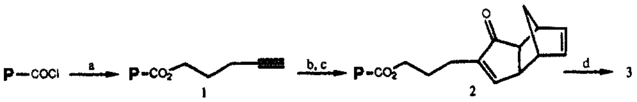
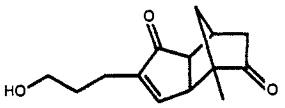
Scheme I[a]



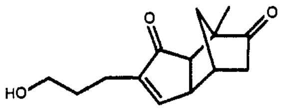
[a] (a) $HC\equiv CCH_2CH_2CH_2OH$, pyridine, 25 → 100 °C, 24 h; (b) $Co_2(CO)_8$, C_6H_6, 25 °C, 3 h; (c) norbornadiene, C_6H_6, 80 °C, 6 h; (d) $(n\text{-}C_4H_9)_4N^+Cl^-$, KOH, H_2O, THF, 80 °C, 48 h.

with $Co_2(CO)_8$ formed the polymer-linked alkyne–$Co_2(CO)_6$ complex.[10] Heating this complex in the presence of 5 equiv of norbornadiene in benzene led to the *polymer-linked* Pauson–Khand product **2**,[11] which upon cleavage of the ester linkage (via the extremely convenient procedure shown) gave free tricyclic enone **3** in nearly analytically pure form. Based on a set of control experiments, which determined the concentration of pentynyl ester groups to be 0.87 mequiv/g of **1**, the overall yield of **3** from **1** was 69%.[12,13]

Pauson–Khand cycloaddition of 4-pentyn-1-ol with 1-methyl-5-norbornen-2-one under the usual homogeneous conditions affords less than 10% of a mixture of impure regioisomeric products **4** and **5**. The corresponding polymer-based reaction, carried out exactly as described above except for a longer heating period for the cycloaddition itself (48 h), gave rise to the same products *in 99% yield after isolation and chromatographic purification*! The 30:70 regioisomer ratio (**4**:**5**) is precisely that found in homogeneous cycloaddition of this alkene with propyne and has been rationalized previously.[14]

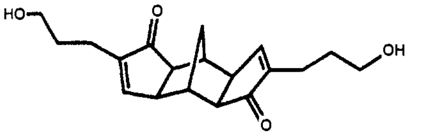


4



5

In order to examine the degree of isolation of polymer-bound alkyne complexes in the context of this chemistry, we repeated the sequence in Scheme I, but only 1 equiv of norbornadiene was used in the cycloaddition. The result was a 20% yield of double-cycloaddition product **6**. This outcome is nonetheless an improvement over that of the same reaction done in homogeneous solution, in which only traces of product were detected.[15] Thus the alkyne moieties are "isolated" enough to reduce their tendency to undergo trimerization, but enough flexibility is retained to permit interaction between the polymer-bound monocycloaddition product (i.e., **2**) and an unreacted polymer-bound alkyne complex.



6

We have previously observed dimerization and polymerization of norbornadiene accompanying its Paulson–Khand cycloadditions;[16] these processes no doubt contribute to limiting the benefits of polymer attachment of the alkyne in these cases. In the case of 1-methyl-5-norbornen-2-one, which is inert to self-condensation under the reaction conditions, suppression of side reactions of the alkyne is sufficient to permit virtually quantitative yields of cocycloaddition to occur, a remarkable result. Thus application of similar methodology to other types of cycloaddition reactions now becomes very attractive, provided that the causes of reaction inefficiency in homogeneous solution may be effectively targeted for suppression by polymer attachment. All of the above reactions benefit from enormous reductions in the effort required to obtain pure produts, more than compensating for the additional polymer-related manipulations. A variety of directions are planned for the development of this methodology, including variation of the degree of cross-linking of the polymer, and polymer attachment of both alkyne and alkene substrates simultaneously, a subset of which will be application to substrates for intramolecular cycloaddition reactions. The results of these studies will be reported in due course.

Acknowledgment. We are grateful to the National Institutes of Health (Grant GM 26294) and the Chevron Research Corporation for financial support of this research. We thank Megan Skaggs and Clarence Silva for performing some control experiments at early stages of this work.

Supplementary Material Available: Experimental details for the preparation and identification of **2**–**6**, tables of ^1H and ^{13}C NMR data, and a spectrum for $C_{19}H_{24}O_2$ (10 pages). Ordering information is given on any current masthead page.

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(10) IR (mull): ν_{CO} 2016, 2052, 2093 cm^{-1}.

(11) IR (mull): 1603, 1710, 3026 cm^{-1}.

(12) Specifically, 0.87 mequiv of free alcohol is obtained from hydrolysis as described (Scheme I) of 1 g of polymeric ester. Thus inefficiency in either attachment or removal of alcohol from the polymer is effectively canceled out through the use of this value, and the yield stated is a true *cycloaddition* yield for the polymer-bound alkyne.

(13) Cycloaddition products have been characterized by ^1H NMR, ^{13}C NMR, IR, high-resolution MS, and, for **3**, elemental analysis.

(14) MacWhorter, S. E.; Sampath, V.; Olmstead, M. M.; Schore, N. E. *J. Org. Chem.* **1988**, *53*, 203. The yield in that reaction was 55%.

(15) The analogous homogeneous reaction of norbornadiene with propyne affords a 17% yield of double-cycloaddition product, analogous to **6**: Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc., Perkin Trans. 1* **1973**, 977.

(16) Schore, N. E. *Synth. Commun.* **1979**, *9*, 41.

Direct Measurement of the Absolute Kinetics of Chlorine Atom in CCl_4[1]

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Ground-state singlet dichlorocarbene is the "standard" in the empirical correlation of carbenic selectivity that was so elegantly developed by Moss.[2,3] Therefore, nearly all singlet carbene reactivity may be directly referred to by the relative reactivity of dichlorocarbene ($:CCl_2$). Unfortunately, due to the lack of suitable photolabile precursors, there has been no direct detection of $:CCl_2$ in solution to date. Recently, there have been intriguing reports, however, by Washio and co-workers,[4] and earlier, by Bühler,[5] that have tentatively assigned the UV band generated by pulse radiolysis of CCl_4 to dichlorocarbene. These reports, in view of the overall importance of $:CCl_2$ to carbene chemistry, warranted further investigation. Herein, we report that the above

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(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-3233 from the Notre Dame Radiation Laboratory.

(2) For a review of carbene selectivity, see: Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58–64.

(3) see, also: (a) Moss, R. A.; Jones, M., Jr. *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley-Interscience: New York, 1981; Vol. 2, Chapter 3. (b) Moss, R. A.; Jones, M., Jr. *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Ed.; Wiley-Interscience: New York, 1978; Vol. 1, Chapter 3. (c) Moss, R. A., Jones, M., Jr., Eds. *Carbenes*; Wiley-Interscience: New York, 1975; Vol. II. (d) Moss, R. A., Jones, M., Jr., Eds. *Carbenes*; Wiley-Interscience: New York, 1973; Vol. 1. See, in particular: Moss, R. A. *Ibid*. Chapter 2. (e) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971. (f) Hine, J. *Divalent Carbon*; Ronald Press: New York, 1964.

(4) (a) Washio, M.; Yoshida, Y.; Hayashi, N.; Kobayashi, H.; Tagawa, S.; Tabata, Y. *Radiat. Phys. Chem.* **1989**, *34*, 115–120. (b) Washio, M.; Yoshida, Y.; Hayashi, N.; Kobayashi, H.; Tagawa, S.; Tabata, Y. *Radiation Research, Proceedings of the 8th International* Congress *on Radiation Research*; Fielden, E. M., Fowler, J. F., Endry, J. H., Scott, D., Eds.; Taylor and Francis: London, 1987; Vol. 1, p 29.

(5) Bühler, R. E. *Radiat. Phys. Chem.* **1983**, *21*, 139–146. Büchler and co-workers also supported their assignment with an ab initio study[6] that predicts a $^1A_1 \rightarrow {}^1B_1$ electronic transition for $:CCl_2$ to occur at 3.90 eV (318.4 nm).

(6) Ha, T.-K.; Gremlich, H. U.; Bühler, R. E. *Chem. Phys. Lett.* **1979**, *65*, 16–18.

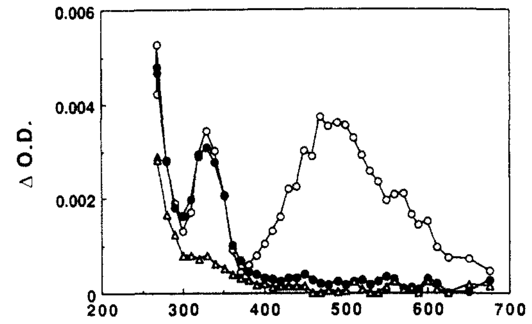

Figure 1. UV-visible time-resolved spectra obtained 20 (○), 250 (●), and 750 ns (△) after pulse radiolysis of N_2-saturated CCl_4.

UV absorption band has been generated by three independent methods and the bimolecular reactivity of this transient shows *no* correlation with known singlet carbene chemistry.[3] The transient species responsible for the absorption spectrum is, in fact, chlorine atom.[7] Several of what represent the first directly monitored absolute bimolecular rate constants for the reactions of chlorine atom in CCl_4 are presented.

A direct comparison of nanosecond time-resolved pulse radiolysis and 266-nm laser flash photolysis (LFP) of liquid CCl_4 reveals that identical transient species are observed. The electronic absorption spectrum observed immediately after pulse radiolysis[8] (10-ns pulse of 8-MeV electrons, dose ≈ 800 rd/pulse)[9] of CCl_4 consists of three distinct species (see Figure 1). The UV (λ_{max} = 330 nm) and visible absorption bands decay independently (τ = 173 and 17 ns, respectively). The UV band (λ_{max} = 330 nm) is produced "instantaneously", i.e., completely formed within the irradiation pulse. The broad visible band is generally believed to be due to some associated form of CCl_3^{+}.[10] The absorption increasing in intensity from 300 to 270 nm is, at least in part, attributed to the $^{\bullet}O_2CCl_3$ radical.[11]

LFP[12] of neat CCl_4, with relatively high focus and laser energy (~20 mJ/pulse) of 266-nm light, results in absorption spectra that are spectroscopically and temporally identical with Figure 1. The UV absorption band (monitored at 330 nm throughout this work) is also produced "instantaneously" and decays with (pseudo)-first-order kinetics[13] ($k_{exptl} = 5.8 \times 10^6$ s^{-1}), and its lifetime[14] (τ = 172 ns) is the same in N_2-, air-, and O_2-saturated solution. However, upon addition of certain substrates, an increase in the observed rate of decay, k_{exptl}, is readily observed. The bimolecular rate constant, k, can therefore be calculated in the usual manner, according to $k_{exptl} = k_0 + k[s]$, where k_0 is the rate of decay is the absence of substrate s. A comparison of rate constants from pulse radiolysis and LFP, (1.0 ± 0.1) and (1.1 ± 0.5) × 10^{10} M^{-1} s^{-1}, respectively, obtained from the cyclopentene bimolecular quenching plots (see Figure 2) demonstrates that the transients observed after each type of irradiation are kinetically identical. This point is also illustrated by the results obtained with CH_2Cl_2 and $CHCl_3$ as reactants by pulse radiolysis [(8.9 ± 1.7) and (1.2 ± 0.3) × 10^7 M^{-1} s^{-1}] and by LFP [(7.2 ± 0.8) and (1.8 ± 0.1) × 10^7 M^{-1} s^{-1}] (see Figure 2, insert).

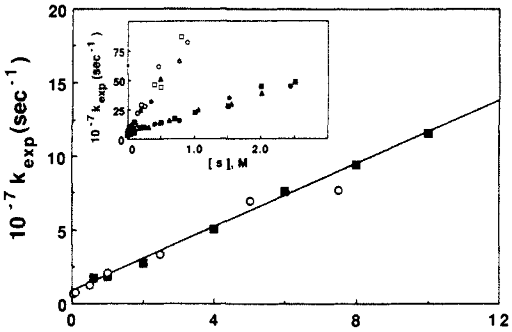

Figure 2. Dependence of the rate of decay of the 330-nm transient in CCl_4 with added cyclopentene generated by pulse radiolysis (○) and 266-nm LFP (■). Insert: quenching plots with added CH_2Cl_2 (open symbols) and $CHCl_3$ (closed symbols) by pulse radiolysis of CCl_4 (○, ●), 266-nm LFP of CCl_4 (□, ■), and 355-nm LFP of Cl_2 (△, ▲); see text.

Absolute rate constants of (12 ± 7), (6.7 ± 0.6), and (6.9 ± 1.1) × 10^9 M^{-1} s^{-1} were obtained by LFP[15] for the reactions of the UV transient with 2,3-dimethyl-2-butene, methyl acrylate, and acrylonitrile, respectively. Although the observed reactivity of this transient may qualitatively mimic that of singlet carbenes, it does not quantitatively coincide with the reactivity of $:CCl_2$. Relative reactivities of 78.4, 0.060, and 0.047 have previously been determined[16] for the reactions of $:CCl_2$ with $Me_2C{=}CMe_2$, $CH_2{=}CHCO_2Me$, and $CH_2{=}CHCN$, respectively. This would represent a discrepancy of 3 orders of magnitude between the relative and absolute data. Furthermore, the absolute reactivities of the 330-nm transient are much greater than those reported for phenylchlorocarbene,[17] which is inconsistent with the "carbene selectivity index and spectrum" of Moss.[2,16]

Absolute rate constants of (9.9 ± 1.3), (8.0 ± 0.8), (5.7 ± 0.3), and (3.8 ± 1.2) × 10^9 M^{-1} s^{-1} were also obtained[15] for reaction with cyclohexene, cyclohexane, methanol, and triethylsilane. Clearly, the indiscriminate nature of the UV transient demonstrates that this species cannot be attributed to $:CCl_2$. The observed kinetics are consistent, however, with chlorine atom reactivity. A limited number of absolute rate constants for chlorine atom in solution have been determined by "probe" techniques.[20-23] Competitive formation of the chlorine atom/DMSO complex has yielded rate constants for reactions of chlorine atom with cyclohexene (1.2 × 10^{10} M^{-1} s^{-1}) and CH_2Cl_2 (9 × 10^6 M^{-1} s^{-1}) in CH_2Cl_2[22] and with methanol (2.7 × 10^9 M^{-1} s^{-1}) in CCl_4.[23]

Spectroscopic and kinetic confirmation that chlorine atom is responsible for the 330-nm band was obtained by independent generation of the species by 355-nm LFP of molecular chlorine Cl_2, in CCl_4. Photodissociation of Cl_2 results in a UV absorption band for chlorine atom identical with that in the pulse radiolysis and the 266-nm LFP of CCl_4 (vide supra), that reacts with CH_2Cl_2

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[7] Recently, it has been demonstrated that the absorption spectra of "free" chlorine atom in halogenated solvents are attributed to charge-transfer transitions, and the band maxima are dramatically solvent dependent. Chateauneuf, J. E. *Chem. Phys. Lett.* Submitted.

[8] The Radiation Laboratory LINAC pulse radiolysis apparatus has previously been discussed in detail. Janata, E.; Schuler, R. H. *J. Phys. Chem.* **1982**, *86*, 2078-2084.

[9] Determined by thiocyanate dosimetry.

[10] For summaries of published assignments, see: Emmi, S. S.; Beggiato, G.; Casalbore-Miceli, G. *Radiat. Phys. Chem.* **1989**, *33*, 29-37. Bühler, R. E. *Ibid.* **1983**, *21*, 139-146.

[11] This radical is formed by reaction of $^{\bullet}CCl_3$ with residual O_2 in solution. The degree of degassing directly determines the amplitude and growth kinetics of this absorption, which dramatically increases in O_2-saturated solution. The UV absorptions of $^{\bullet}O_2CCl_3$ independently generated from $^{\bullet}CCl_3$ + O_2 are known: Shen, X.; Lind, J.; Eriksen, T. E.; Merényi, G. *J. Phys. Chem.* **1989**, *93*, 553-557. Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.* In press.

[12] The LFP equipment is described elsewhere. Nagarajan, V.; Fessenden, R. W. *J. Phys. Chem.* **1985**, *89*, 2330-2335.

[13] The first-order kinetics are attributed to reaction with trace impurities.[14]

[14] τ is crucially dependent on CCl_4 purity. Therefore, CCl_4 was passed through alumina and distilled from K_2CO_3 (35-cm Vigreux column) prior to use.

[15] The kinetics were obtained by 266-nm LFP of CCl_4 purely for experimental convenience.

[16] Moss, R. A.; Munjal, R. C. *Tetrahedron Lett.* **1979**, 4721-4724.

[17] For instance, the k values for reaction of phenylchlorocarbene with $Me_2C{=}CMe_2$,[18] $Me_2C{=}CHMe$,[18] t-$MeCH{=}CHEt$,[18] $CH_2{=}CH$-n-C_4H_9,[18] and Et_3SiH[19] are 28, 13, 0.55, 0.22, and 0.25 × 10^7 M^{-1} s^{-1}, respectively.

[18] Moss, R. A.; Perez, L. A.; Turro, N. J.; Gould, I. R.; Hacker, N. P. *Tetrahedron Lett.* **1983**, *24*, 685-688.

[19] Doyle, M. P.; Taunton, J.; Oon, S.-M.; Liu, M. T. H.; Soundararajan, N.; Platz, M. S.; Jackson, J. E. *Tetrahedron Lett.* **1988**, *29*, 5863-5866.

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[21] Breslow, R.; Brandl, M.; Hunger, J.; Turro, N.; Cassidy, K.; Krogh-Jespersen, K.; Westbrook, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 7204-7206.

[22] Alfassi, Z. B.; Mosseri, S.; Neta, P. *J. Phys. Chem.* **1989**, *93*, 1380-1385.

[23] Sumiyoshi, T.; Miura, K.; Hagiwara, H.; Katayama, M. *Chem. Lett.* **1987**, *7*, 1429-1430.

and $CHCl_3$ with bimolecular rate contants[24] of (8.2 ± 0.8) and (1.4 × 0.1) × 10^7 M^{-1} s^{-1}, respectively (see Figure 2, insert).

In summary, the absorption spectrum observed following pulse radiolysis of CCl_4 has erroneously been assigned to dichlorocarbene.[4,5] The transient species has been identified as chlorine atom. A "clean" method (266-nm LFP) for direct study of the important reactions of chlorine atom, e.g., photochlorination reactions, is presented, and several absolute bimolecular rate constants for the reaction of chlorine atom in CCl_4 are reported.

Currently, the effect of other "inert" solvents on the reactivity of "free" chlorine atom are being pursued.

Registry No. CCl_4, 56-23-5; CCl_3^+, 27130-34-3; $\cdot O_2CCl_3$, 69884-58-8; CH_2Cl_2, 75-09-2; $CHCl_3$, 67-66-3; $:CCl_2$, 1605-72-7; Cl, 22537-15-1; Cl_2, 7782-50-5; 2,3-dimethyl-2-butene, 563-79-1; methyl acrylate, 96-33-3; acetonitrile, 107-13-1; cyclohexene, 110-83-8; cyclohexane, 110-82-7; methanol, 67-56-1; triethylsilane, 617-86-7.

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(24) No evidence of a radical chain depletion of Cl_2 was observed with these substrates.

Phosphorescence and Optical Detection of Magnetic Resonance Studies of Poly(methylpropylsilylene)

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Received April 27, 1989

The nature of the excited states of polysilylenes has attracted considerable attention.[1-4] Fairly intense fluorescence is observed at around 350 nm, and on the basis of the narrow spectral width of the fluorescence, the concept of a high degree of delocalization of the $^1(\sigma,\sigma^*)$ excited state of the polymers has been widely accepted.[3] Most previous studies on the excited states of polysilylenes are, however, limited to singlet states. Observation of the phosphorescence is scarce, except for polymers having aromatic pendants,[5] and the character of the triplet excited states of polysilylenes is not well elucidated. Michl et al.[1] recently reported that the fairly weak long-lived emission observed for poly(methylpropylsilylene), hereafter referred to as $(MePrSi)_n$, at 77 K was the phosphorescence. Harrah and Zeigler[2] also reported phosphorescence for several polysilylenes including $(MePrSi)_n$. The phosphorescence spectrum reported by Michl et al. is broad and structureless, whereas that reported by Harrah and Zeigler shows fine structure. Even though the two reported spectra are somewhat different in structure, they are both fairly broad (half-width of ~4500 cm^{-1}), and this broad feature is in sharp contrast to the narrow (half-width of ~400 cm^{-1}) fluorescence. Both groups of authors[1,2] attributed the broadness to the localized nature of the triplet excited state.

Most of the previous luminescence studies have been carried out at temperatures higher than 77 K. We have investigated the long-lived emission of $(MePrSi)_n$ at 4.2 K or below, and in this communication, we report the existence of the new phosphorescence which should be attributed to the emission from the delocalized triplet state.

$(MePrSi)_n$ was kindly synthesized by Dr. Fujino of NTT. The molecular weights of the synthesized polymer range from ~10^4 to ~10^6, and the main peak is located at molecular weight 2.0 × 10^4. There is another minor peak at molecular weight 1.7 × 10^6. The fluorescence and phosphorescence spectra were measured in a benzene solution and for a spin coated film on a SiO_2 substrate. Both samples give essentially identical spectra. The optical detection of magnetic resonance (ODMR) studies were carried out at 1.3 K for a benzene solution (concentration of 1.0 × 10^{-2} M/monomer repeat) with the apparatus described previously.[6-8] Light from an Ushio 500-W xenon lamp passed through a water filter was used for the excitation source.

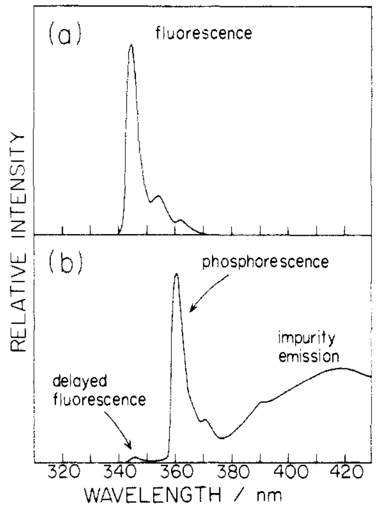

Figure 1. (a) Fluorescence spectrum and (b) long-lived emission of poly(methylpropylsilylene) (spin coated film) at 4.2 K. The assignments of the long-lived emission bands are also shown in b.

The fluorescence spectrum of $(MePrSi)_n$ observed at 4.2 K is shown in Figure 1a. The progression of the 740-cm^{-1} carbon–silicon stretching vibration is built on the intense 0,0 band at 345 nm as was previously observed by Kagawa et al.[3] Figure 1b shows the long-lived emission recorded by means of a phosphoroscope at 4.2 K in the time range of 1–4 ms after the excitation. An intense peak is located at 360 nm, and the vibrational progression of 740 cm^{-1} appears similar to the fluorescence. The quantum yield of the phosphorescence was not determined, but we estimate that it is of the order of ~10^{-4} or less. Besides this intense band, there exists a tiny band at 345 nm, exactly the same position as the fluorescence. For the reasons to be described below, we assign these two bands to phosphorescence and delayed fluorescence, respectively. The broad band at longer wavelengths (~420 nm) is due to an impurity[9] since the excitation spectrum differs from the absorption spectrum. The identification of the two newly observed bands as phosphorescence and delayed fluorescence is mainly due to (1) the decay analysis and (2) ODMR experiments, as discussed in the following sections.

The decays of the 360- and 345-nm bands are both nonexponential. The nonexponentiality is successfully analyzed in terms of a kinetic scheme involving the triplet–triplet annihilation process. If the singlet excited state (S_1) is generated by the annihilation of two triplet excited states (T_1), the populations of T_1 and S_1 should be expressed as follows:[10,11]

$$1/n_T(t) = [1/n_T(0) + k_{TT}/k_P] \exp(k_P t) - k_{TT}/k_P \quad (1)$$

$$[1/n_S(t)]^{1/2} = [\{1/n_S(0)\}^{1/2} + (k_F k_{TT}/f k_P{}^2)^{1/2}] \exp(k_P t) - (k_F k_{TT}/f k_P{}^2)^{1/2} \quad (2)$$

where k_P and k_F are respectively the first-order decay rate con-

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(1) Michl, J.; Downing, W.; Karatsu, T.; McKinley, A. J.; Poggi, G.; Wallraff, G. M.; Sooriyakurmaran, R.; Miller, R. D. *Pure Appl. Chem.* **1988**, *60*, 959.

(2) Harrah, L. A.; Zeigler, J. M. In *Photophysics of Polymers*; Hoyle, C. E., Torkelson, J. M., Eds.; ACS Symposium Series 358; American Chemical Society: Washington, DC, 1987.

(3) Kagawa, T.; Fujino, M.; Takeda, K.; Matsumoto, N. *Solid State Commun.* **1986**, *57*, 635.

(4) Ito, O.; Terazima, M.; Azumi, T.; Takeda, K.; Fujino, M.; Matsumoto, N. *Macromolecules* **1989**, *22*, 1718.

(5) Todesco, R. V.; Kamat, P. V. *Macromolecules* **1986**, *19*, 196.

(6) Yamauchi, S.; Azumi, T. *J. Chem. Phys.* **1977**, *67*, 7.

(7) Murao, T.; Azumi, T. *J. Chem. Phys.* **1979**, *70*, 4460.

(8) Asano, S.; Aita, S.; Azumi, T. *J. Phys. Chem.* **1983**, *87*, 3829.

(9) The origin of the impurity is unknown at present. The impurity emission does not increase upon light irradiation at liquid helium temperatures, and hence, it appears that the impurity is somehow introduced during the synthesis. It may be worth mentioning that the polymer synthesized by anionic polymerization (see: Sakamoto, K.; Obata, K.; Hirata, H.; Nakajima, N.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 7641) also shows similar but somewhat less impurity emission.

(10) Tanaka, Y.; Azumi, T. *Inorg. Chem.* **1986**, *25*, 247.

(11) Tanaka, Y.; Azumi, T. *Chem. Phys. Lett.* **1986**, *132*, 357.

0002-7863/90/1512-444$02.50/0