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Picosecond Time-Resolved Infrared Absorption Studies on the Photoexcited States of Poly(*p*-phenylenevinylene)

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Picosecond time-resolved infrared absorption spectra of the photoexcited states of poly(*p*-phenylenevinylene) [$(-C_6H_4CH{=}CH-)_n$, PPV] have been observed with tunable picosecond light pulses obtained by difference-frequency generation between signal and idler waves from an optical parametric generator and amplifier. The time-resolved photoinduced infrared absorption bands due to a vibrational transition observed at 1550 cm^{-1} and an electronic transition at 3000 cm^{-1} of the photoexcited PPV have fast (≈1.7 ps) and slow (≈50 ps) decay components. By comparison of the picosecond time-resolved infrared absorption spectra of short-lived (fast decay component) and long-lived (slow decay component) transient species with the photoinduced and doping-induced infrared difference spectra of PPV, the short-lived transient species is assigned to bound polaron pairs, and the long-lived transient species is assigned to positive and negative polarons.

1. Introduction

Conducting polymers having conjugated π-electrons not only show high electrical conductivities upon doping but also have interesting optical properties such as photoconductivity and nonlinear optical susceptibility in their pristine states. Poly(*p*-phenylenevinylene) (PPV, Figure 1a) is one of the π-electron conjugated polymers with a nondegenerate ground state. PPV shows nonlinear optical properties,[1−3] photoconductivities,[4−7] electroluminescence,[8] and high electrical conductivities upon doping.[9−12] Self-localized excitations (excitons, polarons, and bipolarons) generated by photoexcitation or chemical doping are considered to play major roles in such interesting physical and chemical properties of π-electron conjugated polymers.[13]

When π-electron conjugated polymers are photoexcited with energies greater than their $\pi-\pi^*$ band gaps, electron−hole pairs are created at first. The very fast (≈10^{-13} s) initial relaxation following photoexcitation involves coupling of the π-electron system to the lattice coordinates and results in formation of self-localized excitations. In the case of PPV, an electron−hole pair on a single chain created via intrachain photoexcitation will initially relax to a neutral singlet exciton. In contrast, an electron−hole pair which is created on separate chains through charge transfer due to interchain photoexcitation will initially lead to the formation of a polaron pair, in which positive and negative polarons are bound to each other on neighboring chains by Coulomb attraction. The positive and negative polarons in the bound polaron pair can move along the polymer chains and evolve into free polarons, which are apart from each other. When two identically charged polarons encounter each other, they will coalesce to form a doubly charged bipolaron. If two oppositely charged polarons and bipolarons meet in the polymer matrix, they should revert to the ground (neutral) state by geminate recombination. The singlet exciton is the first excited singlet state, which is created in the conjugated polymer chain upon photoexcitation. A polaron and a bipolaron correspond, respectively, to a radical ion and a divalent ion. Such self-localized excitations extend over a certain number of repeating units and have structures different from that of the ground-state polymer. The photogenerated exciton, bound polaron pair, and positive and negative polarons in PPV are schematically depicted in Figure 1b, c, and d, respectively, where the elementary excitations localized over about three repeating units are shown as possible examples.

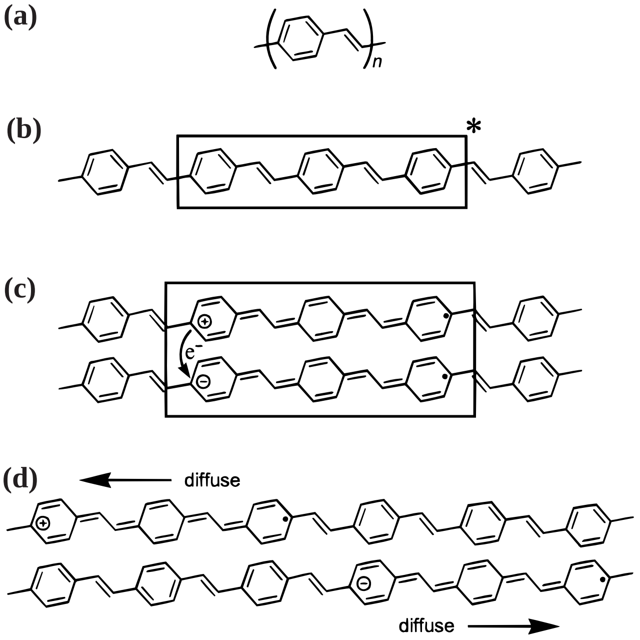

Figure 1. (a) Repeating unit of poly(*p*-phenylenevinylene) (PPV) and schematic structures of (b) exciton, (c) bound polaron pair, and (d) positive and negative polarons photogenerated in PPV. The asterisk (*) indicates an electronically excited state. The dot (•) and the plus (⊕) and minus (⊖) symbols correspond, respectively, to an electron spin and positive and negative charges.

Time-resolved and transient infrared absorption spectroscopy methods have been used successfully to investigate the structure and dynamics of short-lived molecular species in the condensed phase.[14−25] In 1990, Rothberg and Jedju[21] measured femtosecond

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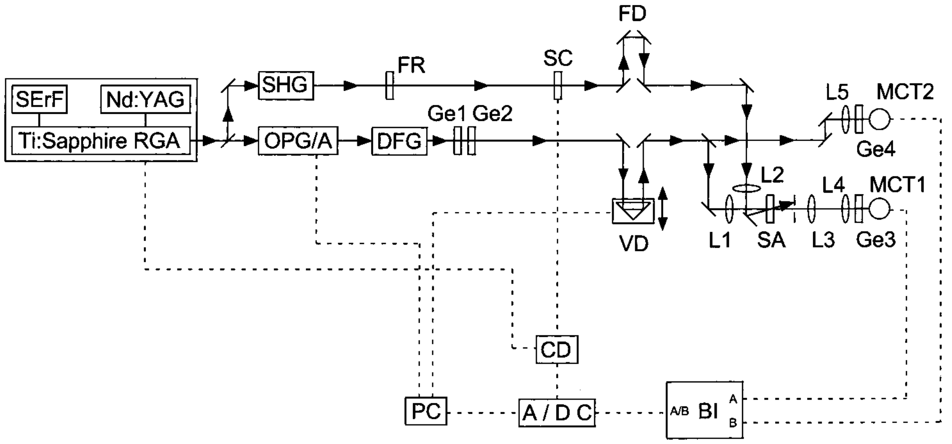

Figure 2. Schematic diagram of the setup used for picosecond time-resolved infrared absorption measurements. Key: (SErF) frequency-doubled, mode-locked, diode-pumped Er-doped fiber laser; (Nd:YAG) CW Q-switched Nd:YAG laser; (SHG) second-harmonic generation; (Ti:sapphire RGA) Ti:sapphire regenerative amplifier; (OPG/A) optical parametric generator and amplifier; (DFG) difference-frequency generation ($AgGaS_2$); (Ge1, Ge2, Ge3, and Ge4) Ge filters; (FR) Fresnel-rhomb prism; (SC) synchronous chopper; (FD) fixed optical delay line; (VD) variable optical delay line; (L1, L2, L3, L4, and L5) lenses; (SA) sample; (MCT1 and MCT2) HgCdTe detectors; (BI) boxcar integrator; (CD) chopper driver; (A/D C) analog-to-digital converter; (PC) personal computer.

time-resolved infrared absorption spectra of *trans*-polyacetylene in the 0.5−0.3 eV (4000−2400 cm^{-1}) region and identified the dynamics of photogenerated solitons and polarons. Recently, Hamm and colleagues[26−28] and Okamoto and colleagues[29,30] succeeded in measuring the subpicosecond time-resolved and picosecond transient infrared absorption spectra in the fingerprint region, where more structural information is contained. A number of groups have carried out time-resolved photoinduced absorption[31−34] and luminescence[35−39] studies on PPV and its derivatives to identify the self-localized excitations created upon photoexcitation. However, a consistent picture for the picosecond dynamics of photogenerated excitations has not yet been established. Picosecond time-resolved infrared absorption spectroscopy covering the fingerprint region is expected to be very useful for characterizing the self-localized excitations and elucidating their structures and dynamics. In the present study, we report picosecond time-resolved infrared absorption spectra of the photoexcited states of PPV. The observed infrared spectra are analyzed by referring to the infrared difference spectra of photoexcited (CW) and H_2SO_4-doped PPVs. Identification of the photoexcited states of PPV and charge-separation dynamics are discussed.

2. Experimental Section

The experimental setup used for picosecond time-resolved infrared absorption measurements is shown schematically in Figure 2. The fundamental output (wavelength 775 nm, pulse width ≈ 2.1 ps, repetition rate 1 kHz) from a picosecond Ti:sapphire regenerative amplifier, seeded by the second harmonic of a mode-locked Er-doped fiber laser (Clark-MXR CPA-2000), was used to excite an optical parametric generator and amplifier (Quantronix TOPAS). Widely tunable picosecond light pulses in the 2500 nm−11 μm (4000−900 cm^{-1}) range were obtained by difference-frequency generation in an $AgGaS_2$ crystal between the signal and idler waves from the optical parametric generator and amplifier. The generated infrared beams were passed through two Ge filters to eliminate the signal and idler waves. The tunable infrared light pulses in a single frequency were used to observe time-resolved infrared absorption spectra of the photoexcited sample by the pump−probe technique. The wavenumber was tuned by changing the phase-matching angles of both the β-barium borate crystal in the optical parametric generator and amplifier and the $AgGaS_2$ crystal for difference-frequency generation.

After the generated infrared beam was passed through a variable optical delay line, a portion of the infrared beam was focused on the sample. The transmitted probe beam was detected by a liquid-nitrogen-cooled HgCdTe (MCT) detector (Hamamatsu P3412-02). Another portion of the infrared beam was used as a reference beam, which was detected by another MCT detector. Amplified signals from the two MCT detectors were gated with a boxcar integrator (Stanford Research Systems SR250). The probe signal intensity was electronically divided by the reference signal intensity. The processed signals were A/D converted and accumulated by a personal computer.

The second harmonic output (wavelength 388 nm) from a Ti:sapphire regenerative amplifier was used to excite the sample. The pump beam was modulated at half the repetition rate of the probe beam (500 Hz) by a mechanical chopper (New Focus model 3501). The modulated pump beam was passed through a fixed optical delay line and focused on the sample noncollinearly against the probe beam. The signals with and without the pump pulses were separately accumulated by the computer. The pump-induced infrared absorption was obtained by dividing the pump-on signal by the pump-off signal. The cross-correlation time between the pump and probe pulses, which was determined by the rise of a transient infrared absorption of photoexcited silicon due to free carriers, was ≈2.8 ps. The spectral resolution was ≈16 cm^{-1}. The data were taken at intervals of 50 cm^{-1} in the 3600−1800 cm^{-1} region and intervals of 15 cm^{-1} in the 1800−1000 cm^{-1} region.

A film of PPV (Figure 1a) deposited on a CaF_2 substrate (8 μm thick) was prepared according to the method reported by Murase et al.[9] Picosecond time-resolved infrared absorption measurements were made for such a film on the CaF_2 substrate at room temperature.

3. Results and Discussion

PPV in its pristine state has a broad electronic absorption band in the ultraviolet to visible region with a maximum at ≈400 nm. The energy of the pump pulse (388 nm) used in the present study was greater than the $\pi-\pi^*$ band gap of PPV. The filled circles in Figure 3a,b show the plots of the infrared absorption intensities of the photoexcited PPV probed at 3000 and 1550

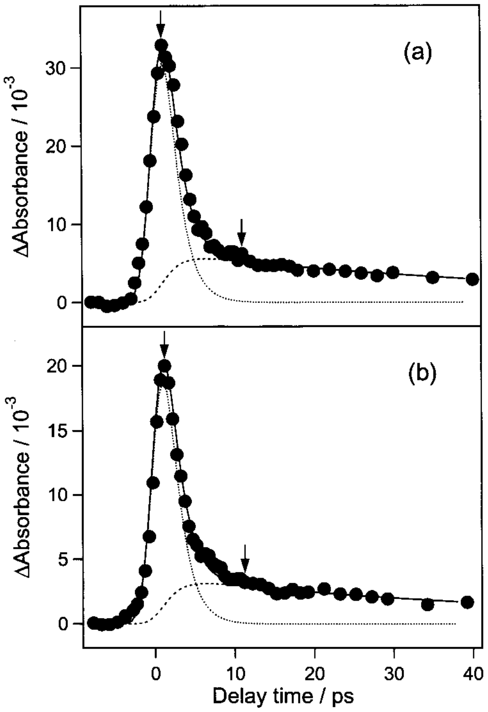

Figure 3. Plots of time-resolved infrared absorption intensities of the photoexcited PPV against the delay time between the pump and probe pulses. Filled circles indicate the time-resolved infrared absorption intensities probed at (a) 3000 and (b) 1550 cm^{-1}. Dotted curves are the results of simulation for a bound polaron pair based on a single-exponential decay function ($\tau_{bd} = 1.7$ ps). Broken curves are the results of simulation for positive and negative polarons based on rise ($\tau_{pr} = \tau_{bd}$) and decay ($\tau_{pd} = 50$ ps) functions. Solid curves are the sum of the dotted and broken curves.

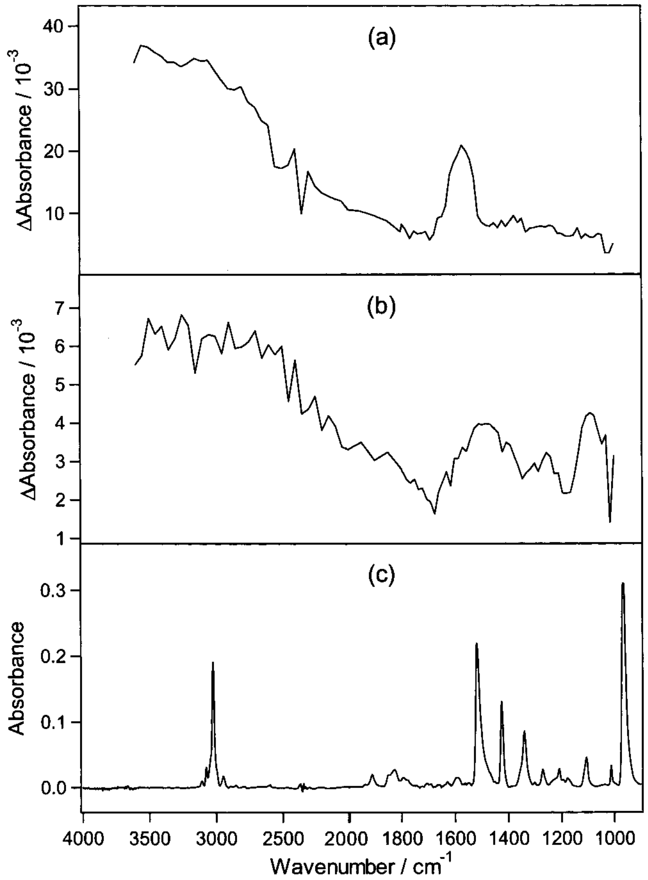

Figure 4. Picosecond time-resolved infrared absorption spectra of the photoexcited PPV at delay times (a) 1 and (b) 11 ps, and (c) infrared absorption spectrum of neutral PPV.

cm^{-1}, respectively, against the delay time between the pump and probe pulses. The photoinduced infrared absorptions at both 3000 and 1550 cm^{-1} (filled circles in Figure 3a,b, respectively) show almost the same temporal behavior and consist of fast and slow decay components. To identify the origins of the fast and slow decay components, we measured time-resolved infrared absorption spectra of the photoexcited PPV.

The picosecond time-resolved infrared absorption spectra of the photoexcited PPV at delay times 1 and 11 ps are shown in Figure 4a,b, respectively, together with the infrared spectrum of a neutral PPV film (Figure 4c). The arrows in Figure 3a,b show the positions of delay times at which the spectra in Figure 4a (1 ps) and b (11 ps) were measured. The transient self-localized excitation corresponding to the fast decay component in Figure 3a,b is observed in the time-resolved spectrum at delay time 1 ps (Figure 4a). The time-resolved spectrum at delay time 11 ps (Figure 4b) is mainly attributed to the transient excitation corresponding to the slow decay component in Figure 3a,b. The time-resolved infrared absorption spectra of the photoexcited PPV (Figure 4a,b) are quite different from the infrared spectrum of neutral PPV (Figure 4c).[40−43] Broad infrared absorption bands are observed in the 4000−1800 cm^{-1} regions in Figure 4a,b. The formation of charged self-localized excitations is accompanied by the appearance of corresponding electronic states in the band gaps.[13] Thus, a new electronic absorption appears in the near-infrared to infrared region, in addition to a new electronic absorption in the visible region.[13] The broad absorptions in the higher wavenumber region in Figure 4a,b are assigned to the subgap electronic transition in the near-infrared to infrared region characteristic of charged self-localized excitations. Hsu et al.[33] reported a similar electronic absorption band centered near 0.5 eV (4000 cm^{-1}) in addition to an absorption band at 1.5 eV (830 nm) in the picosecond photoinduced absorption spectra of 2-methoxy-PPV.

In contrast with the higher wavenumber region where similar broad electronic absorptions are observed, the spectral patterns in the 1800−1000 cm^{-1} regions of Figure 4a,b are considerably different from each other. In the fingerprint region of Figure 4a,b, infrared absorption bands arising from vibrational modes of self-localized excitations created upon photoexcitation are observed. Therefore, this difference in the spectral patterns clearly indicates that the spectra in Figure 4a,b arise from different transient species.

The 1800−1000 cm^{-1} regions of Figure 4a,b are expanded in Figure 5a, b together with the photoinduced infrared difference spectrum of PPV at 78 K (Figure 5c) and the infrared difference spectrum of H_2SO_4-doped PPV (Figure 5d). The spectrum in Figure 5c was obtained by subtracting the spectrum of a neutral PPV film on a CaF_2 substrate at 78 K from the spectrum of the same film excited with the ultraviolet lines from an Ar^+ laser in the 351.1−363.8 nm region. This photoinduced infrared difference spectrum of PPV (Figure 5c) is almost the same as those observed in previous studies.[44−46] Because the spectrum in Figure 5c was measured with steady-state (CW) excitation at 78 K, only photogenerated species with very long lifetimes can be detected in it.

When we take into account the differences of spectral resolution and temperature in measuring Figure 5b ($\approx$16 cm^{-1} and room temperature) and c (4 cm^{-1} and 77 K), the picosecond time-resolved infrared absorption spectrum of PPV at delay time 11 ps (Figure 5b) is similar to the photoinduced infrared difference spectrum (Figure 5c). The photoinduced infrared

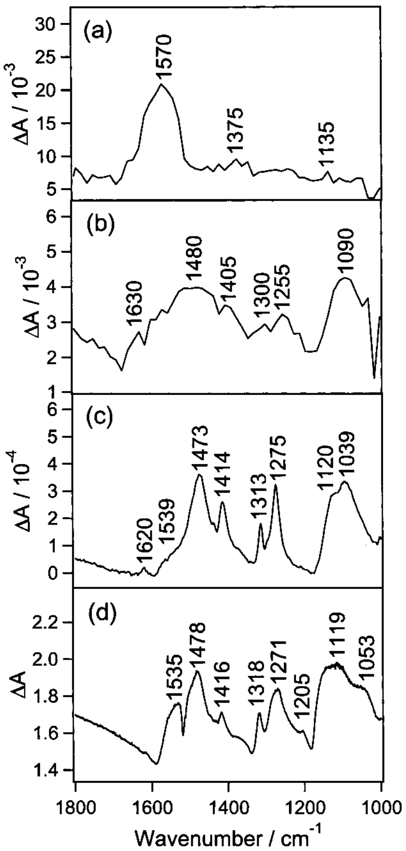

Figure 5. Picosecond time-resolved infrared absorption spectra of PPV at delay times (a) 1 and (b) 11 ps, (c) photoinduced infrared difference spectrum of PPV, and (d) infrared difference spectrum of H_2SO_4-doped PPV.

difference spectrum (Figure 5c) also resembles the infrared difference spectrum of H_2SO_4-doped PPV (Figure 5d), obtained by subtracting the spectrum of the intact polymer from that of the doped one.[47] In our previous studies,[47,48] the doping-induced infrared bands of H_2SO_4-doped PPV have been assigned to positive polarons on the basis of the resonance Raman results. Therefore, the similarity among the three spectra in Figure 5a−c suggests that (1) polarons are the dominant self-localized excitations at ≈11 ps after picosecond photoexcitation at room temperature in PPV and (2) these photogenerated polarons are long-lived at 78 K and can be detected at steady-state photoexcitation. In other words, positive and negative polarons are considered to be geminately created at delay time 11 ps via charge separation of photogenerated electron−hole pairs, and they would give rise to similar, overlapping photoinduced transient infrared spectra.

Because the long-lived transient species (corresponding to the slow decay component in Figure 3a,b) are assigned to positive and negative polarons, the short-lived transient species observed in Figure 5a (corresponding to the fast decay component) must be due to either singlet excitons or bound polaron pairs. From the results of the present measurements alone, it is not possible to determine which species is responsible for the infrared spectrum observed at delay time 1 ps (Figure 4a). As mentioned earlier, the broad electronic absorption is observed in the wavenumber region higher than 2000 cm^{-1}. This broad absorption is considered to arise from the same origin as the absorption around 0.5 eV (≈4000 cm^{-1}) in the picosecond photoinduced absorption spectrum of 2-methoxy-PPV observed by Hsu et al.[33] They reported another absorption centered near 1.5 eV (830 nm), and these two absorption bands were observed within the time resolution (<1 ps) of their measurements. Hsu et al. assigned these two absorptions to bound polaron pairs. If their assignment is correct, it would be reasonable to assign the transient species giving rise to the infrared spectrum at delay time 1 ps to bound polaron pairs. A recent calculation[49] has shown that polaron pairs can satisfactorily account for the peaks in the picosecond photoinduced absorptions observed in ref 33.

To confirm the self-consistency of the above assignments, we have simulated the observed temporal profiles in Figure 3a,b (filled circles) using the following model based on our assignments. Bound polaron pairs are created instantaneously after photoexcitation and decay with a lifetime of τ_{bd}. Positive and negative polarons are formed from bound polaron pairs with a rise time of τ_{pr} ($=\tau_{bd}$) and decay with a lifetime of τ_{pd}. The dotted curves in Figure 3a,b are the results obtained for bound polaron pairs by using a single-exponential decay function ($\tau_{bd} = 1.7$ ps) convoluted with the cross-correlation function between the pump and probe pulses. The broken curves in Figure 3a,b show the results for positive and negative polarons based on the rise ($\tau_{pr} = 1.7$ ps) and decay ($\tau_{pd} = 50$ ps) functions. The solid curves in Figure 3a,b are the sum of the contributions from bound polaron pairs (dotted curves) and positive and negative polarons (broken curves). The solid curves well reproduce the observed time-resolved infrared absorption intensities (filled circles in Figure 3a,b).

Although we have assigned the observed fast and slow decay components, respectively, to bound polaron pairs and polarons (positive and negative), singlet excitons must also be formed. In fact, some time-resolved luminescence studies on PPV have reported that the lifetimes of luminescence due to singlet excitons are in a range from 40 to 100 ps, depending on the sample, at room temperature.[35−37] At present, we consider that the time-resolved infrared spectra obtained in this study were observable due to the large infrared absorption intensities inherent to radical ion species. Recently, it has been reported that the infrared intensities of radical cations and anions of polycyclic aromatic hydrocarbons in the fingerprint region are much larger than those of the neutral species.[50−65] The large infrared intensities have been explained on the basis of electron−vibration interactions in charged species.[66] In contrast with the large infrared intensities of charged species, it has been reported that the infrared intensities in the fingerprint region of *trans*-stilbene (the smallest model compound of PPV) in the lowest excited singlet (S_1) state are comparable to those in the ground state.[30,67] The infrared intensities calculated at the B3LYP/6-31G* level for the radical cation and anion of *trans*-stilbene are much larger than those calculated at the CIS/6-31G* level for *trans*-stilbene in the S_1 state.[68] Since a bound polaron pair and a polaron correspond, respectively, to a radical-ion pair and a radical ion created in PPV, their infrared intensities are considered to be much larger than that of a neutral singlet exciton which corresponds to the first excited singlet state. Therefore, bound polaron pairs and polarons were selectively observed in the picosecond time-resolved infrared spectra, although singlet excitons may also be present in the picosecond time range.

4. Concluding Remarks

In the present study, we have demonstrated the potential of picosecond time-resolved infrared absorption spectroscopy in the characterization of self-localized excitations created in conducting polymers upon photoexcitation. Both an electronic transition in the high-wavenumber region and vibrational transitions in the fingerprint region have been observed in the time-resolved infrared absorption spectra of the photoexcited PPV. The infrared absorption intensities of the photoexcited PPV due to an electronic transition at 3000 cm^{-1} and a vibrational transition at 1550 cm^{-1} show the same temporal profile and have two decay components in the picosecond time range. The picosecond time-resolved infrared absorption spectra arising from the fast and slow decay components have been analyzed on the basis of the photoinduced infrared difference spectrum of PPV and the infrared difference spectrum of H_2SO_4-doped PPV. The fast decay component with a lifetime of $\approx$1.7 ps is assigned to bound polaron pairs and the slow decay component with a lifetime of $\approx$50 ps is assigned to positive and negative polarons.

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