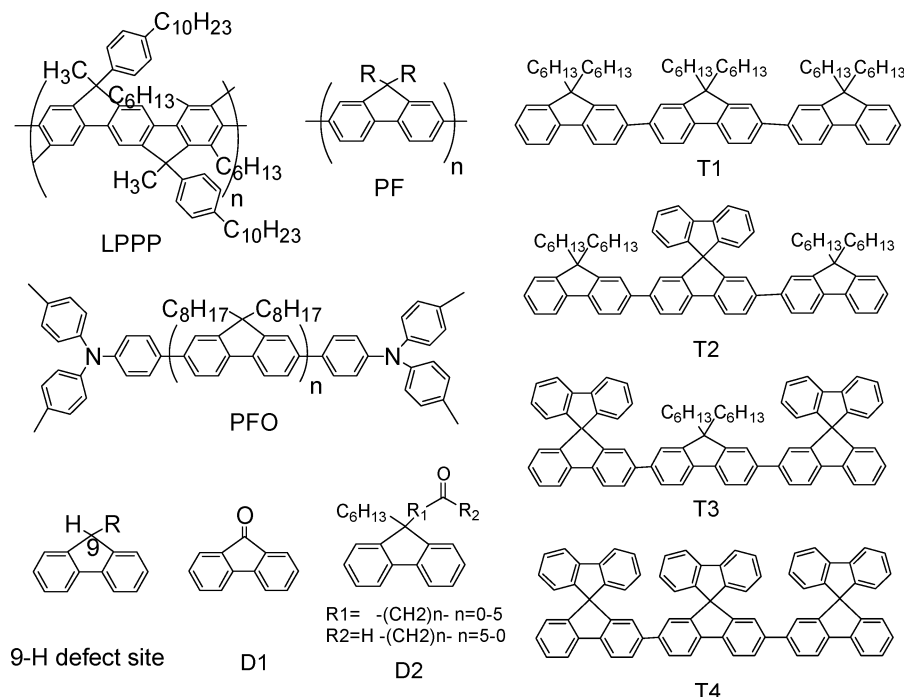
moieties are formed either from defects already present in the polymer (when monoalkylated fluorenes were present as impurities and incorporated into the polymer during polymerization) or later by thermal-oxidative, photooxidative, or electrooxidative degradation processes of PFs. The existence of monoalkylated fluorene monomer can be detected with use of potassium *tert*-butylate, due to the formation of strongly yellow colored fluorene-9-yl anions.⁶ The pristine 9-monoalkylated PF has been found to contain 9-fluorenone sites after polymer synthesis.

A new hypothesis claims that fluorenone formation is a necessary but not sufficient condition for the appearance of the green band, and the additional interchain (or intersegment) interactions are required for the appearance of the green band (e.g., fluorenone excimers).⁷ At the same time, the observations, which support the on-chain fluorenone defect emission from single polyfluorene molecules in the absence of the intermolecular interactions, are reported.⁸ Although great efforts have been made in the investigation of relationships that exist between the ketone defect formation in polymer chain and the resulting luminescence properties, the understanding of these interrelated properties is still debatable.

To resolve this problem many attempts have been reported such as purification of monomers, physical and chemical doping of polymers, etc.⁹ One of the most effective attempts to obtain stable blue emission is the introduction of stable aromatic substitutions at the bridged 9-site carbon.¹⁰ These substitutions are reported to give stable emission during heat treatment. All these results show the relationship between the nature of substitutions and the stability.

In earlier research on the formation of ketonic defects in LPPP, we have reported the kinetics of oxidation is an autocatalytic radical chain process leading to a high level of degradation that exceeds the proportion of monoalkylated fluorene sites, which is explained by the degradation of dialkyl-

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CHART 1: The Molecular Structures of LPPP, PF, 9-H Defect Site, PFO, Fluorene Trimers with Different Substituents, and Degradation Products (D1, D2)

substituted fluorene and the assistance of the alkyl side chain during the degradation.¹¹ In this paper, we report the degradation of PFs and fluorene oligomers. Our work focuses on probing the role of the alkyl side chain with the following two points, namely, (a) the photodegradation of fluorene-based compounds with different proportions of alkyl and spiro substitution and (b) products of side chain degradation. Due to definite structures of oligomers as model compounds, we have used fluorene trimers.

Experimental Section

UV-vis and fluorescence spectra were obtained on a Shimadzu UV-3100 spectrophotometer and a Shimadzu RF-5301PC spectrophotometer, respectively. IR spectra were recorded from 4000 to 800 cm⁻¹ on a Bruker IFS-66V FT-IR spectrophotometer with a Mid-IR (MIR) global source. The interferograms were recorded 32 times at the resolution of 4 cm⁻¹. A wide-band mercury-cadmium-telluride (MCT) detector was used for the FT-IR measurement. The mass spectra were recorded on a Kratos MALDI-TOF mass system. Samples were dissolved in toluene or THF. For the UV and PL measurements, samples were spin coated onto a quartz substrate. Samples for FT-IR spectra were cast onto CaF₂. Then the films were irradiated by a high-pressure mercury-arc light source (125 W) in air and recorded by PL, UV, IR, and mass spectra as a function of irradiated time. For mass spectral measurements, the pristine trimers and the soluble part of degraded trimers were cast onto copper substrates. We have tried our best to make sure that every film can undergo the same conditions.

The PFO was purchased from American Dye Sources (ADS329BE) and was used without further purification. The fluorene oligomers with different substitutions were synthesized by the Suzuki coupling reaction of monomers with different substituents,¹² and were fully characterized by ¹H NMR, ¹³C NMR, element analysis, and MALDI-TOF-MS as described in the Supporting Information.

Results and Discussion

Chart 1 shows the molecular structures of the polymers and trimers. Figure 1 shows the typical phenomenon of polyfluorene degradation. The poly(9,9-dioctylfluorene) (PFO) film displays a strong increase in the low-energy emission band when the samples are irradiated in air, and the corresponding FT-IR spectra show the increase in intensity of the C=O stretching mode (1680–1750 cm⁻¹ region). The low-energy emission and broad vibrational absorption band of PFs are very similar with those of the LPPP.^{5d,11b} In LPPP various kinds of ketonic defects have been observed, which is one of the contributing factors for the broad absorption,^{5d,11b} while fluorenone is reported as the only degraded product in PF. Sims et al. have explained that many local environments of the fluorenone correspond to the apparent broadening of this peak in PFO.⁷ To study the kinetics of the degradation and the effects of the substitution on oxidation in detail, we have synthesized a number of fluorene trimers with a different substitution pattern (Chart 1). We use spiro substitutions, as a relatively stable side chain, to dilute the proportion of the alkyl substituents. The fluorene trimer with all spiro substitutions is also prepared to determine the photostability of spiro substitution in our experimental conditions.

The absorption and emission spectra (Figure 2) show typical characteristics of fluorene trimers.¹² The absorption bands at 360 and 310 nm are assigned to the $\pi \rightarrow \pi^*$ electronic transition of the backbone and spiro side chain, respectively. The optical properties of the trimers with different substitutions are very similar. Figure 3 shows the absorption and emission spectra of the four trimers in spin-coating films. Both the absorption and emission spectra show a small red shift compared with the spectra in solutions. The emission of the high-pressure mercury-arc light source at 312 and 365 nm overlaps well with the absorption of the trimers, which would give an effective excitation during the degradation. Especially, the excitation of 312 nm would indicate the stability of the spiro side chain directly.

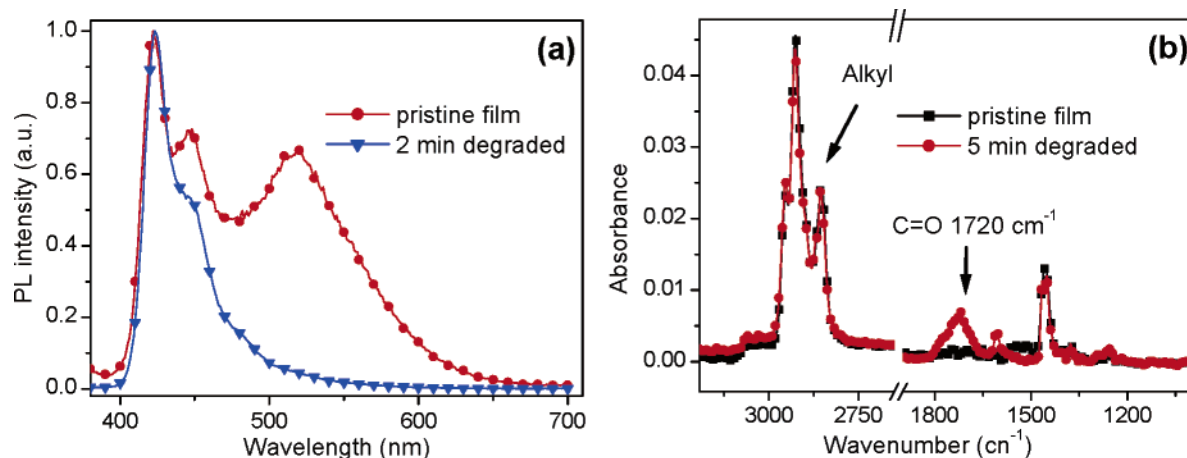


Figure 1. The emission (a) and FT-IR (b) spectra of PFO in pristine film and the subsequent photodegradation under air.

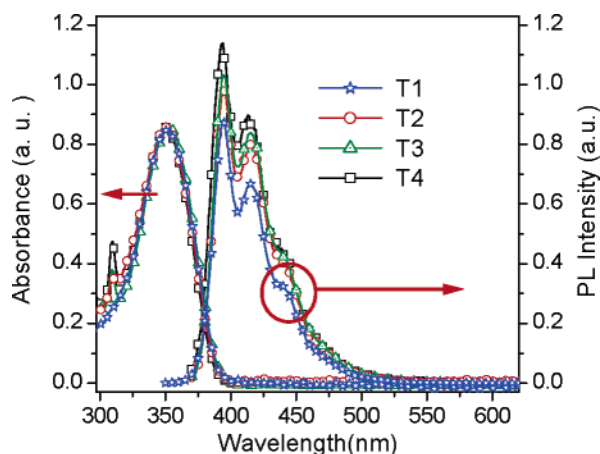


Figure 2. The absorption and emission spectra of the four oligomers in dilute toluene solutions.

Figure 4 shows the absorption spectra of a pristine film and the subsequent photodegradation under air of these four trimers. A relatively larger decrease is observed with UV irradiation for 2 min in **T1**, while little decrease is observed in this period in three other trimers at both 310 and 360 nm, which implies that the photoinduced degradation has not significantly altered the conjugated structure and spiro side chain. The decrease of absorption spectra would be due to the decrease in the oscillator strengths of the $\pi-\pi^*$ transitions, when fluorene units are replaced by fluorenone units, as described by Zojer et al.¹³

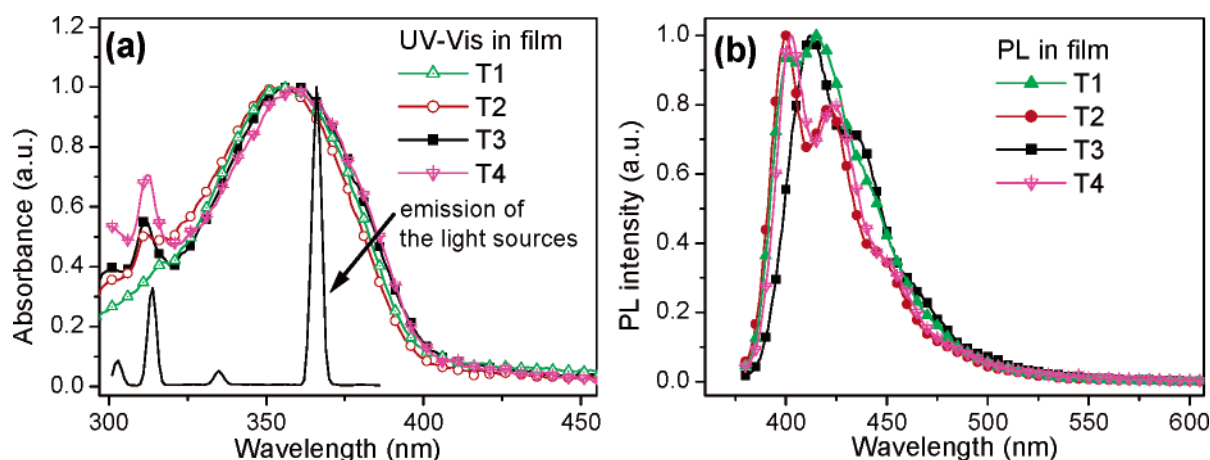


Figure 3. The absorption (a) and emission spectra (b) of the four trimers in spin-coating films. The emission spectrum of the light sources used in the photodegradation experiment is also shown in part a.

Figure 5a shows the emission spectra of a pristine **T1** spin-coating film and the subsequent photodegradation film under air. The emission of the pristine film shows a typical deep blue characteristic of the conjugated fluorene (~ 410 nm), and the low-energy emission bands around 510 nm (2.4 eV) are emerging after degradation and the intensity increases with the increase of the degradation time. When 1/3 alkyl substitution is replaced by the aromatic substitution (**T2**, Figure 5b), the low-energy emission bands can also be observed but not as strong as in **T1**. With 2/3 replacement (**T3**, Figure 5c), the low-energy emission bands cannot be clearly observed in the given degradation period, which is almost as stable as **T4** (Figure 5d). The only difference between these films is the substitution at the 9-carbon, which implies a direct relationship between the low-energy emission and substituents. To determine the role of the oxygen and morphology change, a similar experiment in a vacuum was performed for comparison according to the literature.^{3a} When the samples were irradiated in a vacuum, there was no low-energy emission, which indicated that the oxygen rather than the aggregate as the origin of the low-energy emission.

It is confirmed that the appearance of the green emission corresponds to the change of the chemical structure also revealed by FT-IR spectra before and after photooxidation. Figure 6 shows the evolution of IR spectra of a pristine film and the subsequent photodegradation under air for 5 min for **T1**, **T2**, **T3**, and **T4**. The modes at 2956, 2922, and 2852 cm^{-1} are assigned to the stretching of the alkyl side chains and those at

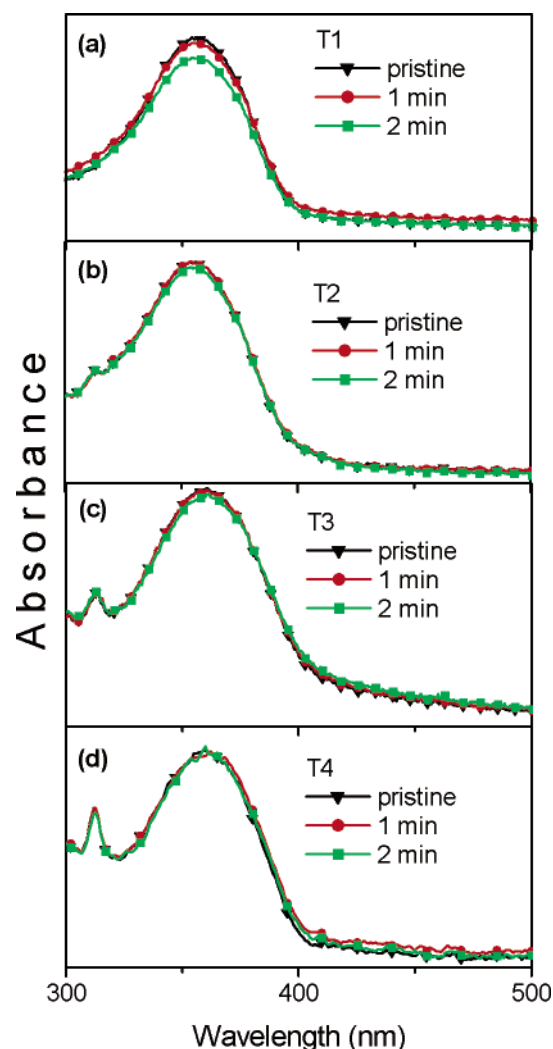


Figure 4. The absorption spectra of a pristine film and the subsequent photodegradation under air for the times specified in the legend: (a) T1, (b) T2, (c) T3, and (d) T4.

3040 and 1450 cm^{-1} to aromatic C–H stretching, which show negligible change during degradation. A new absorption band was observed at 1720 cm^{-1} in the degraded films, which correspond to the C=O stretch modes. Again, they are much more pronounced for T1 and T2 than for T3. Figure 6d shows the evolution of IR spectra of a pristine film and the subsequent photodegradation under air for 5 min for T4. We do not observe the absorption of fluorenone after degradation.

To further understand the degradation mechanism, we sum up the degradation in PL and IR spectra as a function of proportion of alkyl-substituted units (Figures 7 and 8). In PL spectra, we display the intensity ratio ($r = I_{\text{green}}/I_{\text{blue}}$) of the green emission (~ 510 nm) to the bulk blue emission band as shown in Figure 5a (to restrain the influence of reabsorption, the 0–1 band is chosen), and the result is shown in Figure 7. In the pristine films, these ratios are all near zero, which indicates the absence of the low-energy emission. After a minute degradation, the ratio for T1 is 0.3, and it is significantly higher than those for T2, T3, and T4 which are 0.17, 0.09, and 0.05, respectively. After two minutes degradation, the results are very similar ($r_{\text{T1}} = 0.72$, $r_{\text{T2}} = 0.25$, $r_{\text{T3}} = 0.13$, $r_{\text{T4}} = 0.08$). The low-energy emission decreases with the decrease in the proportion of the alkyl-substituted fluorene units, and the tangential slope of the curve increases with the increase in the alkyl proportion. However, we emphasize that the intensity in the

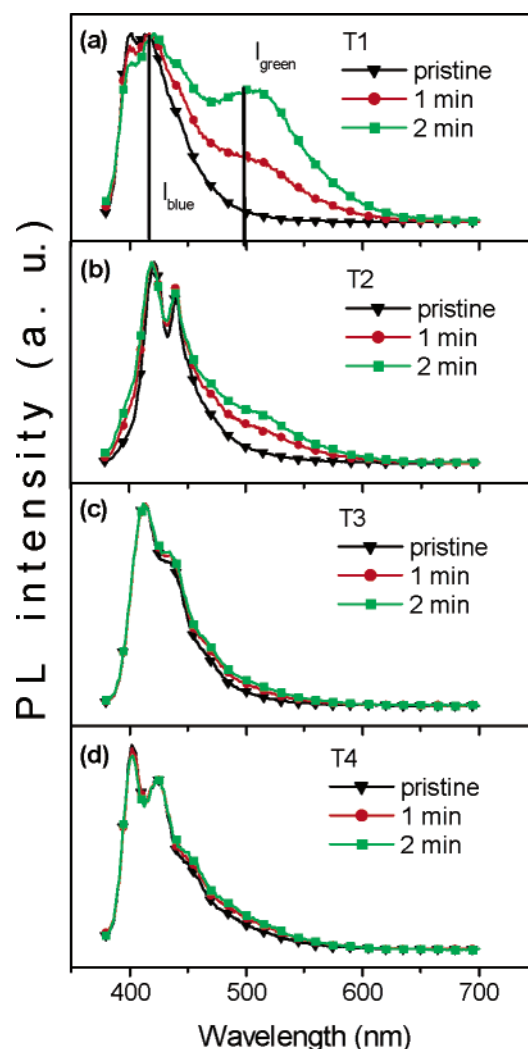


Figure 5. The normalized emission spectra of a pristine film and the subsequent photodegradation under air for the times specified in the legend: (a) T1, (b) T2, (c) T3, and (d) T4. All the films were excited with UV light of 360 nm wavelength.

emission spectra is not a direct reflection of the degradation, because the solid emission would include complex quenching, the energy transfer process, and/or interchain interaction. And these results are further evaluated by FT-IR spectra.

The intensity in IR spectra would be a direct reflection of the degradation ratio based on Lambert–Beer's law. In Figure 8, we take the intensity ratio ($R = A_{\text{CO}}/A_{\text{bulk}}$) of the ketone absorbance (1720 cm^{-1}) to bulk trimers absorbance (alkyl absorbance divide by the proportion of units substituted by alkyl), which is normalized by the intensity ratio of T1 (R_{T1}). The relative intensity ratios of T1, T2, and T3, which represent the proportion of the average rate in 5 min, decrease with the decrease in proportion of the alkyl-substituted units. If the degradation is a direct oxidation that stands on first order, the average rate in the decided period should be proportional to the concentration of the pristine reactant, and the relative intensity ratios of T1, T2, and T3 would be equal to their proportion of the alkyl-substituted units (1:0.67:0.33). (Assuming the alkyl-substituted fluorene units include the same proportion of monoalkylated fluorene units in T1, T2, and T3, the proportion of monoalkylated fluorene units in T1, T2, and T3 would also be 1:0.67:0.33.) But the relative intensity ratios of T1, T2, and T3 are 1, 0.52, and 0.22, respectively, which means the average rates in 5 min are lower than the proportion of alkyl-

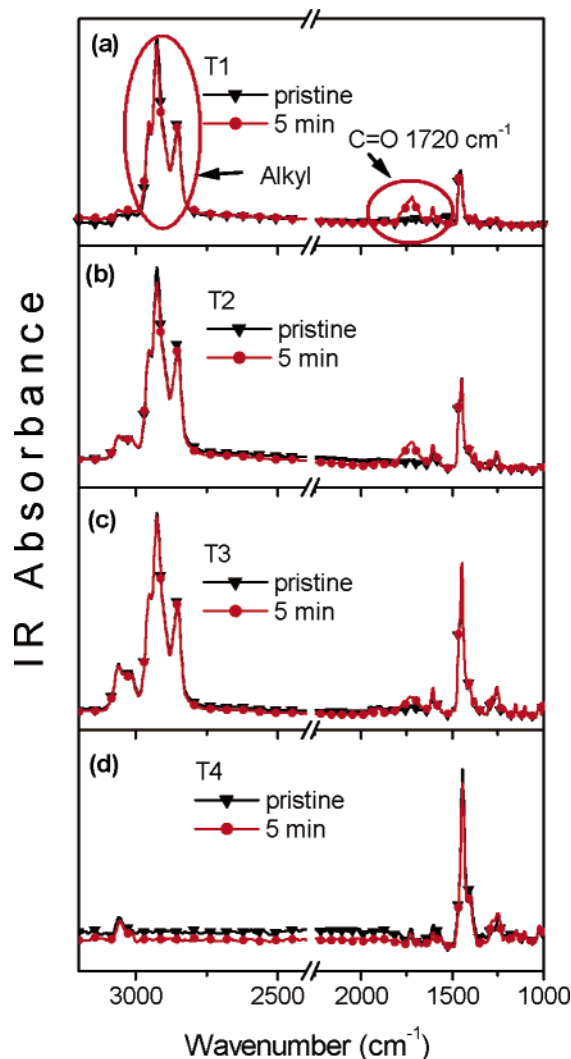


Figure 6. The IR absorption spectra of a pristine film and the subsequent photodegradation under air for 5 min: (a) **T1**, (b) **T2**, (c) **T3**, and (d) **T4**.

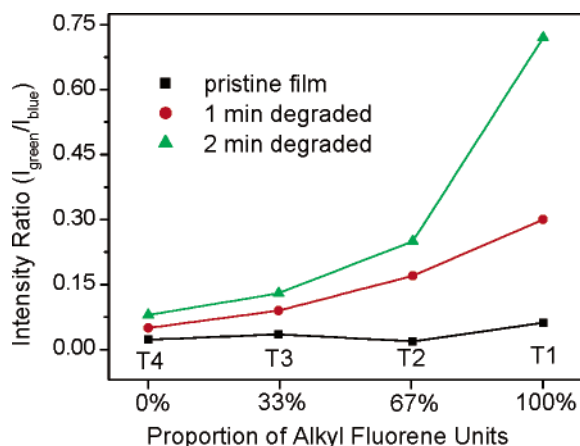


Figure 7. The intensity ratio ($I_{\text{green}}/I_{\text{blue}}$) of the green emission (~ 510 nm) to the bulk blue emission band as a function of the proportion of alkyl fluorene units (to restrain the influence of reabsorption, the 0–1 band is chosen as marked in Figure 5a).

substituted units for **T2** (0.67) and **T3** (0.33) when normalized by **T1** (1). Thus our results in fluorene trimers are similar to that in the fluorene-based ladder-type polymer as we reported before,^{11b} and point out that the degradation is not a direct oxidation and the reactive sites are not only the monoalkylated

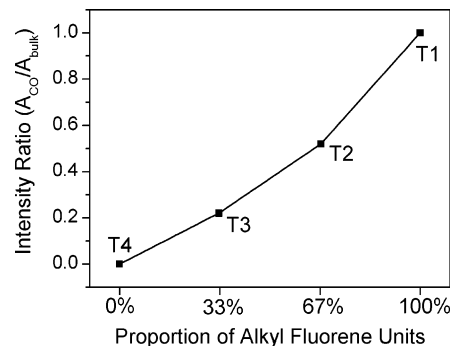


Figure 8. The intensity ratio ($R = A_{\text{CO}}/A_{\text{bulk}}$) of the ketone defects (1720 cm^{-1}) to the bulk absorption (alkyl absorbance divided by the proportion of alkyl-substituted units) as a proportion of alkyl fluorene units. The four samples are photodegraded under air for 5 min.

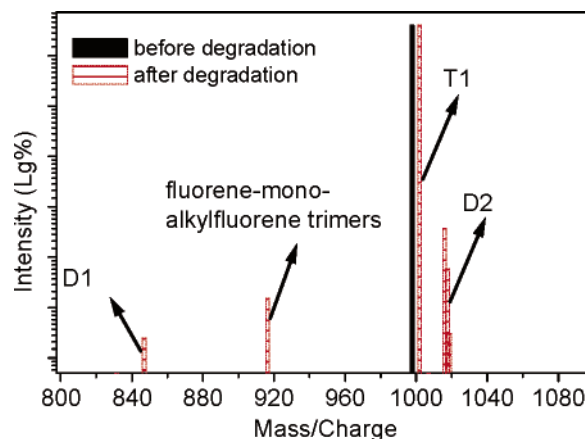


Figure 9. MALDI-TOF mass spectra of **T1** and the soluble part of 30 min photodegraded **T1**. The arrows point toward the possible products with different mass.

fluorene units but also dialkylfluorene units. The radical chain degradation would be a rationale to explain the accelerated process. For the definite structures of trimers, we can confirm this hypothesis using the structures of products.

For a long time, the degradation products were only characterized by IR spectra, or GPC,^{5f} due to the difficulties in the characterization of polymer. For the degradation of trimers, we can use the mass spectra to determine the species of degradation products by their masses. It turned out that MALDI-TOF mass spectrometry is an ideal tool for the investigation of model compounds such as conjugated carbazole and fluorene trimers. Since molecules such as fluorene trimers strongly absorb ionizing laser light and are able to form extremely stable radical cations, no signals except that of the M^+ ion are visible. This makes MALDI-TOF a powerful tool for analysis of model compounds and oligomeric mixtures.¹⁴ Figure 9 shows the MALDI-TOF mass spectra of **T1** and the soluble part of its UV degradation resulting products, which is the clearest out of the four trimers. Pristine **T1** gives one peak at 998, which corresponds to its theoretical mass (999), while in degraded **T1**, the peak of **T1** shifts to 1000. (We do not know why this difference is observed between pristine and degraded films, but we observed similar results in all four trimers.) The degraded film of **T1** also gives three additional peaks, which may correspond to the three types of degradation products. The peak at 845 can be assigned to fluorene–fluorenone trimers (one of the dialkyl fluorene units is replaced by **D1** in Chart 1), which is another evidence of the fluorenone formation. The peak at 915 can be assigned to fluorene–monoalkylfluorene trimers (one of the dialkyl fluorene units is replaced by the 9-H defect site in

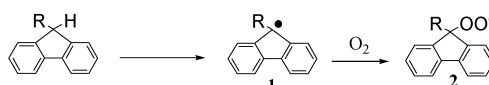
Chart 1). For masses of these two compounds that are smaller than **T1**, we are not sure whether they are molecular fragments or degraded products, especially for fluorene–monoalkylfluorene trimers. But for these peaks that are not observed in pristine film, the peak at 915 would indicate the increase of probability of monoalkylfluorene formation at least. There is another peak around 1014 with a mass bigger than that of **T1**, and so we are sure that these peaks are from oxidation products of **T1** and not fragments. As its mass is easily 14 bigger than that of **T1** (two hydrogen (2) are replaced by one oxygen (16)), it would be assigned to the products of side chain oxidation (one of the dialkylfluorene units is replaced by **D2** in Chart 1). This result is a direct evidence of the side chain degradation. Because the alkyl ketone gives a characteristic peak around 1720 cm^{-1} in FT-IR spectra as does fluorenone, it is difficult to determine by FT-IR spectra. Alkyl ketone does not give low-energy emission as fluorenone, but it would be a fluorescence quencher. All of these three masses can correspond to more than one structure (9-site and side chain in trimers can degrade to different structures with the same mass), thus three masses may include more than 10 kinds of products, which is the reason for the failure to separate the mixture by LC-MS. The intensity of peaks cannot indicate the concentration as every degradation product shows a different ability for ionization. The solubility of the degraded trimers is strongly dependent on the degradation time. For a short-time degradation, the entire film is soluble, but the ratio of the degradation is too low to be detected by the mass spectra. However, for a long-time degradation, part of the film is insoluble. These insoluble parts are widely reported for PF degradation, and are caused by the high degree of degradation and/or cross-linking.^{5f,7} Thus the concentration of each defect depends on the experimental conditions.

From these results, we conclude that the degradation of polyfluorene and fluorene oligomers strongly depends on the proportion of alkyl side chain units. The assistance of alkyl during degradation is directly confirmed by the observation of alkyl oxidation product. As described earlier,¹⁰ the aromatic side chain is very stable toward oxidation. In Scheme 1, we have outlined a likely mechanism to explain the degradation by the chain reaction. The 9-H site is removed to initiate the chain reaction by forming radicals **1** and by reaction with oxygen to form peroxy radicals **2**. The peroxy radicals **2** abstract hydrogen from the side chain to form peroxide **3** and radical **1'** in the side chain. Radical **1'** in the side chain can also react with oxygen and abstract hydrogen from the polymer to form peroxide **3'**. If the hydrogen is abstracted from the α -site of the alkyl side chain (**1''**), it then forms peroxide **3''** and can undergo a final rearrangement to form a second radical **1** in the backbone. The peroxides **3** and **3'** undergo a similar oxidation process to form fluorenone (**D1**) and alkyl ketone (**D2**). We attribute the accelerated process observed in PL and FT-IR spectra to the radical chain degradation. The decrease of the alkyl proportion will decrease the radical propagation process, so an increase in stability is very obvious.¹⁵

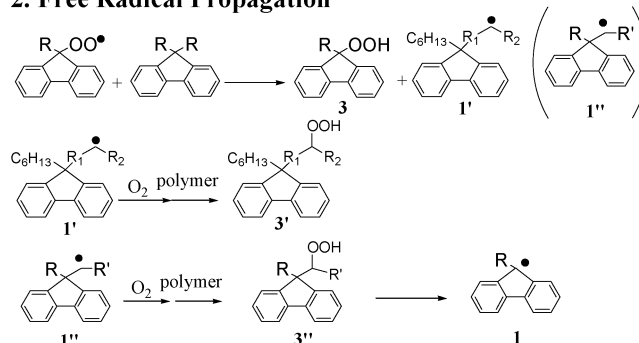
On the basis of the proposed mechanism, the good stability of fluorene oligomers with aromatic side chains is connected to the absence of any aliphatic hydrogens, which suppresses the initiation and propagation of the radical oxidation cascade. First, The alkylation procedure for the alkylated fluorene would induce monoalkylated sites, which can be transformed to keto sites. On the other hand, the aromatic fluorene is synthesized by the ring-closure reaction via a polymer-analogous intramolecular Friedel–Crafts alkylation, which would not introduce any structure that can be transformed to keto sites.^{10a} But this

SCHEME 1: Proposed Mechanism of the Ketone Defects Formation in PF and Fluorene Trimers

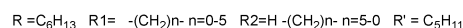
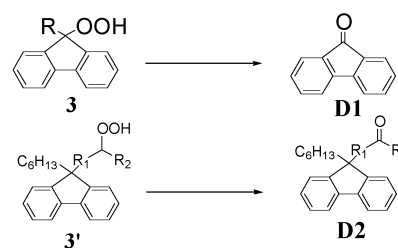
1. Initiation



2. Free Radical Propagation



3. Formation of ketonic defects



procedure is very similar to that of LPPP, and the ketone defect formation in LPPP is reported, which indicates the explanation of different synthetic routes is not enough.^{5d} Second we emphasize the important role of alkyl during free radical propagation as discussed above. Thus to reach a stable blue emission, the alkyl chain should not be linked at the 9-site directly.

Conclusion

We have compared the photostability of fluorene trimers with different substituents. The degradation of polyfluorene and fluorene oligomers is a radical chain reaction, which strongly depends on the proportion of alkyl side chain units. The assistance of the alkyl during degradation is directly confirmed by the observation of alkyl oxidation products. The aromatic substitution is essential for improving the stability, because it can effectively restrain the radical chain reaction. From our experiment, we propose replacing the alkyl side chains with other substitutions that can well restrain the propagation of the radicals or doping with antioxidant that can restrain the initiation in order to reach a stable blue emission.

Acknowledgment. We are grateful for financial support from National Science Foundation of China (grant nos. 20573040, 20474024, 20125421, 90101026, and 50303007), from the Ministry of Science and Technology of China (grant nos. 2002CB6134003 and 2003CB314703), and from PCSIRT.

Supporting Information Available: Characterization of trimers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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