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Author(s)	Gohdo, Masao; Tagawa, Seiichi; Kan, Koichi et al.
Citation	Radiation Physics and Chemistry. 2022, 196, p. 110105
Version Type	AM
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Direct ionization-driven observational approaches for radical cation formation in solution for pulse radiolysis

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Abstract

Radical cations' dynamics in early stage reactions in the ionizing radiation induced reaction is essential to understanding the whole reaction scheme. The observation of radical cations in tetrahydrofuran (THF) solutions was demonstrated for time-resolved measurements using pulse radiolysis. The designedly concentrated solutions enabled the observation of the direct ionization-driven radical cations. In THF, the transient absorption spectra of the biphenyl radical cations, which were generated through direct ionization of biphenyl under electron beam irradiation, were found to be associated with the biphenyl radical anions generated by the attachment of an excess electron to the biphenyl. Furthermore, when polystyrene (PS) was used as the solute in THF solutions, transient absorption spectra of the dimer radical cations containing solvated electrons of PS were observed. The findings, therefore, indicate that the time-resolution-based limitation on the radical cation-forming process observation, which was imposed by the diffusion-limited reactions of the solvent radical cations with the solute, could be overcome by employing direct ionization in THF. This method can be employed to study the reactivity of radical cations with solvents and the stability of radical cations in fluid media.

Keywords

Pulse radiolysis; direct ionization; transient absorption; radical cation observation technique;

List of abbreviations

THF, PS, Et₃N, FWHM. ¹

¹ Abbreviations: THF: Tetrahydrofuran; PS: Polystyrene; Et₃N: Triethylamine; FWHM: Full width at half maximum

1. Introduction

Radical cations are one of the key intermediates in ionizing radiation-induced reactions. However, it is difficult to observe the primary reactions of the solute radical cations in solution because the cation formation is driven by a diffusion-controlled hole-transfer reaction of the solvent hole species and solute molecules. The diffusion-controlled process requires a considerable amount of time to initiate the early stage reactions, thereby rendering the observation of the primary reaction process of the cation extremely difficult. Pulse radiolysis is one of the most valuable methods to observe radiation-induced reactions and significant transients like hydrated electrons (Hart and Boag, 1962; Keene, 1963). Additionally, pulse radiolysis is a powerful technique to investigate the reaction dynamics of ionizing radiation-induced reactions (Wishart and Rao, 2010), electron transfer reactions (Patel and Willson, 1973; Miller et al., 1984), as well as subsequent reactions following single-electron oxidation/reduction of various molecules, including biochemical redox reactions (Kobayashi, 2019) and nano-particle formations (Belloni et al., 2020). Pulse radiolysis has recently been expanded to determine the redox potentials of solutes in solution without the use of an electrolyte (Bird et al., 2020a, 2020b). Numerous transient absorption spectra of solute molecules have been reported using this technique, laying the foundation for understanding ionizing radiation-induced phenomena and reactions (Wishart and Rao, 2010; Tabata et al., 1991; Ferradini and Jay-Gerin, 1991). Additionally, the choice of the solvent decrees which radical ions, anions, or cations are formed, or whether both radical ions are formed.

Focusing on organic solutes, one of the essential solvents for observing radical cations is chlorinated hydrocarbons such as dichloromethane and 1,2-dichloroethane. Both solvents have been reported to generate radical cations in the solute by hole transfer of the solvent's radical cation species (Arai et al., 1969; Burrows et al., 1972; Sumiyoshi et al., 1988). It is also worth noting that the excess electrons can be stabilized in these cation-forming solvents by reacting the solvents themselves to form chloride, which is relatively inert. As a result, the solute radical cation is observed, and the lifetime of the solute radical cation is prolonged. Through a hole transfer reaction involving the transfer of solvent-derived radical cations to the target solute molecules, the established reaction system efficiently generates radical cations. These measurements are typically carried out at relatively low solute concentrations, such as 0.01 mol dm⁻³ or less than 0.1 mol dm⁻³. The excess electrons are scavenged by the solvent yielding relatively stable anion species such as Cl⁻, which is optically inert in the UV-Vis-NIR region (Arai et al., 1969; Burrows et al., 1972).

On the other hand, the observation of radical anions has been established using polar solvents and a wide range of polar and non-polar solvents with cation scavengers such as trimethylamine (Et₃N). The primary reaction that forms the solute radical anions comprises the scavenging of solvated electrons or excess electrons by the solute molecule. Among these radical anion-forming solvents, THF is generally the preferred choice since THF radical cations undergo self-decomposition to form relatively inert cation species and neutral radical(s), which restricts the observation of hole-transfer yielding solute radical cations. As a result, the reaction system in THF was more apparent in comparison to other solvents with cation scavengers.

As mentioned above, these methods of cation observation in dilute solutions are unfavorable for investigating intramolecular reactions of radical cations in high time-resolved measurements. This may be attributed to the formation of the radical cations that involve hole transfer of the solvent-originated radical cations to the solute molecules, as well as to the reaction being primarily diffusion-limited. As a result, the primary process of targeted cation dynamics is obscured by this diffusion process. Thus, to investigate the early stage intramolecular processes,

a novel observation approach involving the formation of the solute radical ions that are not governed by diffusion is required. Additionally, ultra-high time-resolved measurements require precise timing for the generation of radical cations. As a result, the desired condition for measurements involves the generation of an electron beam pulse by the targeted radical cation with a duration that is identical to that of the electron beam pulse.

In the current study, a radical cation was generated by directly ionizing the solute molecule, and radical cation observation in THF was demonstrated. The facile method that is proposed is critical for ultra-high time-resolved pulse radiolysis since it identifies when radical cations are formed in the reaction system. For the experimental demonstration of this technique, biphenyl and polystyrene (PS) were chosen as the solute molecules. Biphenyl is one of the most well-established molecules (Tagawa et al., 1982; Tagawa et al., 1983), and its radical anions and cations have been examined in various solvents such as THF, benzene, ethyl acetate, cyclohexane, 3-methyl pentane, and acetone (Carmichael and Hug, 1986). Additionally, biphenyl kinetics under ionizing radiation has also been well examined (Tagawa et al., 1982; Tagawa et al., 1983), which establishes biphenyl as a standard molecule for time-resolved spectroscopy. As a result, biphenyl can be used as a general and standard molecule for the observation of anions and radical cations via pulse radiolysis.

On the other hand, the use of PS has also been well established by pulse radiolysis and laser flash photolysis (Tagawa and Schnabel, 1980; Itagaki et al., 1983; Tagawa et al., 1984; Tagawa, 1986; Miyasaka et al., 1993; Okamoto et al., 2006; Okamoto et al., 2001). Although PS is also known to form radical cations and dimer radical cations. Additionally, the scavenging of excess electrons or the formation of PS radical anions has not been observed in fluid solutions. As a result, PS is highly unlikely to scavenge excess electrons in fluid solutions. Thus, PS is a unique molecule that has the ability to form radical cations and dimer radical cations in fluid solutions but lacks the ability to form radical anions. Thus, PS can be used to study radical cations and their intra-molecular reactions yielding dimer radical cations. The observation of dimer radical cations of PS by hole transfer from solvent radical cations to PS molecules via pulse radiolysis has been reported previously (Okamoto et al., 2001; Okamoto et al., 2006). However, the formation dynamics of the dimer radical cations of PS were limited by the diffusion-controlled reaction. Consequently, observation of the intramolecular formation dynamics of the dimer radical cations is an excellent candidate for the demonstration of the technique proposed in this study without employing diffusion-controlled hole transfer reactions from solvent radical cations.

The purpose of the present study is to demonstrate the direct ionization as an effective approach for observing radical cations in THF and to achieve the real-time observation of the intra-molecular dimer radical formation using the proposed approach.

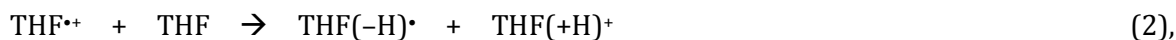
2. Materials and Methods

The pulse radiolysis experiments were conducted using electron linacs, at the research laboratory for quantum beam science at SANKEN, Osaka University. The picosecond-pulse radiolysis experiments were conducted using an accelerated electron with the energy and pulse width of 32 MeV and ~ 1 ps full width at half maximum (FWHM), respectively. An S-band photocathode RF-gun with an electron linear accelerator system was used as the source of ionizing radiation. The probe light originated from a fs-laser pulse generated using a Ti:Sapphire fs-laser coupled

with regenerative amplifier and OPA (Tsunami with Spitfire and TOPAS, Spectra physics). Furthermore, a Silicon avalanche photodiode (S8890-02, Hamamatsu photonics) and an InGaAs avalanche photodiode (G8931-20, Hamamatsu photonics) were used as detectors for visible and NIR wavelengths, respectively. The details of the experimental setup were described in detail elsewhere (Toigawa et al., 2016). The ns-pulse radiolysis experiments were conducted using an accelerated electron with the energy and pulse width of 26 MeV and 8 ns pulse (FWHM), respectively, employing an L-band electron linear accelerator system as the source of ionizing radiation. For pure water, the typical dose of 62 Gy/pulse was maintained. The probe light comprised of a xenon flash lamp (XF-80, Tokyo instruments). A Silicon photodiode (S1722-02, Hamamatsu photonics) and an InGaAs photodiode (DET-10C, Thorlabs) were used as the detector at the wavelength ranges of 300–800 nm and 800–1600 nm, respectively. Details of the experimental setup were described in detail elsewhere (Toigawa et al., 2016). Biphenyl (99.5+%, TCI), PS ($M_w = 2420$, $M_w/M_n = 1.06$, atactic, Pressure chemical, please see supporting information for the purity), THF (HPLC grade, Kanto chemical; spectroscopic grade, Nacalai tesque) and Et₃N (99+%, Nacalai tesque) were used as received. Both biphenyl and PS were dissolved in THF separately and were subsequently deoxygenated by argon bubbling to generate the sample solutions. All sample solutions were colorless and clear. The experiments were conducted using quartz cuvettes with an optical length of 5 or 10 mm. All PS concentrations were expressed as concentrations of the monomer unit. Furthermore, all experiments were conducted at a temperature of 296 ± 2 K.

3. Results

The transient absorption spectra of THF were examined, as illustrated in Figure 1. As evident from the figure, the well-known spectra of the THF solvated electrons could be observed in the NIR region, with a rate constant of 6.5×10^7 s⁻¹. The absorption maximum of the solvated electrons has been reported to be ~ 2100 nm (Dorfman et al., 1971; Jou and Dorfman, 1973) which was beyond the detection range of our instruments. Additionally, the observed absorptions decayed at a double exponential rate in the 300–700 nm range and at a single exponential rate in the 750–1600 nm range. As illustrated in Figure S1(a) in the supporting information, the fitted results of the kinetic analysis revealed that the solvated electron absorption band spread throughout the spectra range of the present experiment. In addition to the absorption caused by solvated electrons, two additional components were observed at wavelengths of 300–380 nm with the rate constant of 3.4×10^5 s⁻¹ and 400–700 nm with the rate constant of 4.1×10^6 s⁻¹ [Figure S1(b)]. Since the absorption band spectrum for the shorter wavelength approached 300 nm, the peak of the absorption band may have a wavelength shorter than 300 nm. As illustrated in Figure S1 in the supporting information, the other absorption band did not exhibit any characteristic spectrum. These absorptions are highly likely to have resulted from radicals. To our knowledge, the exact structure of these radicals has not been reported. It is reasonable to assume that the proton (H⁺) would not be an observable intermediate for transient absorption in the 300–1600 nm wavelength range. As a result, the observed transient absorption can be attributed to neutral radicals. Because identifying these radicals is beyond the scope of this paper, they were treated as unknown radical(s). The pulse radiolysis measurement of pristine THF, therefore, showed an absorption band in the 300–1600 nm range due to the solvated electrons in THF, as well as two unknown absorption bands at UV and visible regions. The main radiolysis kinetics is written as follows (Tran-Thi and Koulkes-Pujo, 1983):



The THF originating radicals have not been known. We believe THF(+H) can be assumed to be H⁺ because THF radiolysis product may contain H₂ due to the recombination of two H[•] which is formed by the reaction with the solvated electron just like radiolysis of 1,4-dioxane (Baxendale and Rodgers, 1967). The counterparts of THF(+H)⁺, there are several candidates for THF(-H)[•]. We believe these neutral transient radicals have not been identified. Deprotonated products give carbon centered radical which has radical at position 2 or 3. In addition, the corresponding ring-opening products are also considered as the candidate intermediates. These transients most likely gave transient absorption at UV region shown in Figure S1 denoted as unk1 and unk2.

Biphenyl is known to react with excess electrons in the fluid media, yielding biphenyl radical anions (Balk et al., 1957; Tagawa et al., 1982; Tagawa et al., 1983; Renou et al., 2003a, 2003b; Saeki et al., 2007; Kondoh et al., 2013). Biphenyl dissolves readily in THF, with a solubility of $\approx 3 \text{ mol dm}^{-3}$ at 298 K. In the present experiments, 2.5 mol dm^{-3} solutions were used for the high-concentration sample to avoid crystallization during argon bubbling to remove dissolved oxygen. A solution with a lower concentration of $0.010 \text{ mol dm}^{-3}$ was also used for comparison. At the concentration of 0.010 and 2.5 mol dm^{-3} , the electron densities of the solutions were estimated to be 489.6 and $514.9 \text{ mol dm}^{-3}$, respectively. This is indeed 39.8% of electron in the 2.5 mol dm^{-3} biphenyl solution of THF belongs to biphenyl. On the contrary, biphenyl's electron is only 0.167% at $0.010 \text{ mol dm}^{-3}$ solutions. Therefore, it is expected that at the high concentration solution, the probability of the direct ionization of solute cannot be negligible and expected to contribute the observation.

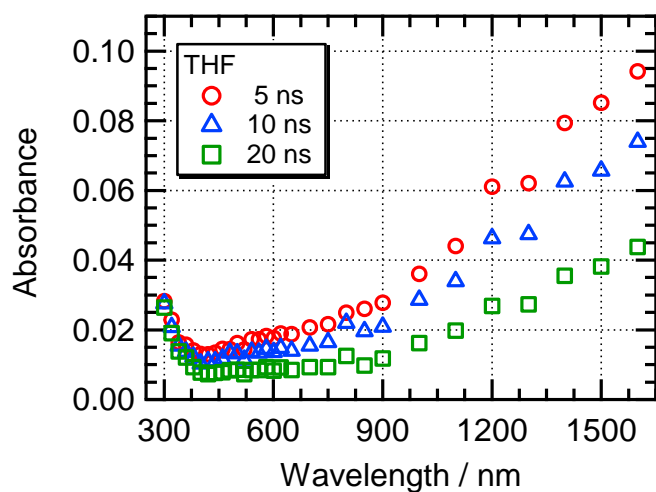


Figure 1. Transient absorption spectra of THF.

The transient absorption spectra of the $0.010 \text{ mol dm}^{-3}$ biphenyl solution of THF are shown in Figure 2(a). As evident from the figure, absorption bands at $\approx 370 \text{ nm}$, as well as $\approx 400 \text{ nm}$ and $\approx 650 \text{ nm}$, caused by the T-T absorption

of biphenyl (Meyer et al., 1970; Porter and Windsor, 1958; Bensasson and Land, 1971; Tagawa et al., 1982; Tagawa et al., 1983) and biphenyl radical anions (Tagawa et al., 1982; Tagawa et al., 1983; Shida, 1988; Saeki et al., 2007; Renou et al., 2003; Renou et al., 2003; Kondoh et al., 2013) were observed. The triplet excited states of biphenyl were formed by the intersystem crossing of the singlet excited states of biphenyl, generated by excitation via electron beam irradiation, including the internal excitation due to the Cherenkov radiation. Additionally, since the solvated electrons were scavenged by biphenyl, no absorption by solvated electrons in THF could be observed. Furthermore, the addition of Et₃N as a cation scavenger induced no change in the absorption spectra and decay kinetics observed in the 300–900 nm wavelength range. As a result, no absorption was attributed to biphenyl radical cations. The absence of solvated electron absorption in THF further indicates that the solvated electrons were scavenged by biphenyl, resulting in the formation of biphenyl radical anions. The reactions are as follows:



The transient absorption spectra for the solution with a higher biphenyl concentration, 2.5 mol dm⁻³ biphenyl THF, are shown in Figure 2(b). The spectral features were consistent with those observed for 0.010 mol dm⁻³ solution. However, a wider absorption band was observed in the visible region, and the absorption maximum shifted to shorter wavelengths with time. Other differences included a wider absorption band in the UV region at shorter wavelengths. As with the 0.010 mol dm⁻³ solutions, no absorption due to the solvated electrons was observed. With the addition of Et₃N, the spectra approached that of 0.010 mol dm⁻³ biphenyl solution, as illustrated in Figure 2(c). Therefore, the transient absorption spectra obtained for 2.5 mol dm⁻³ biphenyl solution was observed to be the sum of the absorption due to the biphenyl radical cations, the biphenyl radical anions, and the triplet excited state biphenyl. Similar spectra have been reported for acetone solutions, which produced both biphenyl radical cations and radical anions with T-T absorption of biphenyl (Arai et al., 1971). The biphenyl radical cations have been reported to exhibit absorption bands with peak wavelengths of 365, 387, and 703 nm in sec-butyl chloride matrix (Shida, 1988), as well as 380, and 690 nm in 1,2-dichloroethane, using pulse radiolysis (Arai et al., 1969). Additionally, the peak absorption wavelengths for the biphenyl radical anions were reported as 380, 396, 408, and 655 nm in methyl tetrahydrofuran matrix (Shida, 1988), and 405, and 637 nm in THF, using chemical reduction (Buschow et al., 1965). These features were found to corroborate with the current observation. Thus, biphenyl radical cations were generated via direct ionization of biphenyl at a high concentration.

On the other hand, biphenyl radical anions were formed by scavenging the excess electrons resulting from the ionization of biphenyl and THF. The increase in the excited triplet yield can be attributed to the increased number of biphenyls that were excited by electron beam irradiation, as well as to the formation of biphenyl excited states via geminate ion recombination of the biphenyl radical anions and radical cations (Arai et al., 1971). This is conclusive since biphenyl's electron accounts for 39.8% of total electron of the 2.5 mol dm⁻³ biphenyl THF solution, as determined from its density. In addition to the reactions listed above, the geminate ion recombination and the escaped ions' charge recombination between the radical cations and the excess electrons or the radical anions also give the excited states. The following reactions occur in a high biphenyl concentration solution of THF:



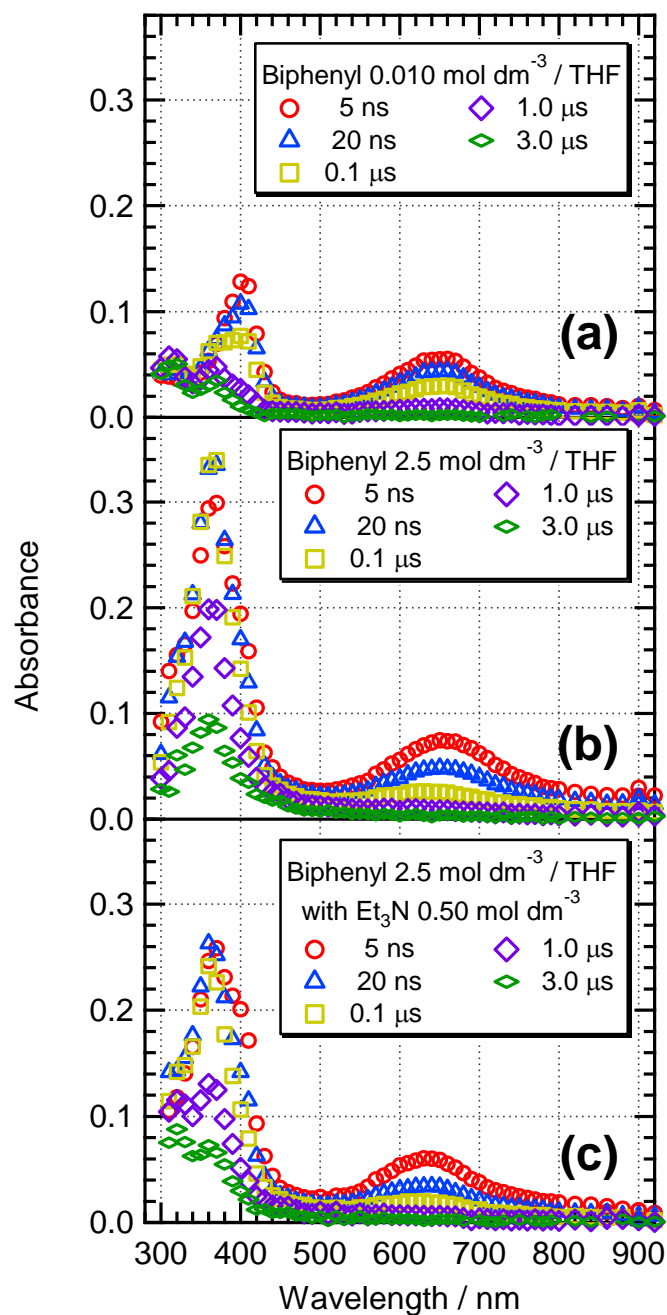
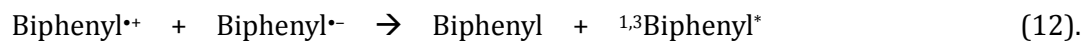


Figure 2. Transient absorption spectra of $0.010 \text{ mol dm}^{-3}$ biphenyl in THF (a), 2.5 mol dm^{-3} biphenyl in THF (b), and 2.5 mol dm^{-3} biphenyl with 0.50 mol dm^{-3} trimethylamine in THF (c).

When PS was used as a solute, a solution of 1.0 mol dm^{-3} PS in THF (electron fraction of PS: 11.2%) exhibited transient absorption due to the solvated electrons and dimer radical cations in PS. As illustrated in Figure 3, the absorption caused by the solvated electron was visible in the NIR region. Additionally, the addition of PS had no effect

on the decay profile of the solvated electron. Thus, PS cannot scavenge the solvated electron in THF, as illustrated in Figure S2. Additionally, the triplet state of PS (UV region) and the excimer of PS (visible region) were observed. The peak absorption wavelength of the dimer radical cation of PS, as well as both the solvated electron and the dimer radical cation were observed without the corresponding decay of the radical ions. In other words, the radical anion species observed decayed significantly faster than the radical cation species observed. According to the electro-neutrality principle, the system must contain an anion species, but the intermediates exhibited silent absorption in the current experimental region.

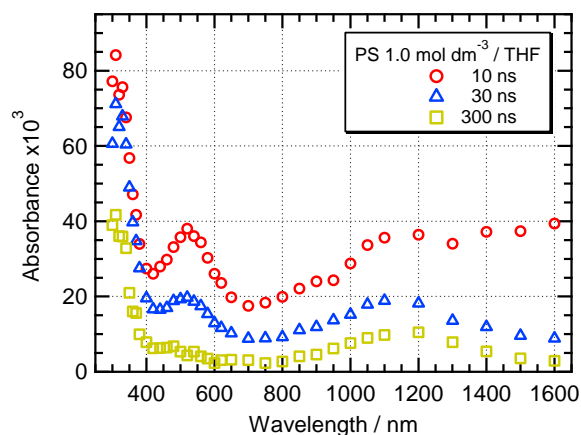


Figure 3. Transient absorption spectra of PS (1.0 mol dm^{-3}) in THF.

It is critical to note that as long as the solute has no ability to scavenge solvated electrons in THF, radical cations of the solute can be observed in THF without the contribution of the solute radical anions. Therefore, it is necessary that the solute dissolves in THF at extremely high concentrations, given that THF is a suitable solvent for many classes of chemicals. The radical cation is predominantly formed by the direct ionization of solute molecules. Therefore, the radical cations can be observed instantly after being irradiated with an electron beam. Thus, ultra-high time-resolution measurements on radical cations using the pulse radiolysis technique can provide critical information on the self-driven reactions of radical cations. Without this technique, radical cation generation requires the solvent radical cations to diffuse into the solute molecules.

Using ps-pulse radiolysis, the formation processes of PS dimer radical cations were investigated. The time profiles of the transient absorption were observed at 1200 nm for 1.0 mol dm^{-3} PS THF solution and pristine THF, as illustrated in Figure 4. At this wavelength, the absorption due to the solvated electron and dimer radical cations are expected to be observed. (S. Tagawa et al., 1986; Okamoto et al., 2006; Okamoto et al., 2001) As seen in Figure 4, the absorption caused by the solvated electron in THF was observed as a monotonically decaying time profile when the pristine THF was measured. For the PS solution, the transient absorption exhibited an increasing trend around 10–40 ps, followed by a minimal decay. The absorptions of both samples exhibited a near-identical decaying profile, around 50 ps–400 ps with nearly the same amount of absorption (Figure 4 inset). Consequently, the decaying component can be attributed to the absorption caused by the solvated electron. Contemporarily, the dimer phenyl

cations are not expected to be observed in the decaying profile during the current time window, as seen in Figure S2. The increasing component should be attributed to the absorption of dimer radical cations of PS. Thus, the direct observation of the forming process of dimer radical cation of PS was successfully achieved. At least three processes are involved in the forming process. The hole transfer reactions between the localized phenyl radical cations and the alkyl radical cation were described previously. Additionally, one should consider the direct generation of dimer radical cations. This direct dimer radical cation formation can occur only when two aromatic rings interact or are stacked at the ground state. It is not easy to quantify the contributions of each of those processes. However, ionization at this stacked-ring position does not produce a rising signal. Therefore, the observed rising signal can be assigned to the formation process of the dimer radical cation from the local radical cation of PS. With respect to the time-scale of sub-ns conformational motions (Miyasaka et al., 2003), the observed process is too fast to be limited by those motions and therefore referred to as the hole transfer of localization to the stacked aromatic ring position in the polymer. As a result, the observed rate constant was estimated as the rate constant of the forming dimer radical cations of PS due to intra-molecular hole transfer and was estimated to be higher than $7 \times 10^{10} \text{ s}^{-1}$ by the single exponential fitting for the rising signal as an apparent rate constant for non-diffusion controlled dimer radical cation formation.

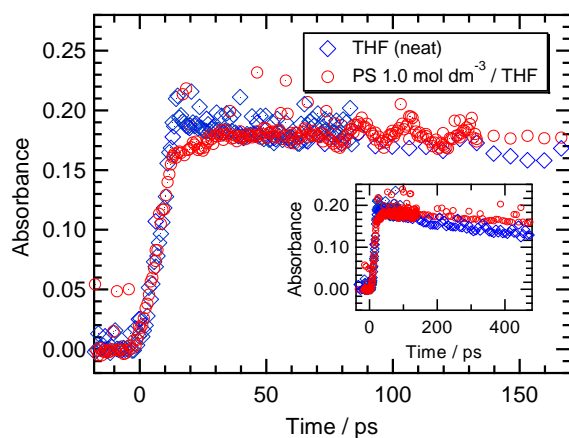


Figure 4. Transient absorption time profiles observed at 1200 nm using ps-pulse radiolysis on 1.0 mol dm^{-3} PS in THF and pristine THF. Inset: Time profile of full scale of measurement.

4. Conclusions

Radical cations of solute molecules were successfully observed in THF using pulse radiolysis. When the high-concentration biphenyl solution of THF was examined, both the radical anions and cations could be observed, in addition to the excited triplet state of biphenyl. Additionally, when the high-concentration PS solution of THF was examined, the dimer radical cation of PS was observed to be associated with the solvated electron present in THF. The observed formation dynamics of the dimer radical cation of PS could be further interpreted as a non-diffusion-controlled process that was initiated by the direct ionization of PS. Moreover, when the concentration of the solute was increased substantially, direct ionization was successfully achieved. The resultant reaction system further

demonstrated that the radical cations obtained could be observed successfully under significantly high concentrations. Additionally, it was demonstrated that the use of ps-pulse radiolysis measurements catered to the instantaneous generation of radical cations due to the direct ionization and the resultant hole transfer in PS molecules. Thus, a designedly high concentrated condition can be one of the ways to investigate reactions and the nature of radical cations using ultra-high time-resolved measurements.

One of the limitations of the present approach is that the solubility of the solute depends on the combination. THF is one of the good solvents for organic molecules. Additionally, the spectroscopic and radiolytic characters are also well known. Therefore, the use of THF can be the first choice, but the essence of this approach is to use considerably high concentration solutions. The optimized concentration for the cation observation needs to be examined even though the probability of the direct ionization of the solute increased as the concentration increased. Moreover, with the demonstrated method, the reactions of the solute radical cation and the solvent and the stability of the radical cation in fluid media can be examined and give an understanding of radical cations' nature.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The author, Masao Gohdo, would like to thank Mr. Takafumi Kondoh for the fruitful discussions and his help with our experiments. Furthermore, we wish to thank all the research laboratory staff for the quantum beam science of SANKEN, Osaka University, for the operation of the linacs. We also wish to thank Mr. Hitoshi Haneoka at the comprehensive analysis center at SANKEN, Osaka University for NMR measurement. This work was supported by JSPS KAKENHI [grant numbers: 21226022, 26249146, 17H01374, 18K04993, and 20H00364].

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