

## Ultrafast dynamics of excitons and solitons in disubstituted polyacetylene

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We studied the ultrafast photoexcitation dynamics in disubstituted polyacetylene (DPA). We found two distinctively different relaxation channels for the photogenerated excitons; ionic and covalent pathways. In DPA films the photogenerated odd-parity ( $B_u$ ) excitons that are responsible for the high photoluminescence quantum efficiency follow the ionic relaxation pathway. During the hot exciton thermalization process, however, a fraction of the  $B_u$  excitons undergo a phonon-assisted transition to the covalent  $2A_g$  state, which consequently decomposes into two neutral soliton-antisoliton pairs that are subject to ultrafast recombination or dissociate into stable neutral solitons. In DPA solutions the ionic channel remains unchanged, however, the covalent channel becomes ineffective due to the different hot exciton thermalization pathways.

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The disubstituted polyacetylene (DPA), of which backbone structure is shown in Fig. 1 inset, is unique among the class of  $\pi$ -conjugated polymers (PCP).<sup>1</sup> On the one hand, DPA has a strong photoluminescence (PL) band, which has been used in optoelectronic applications such as light emitting diodes<sup>2</sup> and solid-state lasers.<sup>1,3</sup> On the other hand, this polymer has been shown to have a degenerate ground state,<sup>1</sup> which supports topological soliton excitations.<sup>4</sup> It has been shown that the PL quantum efficiency in PCP is associated with the order of the lowest lying excited states with odd ( $1B_u$ ) and even ( $2A_g$ ) parities.<sup>5</sup> If the energies  $E(1B_u) < E(2A_g)$ , then the polymer is strongly luminescent; conversely, if  $E(2A_g) < E(1B_u)$ , then the polymer is only weakly luminescent. It has been shown by Mazumdar *et al.* that in DPA  $E(1B_u) < E(2A_g)$  in spite of its polyene backbone, because of transverse conjugation.<sup>6</sup> Surprisingly, it was discovered<sup>1</sup> that the steady-state photomodulation (PM) spectrum of DPA films contains long-lived soliton excitations (neutral solitons,  $S^0$ , as well as charged solitons,  $S^\pm$ ), for which the photogeneration mechanism has remained a mystery. A persistent debate exists whether soliton excitations are by-products of photogenerated intrachain excitons, or conversely, excitons are unstable towards the formation of soliton-antisoliton pairs. Other types of photoexcitations, such as polarons, were also discovered in DPA in solution,<sup>7</sup> where again, their photogeneration mechanism has remained largely unclear.

In this work we elucidate the primary photoexcitation dynamics in DPA solutions and films in the femtoseconds (fs) to picoseconds (ps) time domain using transient PM spectroscopy. In DPA solutions we found that the primary photoexcitations are  $1B_u$  excitons in agreement with the assumed order  $E(1B_u) < E(2A_g)$ . In DPA films, however, we found that along with  $1B_u$  excitons in the ionic channel, neutral solitons are also photogenerated in the covalent channel, via the process of phonon-assisted transitions from  $1B_u$  to  $2A_g$ . Due to the ground-state degeneracy of DPA the  $2A_g$  decomposes into two soliton-antisoliton,  $\bar{S}S$  pairs:<sup>8,9</sup>  $2A_g \Rightarrow 2(S^0 + \bar{S}^0)$ . The generation, separation, and recombination dynamics of  $\bar{S}S$  pairs in DPA solid films are similar to those

previously observed for the high-energy band in films of transpolyacetylene [ $t-(CH)_x$ ],<sup>10</sup> and thus our results in DPA may also clarify the ultrafast transient processes in  $t-(CH)_x$ .

In our studies we have employed both steady-state and fs transient PM spectroscopies. The studies of ultrafast photoexcitation dynamics were performed utilizing the pump-probe correlation spectroscopy with 100-fs resolution in a broad spectral range from 0.5 to 2.7 eV.<sup>11</sup> The pump beam was extracted from a Ti-sapphire fs regenerative laser amplifier that was doubled to 3.1 eV, whereas the probe beam was either a fs white light continuum in the spectral range from 1.1 to 2.5 eV, or extracted from an optical parametric amplifier (OPA) in the spectral range from 0.5 to 1.1 eV. The probe beam was mechanically delayed with respect to the pump beam using a computerized translation stage in the time interval  $t$  of up to 200 ps. The changes  $\Delta T$  in the probe optical transmission  $T$  due to the pump were measured by a phase sensitive technique with a resolution in  $\Delta T/T$  of about  $10^{-4}$ , which corresponds to photoexcitations density of about  $10^{17} \text{ cm}^{-3}$ .  $\Delta T/T$  is either negative for photoinduced absorption (PA), or positive for stimulated emission (SE) and photo bleaching (PB). In addition, since the pump and probe beams were linearly polarized, we could also measure  $\Delta T$  for pump and probe with polarization parallel (par) and per-

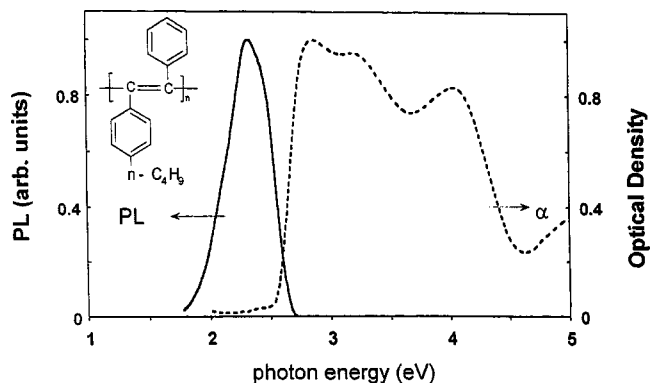


FIG. 1. Room-temperature optical spectra of PDPA- $n$ Bu film absorption  $\alpha$  and photoluminescence (PL). The polymer repeat unit is shown in the inset.

pendicular (per) to each other.

For the steady-state PM spectroscopy we used a standard cw experimental setup with a number of solid-state detectors, diffraction gratings, and optical filter combinations.<sup>1</sup> The pump beam was a modulated cw Ar<sup>+</sup> laser beam, and the probe beam was extracted from an incandescent lamp in the spectral range 0.3–2.5 eV.  $\Delta T/T$  was measured with a standard lock-in amplifier at frequencies in the range of 1 KHz that corresponds to photoexcitation lifetime of the order of a millisecond.

The DPA polymer was a disubstituted biphenyl derivative of transpolyacetylene, where one of the hydrogen-substituted phenyl groups was attached to a butyl group, which we referred to as PDPA-*n*Bu (see Fig. 1, inset).<sup>12</sup> The polymer films were cast on sapphire substrates from a toluene solution; the same solution was used for measuring the photoexcitation dynamics in a PDPA-*n*Bu solution. During the ps transient PM measurements the polymer films were kept at room temperature in an optical cryostat under a dynamic vacuum to prevent photo-oxidation;<sup>13</sup> no special precautions were taken for the ps transient measurements of the polymer solution.

The optical-absorption and PL spectra of a PDPA-*n*Bu film at room temperature (Fig. 1) have been recently studied in detail;<sup>14</sup> the respective spectra in PDPA-*n*Bu solution are very similar. The relatively broad absorption band with an onset at 2.65 eV, and peaks at about 2.85 and 3.05 eV, respectively, are due to delocalized  $\pi$ - $\pi^*$  transitions involving optical transitions from the ground state ( $1A_g$ ) to the first odd-parity exciton band ( $1B_u$ ), and phonon replicas. This absorption band is broadened by the inhomogeneity in the sample caused by a distribution of the polymer chain conjugation lengths. The band at 4 eV is due to delocalized to localized transitions.<sup>6</sup> The featureless PL band with an onset at 2.65 eV and peak at 2.4 eV somewhat resembles the first absorption band, with an apparent Stokes shift of about 0.45 eV between the peaks of the respective bands. We found that the PL emission has a quantum efficiency of about 50% both in solid films and solutions, which is considered to be relatively large in the class of PCP, and is thus in agreement with the assumed order  $E(1B_u) < E(2A_g)$ .<sup>6</sup>

The ultrafast excitation dynamics in dilute PDPA-*n*Bu solution are studied via the transient PM spectra as shown in Fig. 2(a). Upon photoexcitation (or at  $t=0$ ) a SE band at 2.4 eV and two PA bands with peaks at 1.2 eV (PA<sub>1</sub>) and 2.0 eV (PA<sub>2</sub>), respectively, are formed. We found that the SE band is polarized preferentially parallel to the pump polarization (see below), i.e., mainly along the polymer chains, and therefore we assign it as due to *intrachain excitons*. Since the SE and the cw PL bands [Figs. 1 and 2(a)] are essentially the same, we therefore attribute the PL in PDPA-*n*Bu to intrachain excitons with dipole moment lying along the polymer chains. Figure 2 inset shows that the SE lifetime is about 120 ps, similar to those of the two PA bands. This demonstrates that intrachain excitons in PDPA-*n*Bu have a strong SE band in the visible spectral range and two correlated PA bands in the visible/near-infrared spectral range, similar to intrachain exciton spectra in other luminescent PCP's.<sup>15</sup>

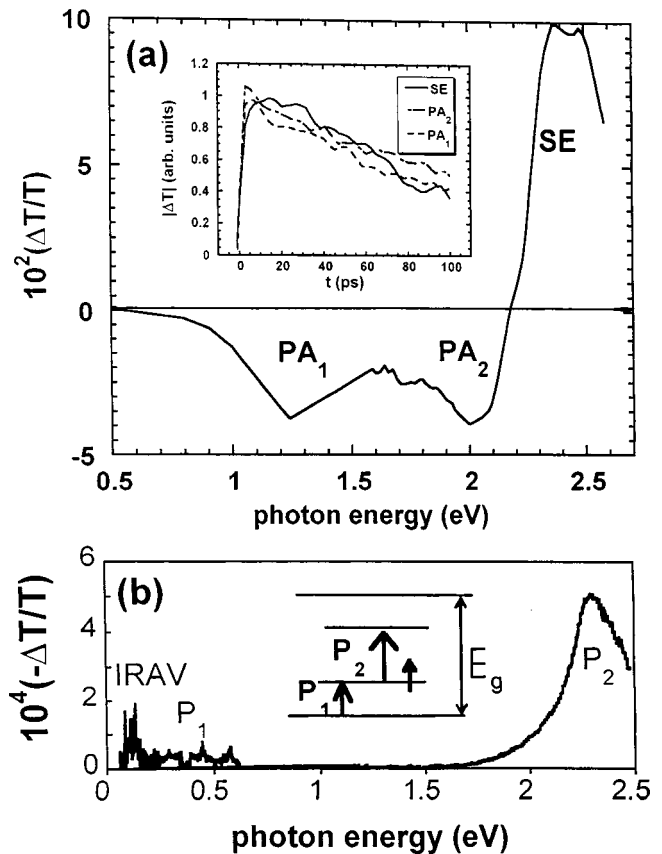


FIG. 2. (a) Transient PM spectrum of PDPA-*n*Bu solution at  $t=0$  showing a SE and two PA bands. The decay kinetics of the SE (full line) and two PA bands (dashed lines) are shown in the inset. (b) The steady-state PM spectrum showing other two correlated PA bands and photoinduced IRAV's. The inset shows the energy levels and optical transitions associated with a positively charged polaron excitation in PCP's.

Figure 2(b) shows the room-temperature steady-state PM spectrum of PDPA-*n*Bu in solution. The PM spectrum consists of two correlated PA bands at 0.25 and 2.35 eV, respectively, followed by PB of the  $\pi^*$ - $\pi$  transition (not shown). The lower energy PA band is correlated with photoinduced infrared active vibrations (IRAV) seen at energies below about 0.2 eV. We therefore conclude that the underlying long-lived species are charged, and, in accordance with previous studies using PA-detected magnetic resonance,<sup>1</sup> have spin  $\frac{1}{2}$ . Therefore the two PA bands are due to long-lived charged polarons [Fig. 2(b), inset].<sup>16</sup> Compared to the ps transient results above we conclude that the long-lived polarons are generated in PDPA-*n*Bu solution via exciton dissociation, and are therefore not the primary photoexcitations. This was also recently seen in another ps transient dynamics study of PDPA in solution, where the time in which excitons dissociate into polarons was measured to be about 200 ps.<sup>7</sup>

Figure 3(a) shows the ps transient PM spectra in a PDPA-*n*Bu film. In addition to the SE band and two PA bands at 1.1 eV (PA<sub>1</sub>) and 2.0 eV (PA<sub>2</sub>), respectively, which, as in Fig. 2(a) for PDPA-*n*Bu solution are due to photogenerated  $1B_u$  excitons, the transient PM spectrum in the polymer film also shows a PA band at 1.7 eV (PA<sub>g</sub>). At

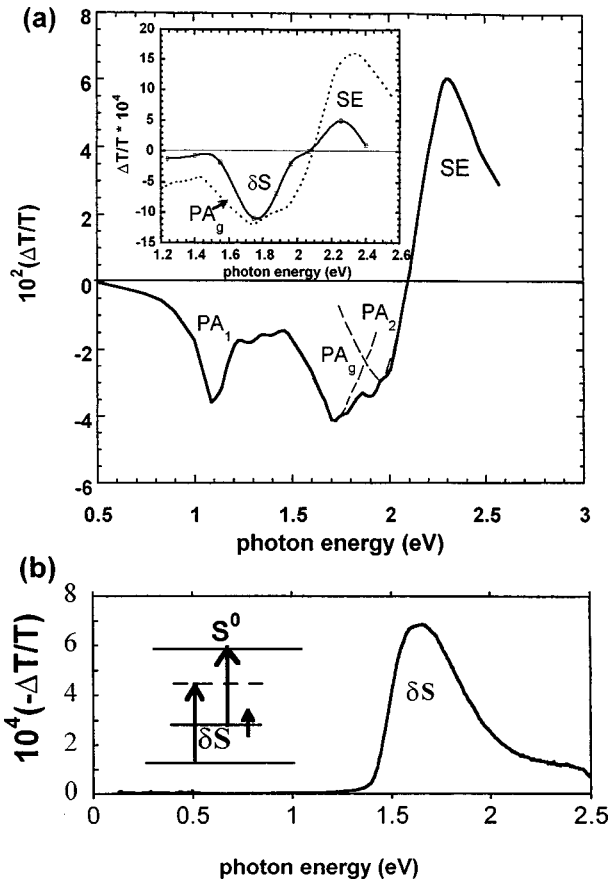


FIG. 3. (a) Transient PM spectrum of PDPA-*n*Bu film measured at  $t=0$  showing a SE and two PA bands. The higher energy PA band is decomposed into two separate PA bands, PA<sub>g</sub> and PA<sub>2</sub>. The inset compares the normalized transient photomodulation spectra at  $t=0$  (full line) and  $t=200$  ps (dotted line), where PA<sub>g</sub> transforms into  $\delta S$ . (b) The steady-state PM spectrum of the PDPA-*n*Bu film at 80 K showing a single, neutral PA band  $\delta S$ . The inset shows the two degenerate optical transitions  $\delta S$  associated with a neutral soliton excitation  $S^0$ .

200 ps PA<sub>g</sub> significantly narrows [Fig. 3(a) inset]; it becomes the dominant PA feature in the PM spectrum at longer delay times. The transient dynamics of the various PM bands are shown in Fig. 4. It is seen that whereas SE shares the same dynamics as PA<sub>1</sub> and PA<sub>2</sub> [Fig. 4(a) inset] having a lifetime of about 50 ps, it does not show the same dynamics as PA<sub>g</sub>. In fact, whereas SE has an exponential decay, the decay kinetics of PA<sub>g</sub> is complicated. This band decays much faster in the first few ps, but basically stops decaying after about 30 ps. Two possible scenarios can explain this latter dynamics: either PA<sub>g</sub> changes from one type of photoexcitation to another during the time period of about 10 ps, or the photoexcitations associated with PA<sub>g</sub> experience “random-walk-type” geminate recombination with recombination time of about 10 ps.<sup>10</sup>

To get further insight into the excited-state dynamics in a PDPA-*n*Bu film, we measured the time-resolved degree of polarization memory,  $P(t) = [\Delta T(\text{par}) - \Delta T(\text{per})] / [\Delta T(\text{par}) + \Delta T(\text{per})]$ , which reflects the transient reorientation of transition dipole moment.  $P(t)$  dynamics at the SE

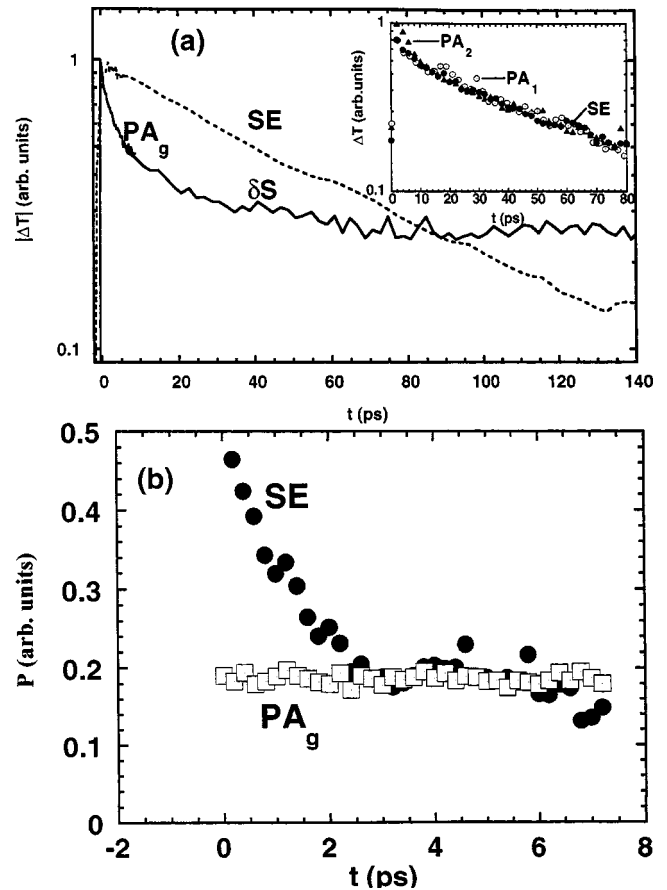


FIG. 4. (a) The transient decay dynamics of PA<sub>g</sub> and  $\delta S$  (full line) and SE (dashed line) in PDPA-*n*Bu film. The inset compares the transient decay dynamics of SE, PA<sub>1</sub>, and PA<sub>2</sub>. (b) The transient decay of the polarization memory  $P(t)$  measured at the SE band (2.3 eV, open circles) and PA<sub>g</sub> band (1.7 eV, full triangles).

(2.3 eV) and PA<sub>g</sub> (1.7 eV) bands appear to be very different from each other [Fig. 4(b)].  $P(t)$  at the SE band decays in about 2 ps to half its magnitude at  $t=0$ , whereas  $P(t)$  at the PA<sub>g</sub> band remains constant in time beyond 100 ps. The relatively fast  $P(t)$  dynamics at the SE band shows that the photogenerated  $1B_u$  excitons are quite mobile in the polymer film, probably via interchain hopping<sup>17</sup> (Fig. 5). In contrast,  $P(t)$  at PA<sub>g</sub> does not change so much during the first 10 ps, and this suggests that the photoexcitations associated with PA<sub>g</sub> are not involved in the interchain hopping process. This may be due to the strong lattice relaxation that follows PA<sub>g</sub> generation,<sup>9</sup> which suppresses interchain hopping.<sup>4,10</sup>

In Fig. 3(b) we show the steady-state PM spectrum in the PDPA-*n*Bu film at 80 K. In contrast to the PM spectrum in PDPA-*n*Bu solution that shows two PA bands [Fig. 2(b)] and associated IRAV's, in PDPA films only a single PA band ( $\delta S$ ) at 1.65 eV dominates the steady-state PM spectrum, and no IRAV's are observed. Using PA-detected magnetic resonance it was shown before<sup>1</sup> that  $\delta S$  is associated with spin- $\frac{1}{2}$  excitations; also the lack of IRAV's shows that  $\delta S$  is due to neutral excitations. This reversed spin-charge relationship, which contrasts other known spin- $\frac{1}{2}$  excitations in condensed-matter physics, is unique to soliton excitations in

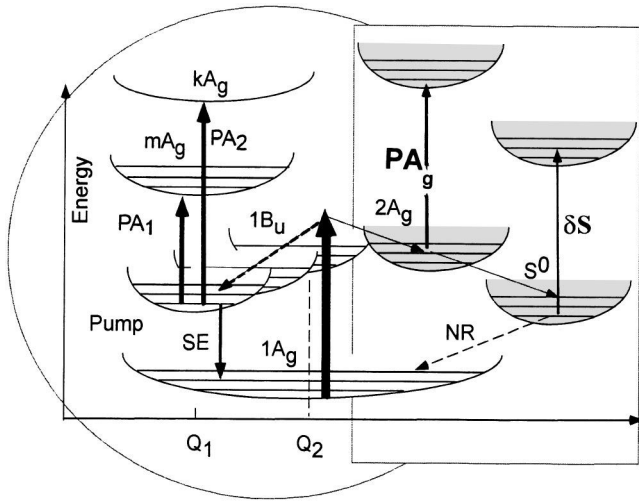


FIG. 5. Schematic representation in configuration coordinates  $Q$  of the energy levels, relaxation processes, and optical transitions in the two relaxation channels of PDPA-*n*Bu, namely the ionic (left) and covalent (right). The full vertical lines are optical transitions, whereas the dashed lines represent relaxation processes. The different parabolas associated with  $1B_u$  stand for intrachain exciton levels of polymers with various conjugation lengths, where the dashed line represents interchain hopping.  $mA_g$  and  $kA_g$  are upper energy states with even parity, which can be reached from the  $1B_u$  exciton by optical transitions ( $PA_1$  and  $PA_2$ , respectively).

degenerate ground-state PCP's.<sup>4</sup> We therefore identify  $\delta S$  as due to neutral solitons ( $S^\circ$ ), of which optical transitions are shown in Fig. 3(b) inset. From the similarity of the transient  $PA_g$  band at 200 ps and the slightly redshifted ( $\approx 0.1$  eV) steady-state  $\delta S$  band, we conclude that  $PA_g$  at  $t > 10$  ps is also due to neutral solitons. From the almost constant  $P(t)$  transient at  $PA_g$ , and the very similar spectrum at 100 fs and 200 ps we also suggest that the nature of  $PA_g$  remains unchanged with time, and thus it is due to neutral  $\bar{S}S$  pairs. Indeed soliton are topological excitations that cannot participate in interchain hopping.<sup>6</sup> This means that the transient  $PA_g$  decay up to about 10 ps [Fig. 4(a)] is due to ultrafast  $\bar{S}S$  recombination rather than formation of a new transient species.

Figure 5 schematically shows our proposed model for the ultrafast energy relaxation processes in DPA films. It contains two relaxation channels;<sup>18,19</sup> ionic, via  $1B_u$  and covalent, via  $2A_g$ , which is populated following an ultrafast phonon-assisted internal conversion from the photogenerated  $1B_u$  excitons.  $PA_g$  at short time is thus due to transitions from  $2A_g$  (dark) excitons. As in long chain polyenes<sup>20</sup> and  $t-(CH)_x$ ,<sup>21</sup> these excitons are subject to ultrafast recombination dynamics and this explains the ultrafast decay dynamics

seen in Fig. 4(a). In degenerate ground-state polymers  $2A_g$  is unstable with respect to the formation of soliton excitations and therefore undergoes fission into two neutral  $\bar{S}S$  pairs,  $2A_g \Rightarrow 2(S^\circ + \bar{S}^\circ)$ ,<sup>8,19</sup> followed by further separation into individual neutral solitons; the latter state has a slightly narrower PA band ( $\delta S$ ) compared to  $PA_g$ . A similar separation between ionic and covalent relaxation channels happens in other, nondegenerate ground-state PCP's,<sup>22</sup> except that the  $2A_g$  in the covalent channel separates into two triplets rather than into two soliton pairs. The triplets are stable in nondegenerate ground-state PCP's,<sup>9,19,22</sup> and thus soliton pairs are not formed. Comparing our data in PDPA-*n*Bu and the prototype degenerate ground-state polymer  $t-(CH)_x$ , we suggest that in  $t-(CH)_x$  the  $2A_g$  fission process occurs in the sub-ps time domain.<sup>21,23</sup> This may happen in  $t-(CH)_x$  since  $E(2A_g) \ll E(1B_u)$ .

The contrast between the steady-state PM spectra in PDPA-*n*Bu solution, that shows long-lived polarons, and films, that show long-lived neutral solitons [Figs. 2(b) and 3(b), respectively], is quite astonishing and points to a radical change in the photoexcitation dynamics in the two polymer chain environments. The underlying mechanism for this apparent difference may be the suppression of the covalent channel in PDPA-*n*Bu solution. The solvent thermal bath having many low-energy vibrations may enhance the hot exciton thermalization rate in the ionic channel in polymer solution. Since in PDPA-*n*Bu  $E(1B_u) < E(2A_g)$ , then in solution the covalent relaxation channel cannot be reached following the ultrafast hot exciton thermalization. Since solitons are byproducts of  $2A_g$  fission in the covalent relaxation channel then the ultrafast thermalization may explain the lack of soliton photoexcitations in PDPA-*n*Bu in solution.<sup>7</sup>

In conclusion, we unravel the interplay dynamics between  $1B_u$  and  $2A_g$  in disubstituted polyacetylene. In PDPA-*n*Bu solution only the ionic channel with  $B_u$  excitons is observed in the transient PM spectrum, whereas the steady-state PM spectrum is dominated by long-lived polaron excitations following few exciton dissociation. In PDPA-*n*Bu films, however, in addition to excitons, soliton-antisoliton pairs are also photogenerated via the covalent channel. The  $2A_g$  in the covalent channel is populated in the 100-fs time domain via phonon-assisted internal conversion, followed by fission into two neutral  $\bar{S}S$  pairs and their subsequent separation in the course of interchain hopping on a 10-ps time scale. This mechanism may also explain the  $\bar{S}S$  pair photogeneration in  $t-(CH)_x$ .<sup>21</sup>

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