Transient photoconductivity in oriented *trans*-polyacetylene prepared by the Naarmann-Theophilou method

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We present transient-photoconductivity results of oriented *trans*-polyacetylene prepared by the Naarmann-Theophilou method. In addition to the usual fast-decaying photocurrent peak, we report a large long-lived, temperature-dependent tail not previously seen in other forms of polyacetylene. By comparison of the data to that obtained from high-quality single crystals of polydiacetylene, we conclude that the magnitude of this tail implies higher-quality polyacetylene. The anisotropic behavior for different polarizations of the incident light is presented together with the effect of light intensity, temperature, and external field strength.

INTRODUCTION

The role of nonlinear localized excitations such as solitons and polarons in the conducting polymer *trans*-polyacetylene have received considerable theoretical and experimental attention. Nevertheless, the dynamics of charge transport is not fully understood, particularly in the subnanosecond domain. Numerous experiments have probed this short-time domain through photoinduced bleaching,[1] photoinduced absorption,[2-5] and photoconductivity.[6-8] Photoinduced bleaching demonstrates that oscillator strength is rapidly (subpicosecond) removed from the interband transition upon sample illumination with light of energy greater than the band gap. Photoinduced absorption demonstrates that the oscillator strength is deposited in a low-energy peak (0.45 eV) and a high-energy peak (1.35 eV) on a similar time scale. Both photoinduced excitations decay rapidly, within tens of picoseconds. Transient-photoconductivity measurements, which measure the product of the number of charge carriers and their mobility, include contributions from all mobile charged species. Results from photoconductivity experiments also indicate a fast decay followed by a small, long-lived component. Sinclair and co-workers[6] reported transient photoconductivity in unoriented Shirakawa polyacetylene to have a roughly exponential initial decay of lifetime 300 ps. Stretch-oriented polyacetylene samples prepared by the Durham procedure have been measured by Bleier *et al.*,[8] who found a somewhat shorter initial photoconductivity decay time of 100–150 ps.

Recently, Naarmann and Theophilou[9,10] have developed an improved method of synthesizing polyacetylene which yields fewer sp^3 defects and significantly higher electrical conductivity subsequent to doping. In order to characterize the intrinsic properties of polyacetylene, it is necessary to probe the transport during the subnanosecond time domain, i.e., before the transport is dominated by the sample morphology. With this as motivation, we present in this paper the results of transient photoconductivity measurements on stretch-oriented Naarmann-Theophilou polyacetylene.

EXPERIMENTAL RESULTS

Details of the photoconductivity apparatus have been previously reported.[6] The incident laser beam was linearly polarized with a dichroic polarizer and subsequently rotated via a half-wave plate. Photon fluxes were in the range of 10^{14}–10^{15} cm^{-2} per pulse with energy of 2.2 eV (566 nm) and a pulse duration of 20 ps. The polyacetylene samples were free-standing stretch-oriented ($6\times$) films with 200-μm-gap gold electrodes evaporated on it and attached with silver paint to the substrate. The time resolution of the data-acquisition system is approximately 40 ps.

Conductivity measurements performed with an electrometer yield a dark conductivity of 10^{-6} S/cm and a linear (Ohmic) current-to-voltage relationship over all voltages of interest. The samples were of the same batch tested by Basescu *et al.*[10] and found to have a doped (6 mol % of I_3^-) conductivity of 20 000 S/cm, nearly 2 orders of magnitude larger than similarly doped polyacetylene samples obtained by the conventional Shirakawa method. All samples were mounted with the chain-orientation direction parallel to the biasing electric field. Sample preparation was performed in an inert atmosphere, and the photoconductivity experiments carried out under vacuum of 10^{-4} torr or less.

Figure 1 shows the transient photoconductivity at room temperature and at 80 K due to a 0.25-μJ pulse of 2.2 eV polarized perpendicular to the chains with a bias field of 1.5×10^4 V/cm. By careful waveform averaging with regard to trigger jitter, we are able to resolve an intense and sharp peak at short times (< 100 ps), which we believe was averaged out in previous studies.[6-8] In the room-temperature curve, a long-lived tail is clearly present, considerably longer and more intense than previously reported for aligned Durham[8] or for unoriented Shirakawa material.[6] Assuming an effective quantum efficiency at 50 ps of 0.01 (Refs. 3 and 4) (which includes the probability of escaping early recombination), this yields a mobility of 2 cm^2/V s, similar to that obtained for other forms of polyacetylene[6,8] and inferred from photoinduced dichroism.[1] Both peak and long-lived pho-
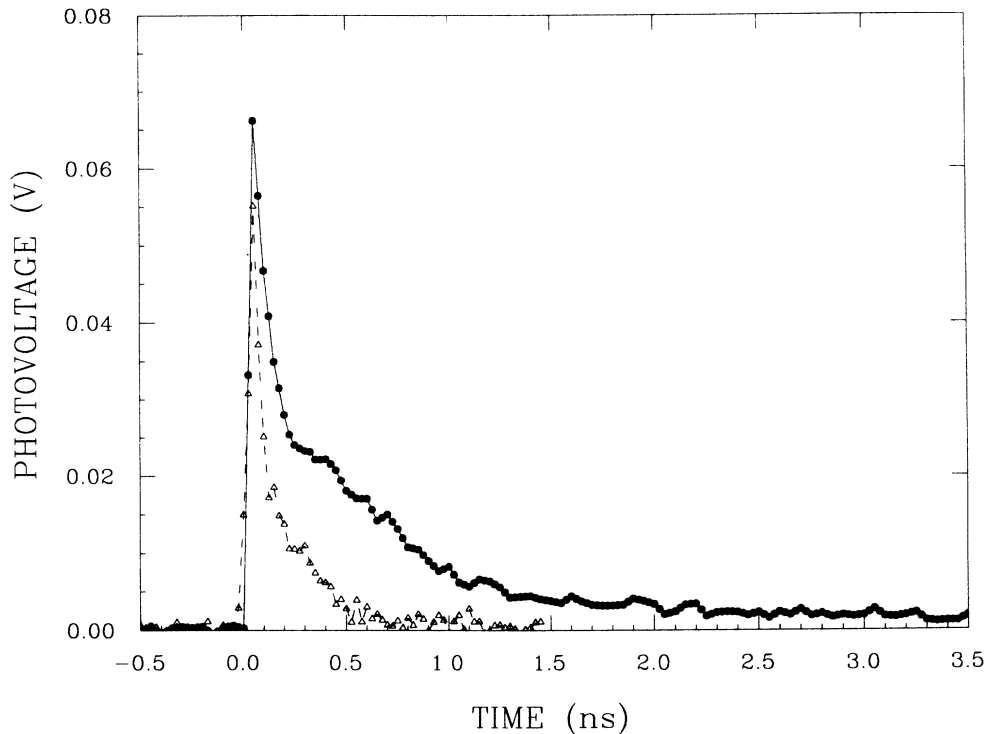
FIG. 1. Transient photocurrent across 50 Ω (see text). ●, 300 K; △, 80 K.

tocurrents scale in a roughly linear fashion with the applied electric field over 2500–15000 V/cm. The transient photoconductivity obtained for light polarized parallel to the chains is similar with a slightly faster (25%) decaying tail and a factor-of-3 smaller signal due to a combination of the greater reflectivity for this polarization and some intrinsic anisotropy favoring the perpendicular polarization, which will be discussed later. Due to this reduced signal level, the majority of data presented in this paper were obtained for the perpendicular-polarization case.

The transient photoconductivity at 80 K has the long-lived tail almost completely suppressed. The low-temperature peak is only slightly (17%) smaller than that found at room temperature and the decay time has shortened to 250 ps. Upon further cooling to 30 K, these parameters remain unchanged. Hence, the low-temperature photocurrent is very similar both in magnitude and decay time to the temperature-independent peak found by both Sinclair et al.[6,7] and Bleier et al.[8] in Shirakawa and Durham polyacetylene, respectively. Figure 2 illustrates the temperature dependence of the photoconductivity signal at 1.5 ns. Over the region 305–200 K the tail is approximately exponential in inverse temperature $(1/T)$ with an activation energy of 0.045 eV.

Figure 3 displays the first 800 ps of the 300-K data of Fig. 1 together with a convolution of $t^{-0.50}$ and a 36-ps rise-time Gaussian. The Gaussian represents the instrumental resolution and the time constant of 36 ps taken from the rise time of the data. The power-law decay dependence is more clearly seen in Fig. 4. At early times (before 700 ps) the decay is $t^{-0.5}$, changing to t^{-1} at approximately 1 ns.

Figure 5 shows the anisotropy of the peak photo-

current for both the raw data and corrected for reflectance by the function, $(1-R_\parallel)\cos^2(\theta)$ $+(1-R_\perp)\sin^2(\theta)$, where θ is the angle between the light-polarization vector and the chain direction. The reflection coefficient for light polarized parallel $(R_\parallel)$ and perpendicular $(R_\perp)$ to the chain direction is 0.50 and 0.05, respectively.[11] Even after the reflection correction, there is still a net anisotropy which varies as $1+0.7\sin^2\theta$ favoring the perpendicular polarization.

Figure 6 shows the dependence of the photoconductivity as a function of light intensity at three separate delay times after the laser pulse. All three curves were taken
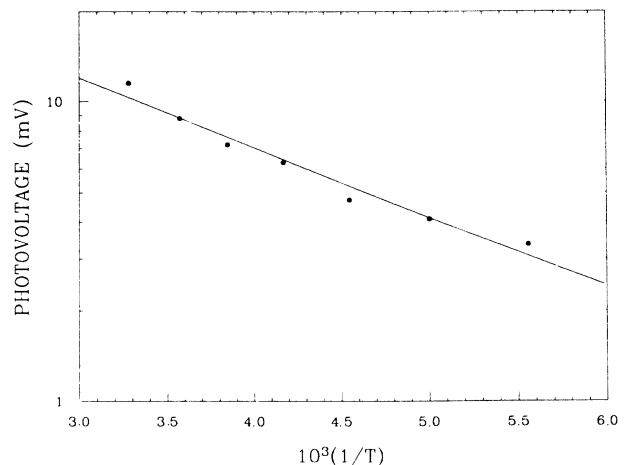

FIG. 2. Temperature dependence of photocurrent (across 50 Ω) at 1.5 ns.
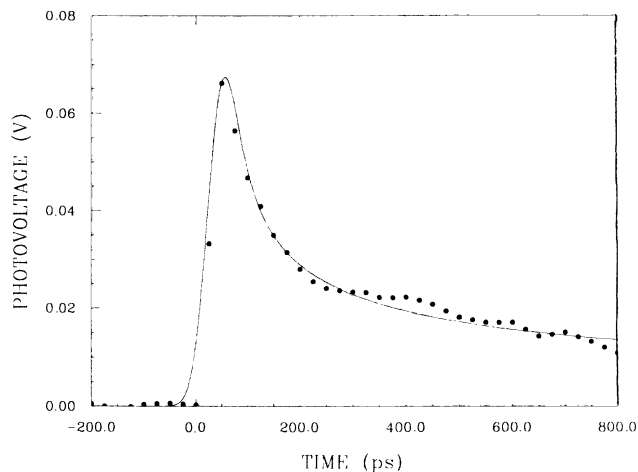
FIG. 3. The first 800 ps of photocurrent in Fig. 1. ●, sub-nanosecond photocurrent, 300 K; ———, convolution of $t^{-0.5}$ and 36 ps Gaussian.

with a 1.1-GHz amplifier with a rise time of several hundred picoseconds. The intensity dependence of the peak thus contains some averaging with longer times (which have a sublinear dependence); hence, the 0.92 exponent should be taken as a lower limit and the true peak dependence is probably linear, as reported by other authors.[6,8] At longer times (1.5 and 4.0 ns), the dependence becomes clearly sublinear.

DISCUSSION

Naarmann polyacetylene has attracted considerable interest because of the remarkably high conductivity[9,10] of the doped material. This enhanced conductivity is believed to be related to the higher quality of the polymer as inferred from the low sp^3-defect content found in this material.[9] This motivated us to investigate the effects the low defect content may have on the photoinduced conductivity at short times after photoexcitation. The most
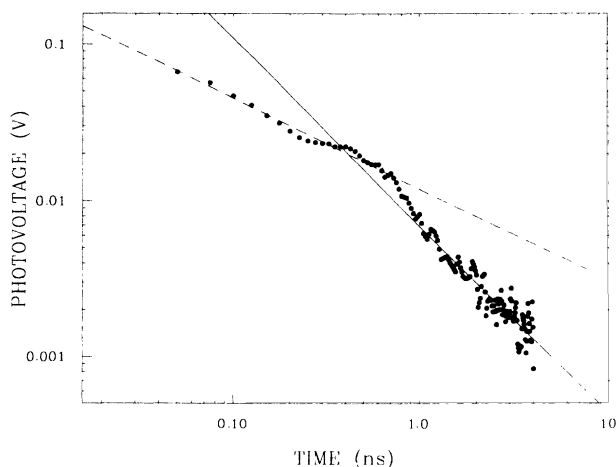

FIG. 4. Power-law decay of photocurrent from Fig. 1. — — —, $t^{-0.55}$; ———, $t^{-1.1}$.

striking result is the long-lived temperature-dependent tail seen in Fig. 1; this tail is not observed in other forms of polyacetylene. We believe that the sp^3 defects prevalent in Shirakawa and Durham polyacetylene serve as deep traps or barriers from which charge carriers cannot easily escape at room temperature. The Naarmann-Theophilou material contains fewer deep sp^3 defects and, consequently, has a longer-lived photocurrent at room temperature. This is consistent with the fact that Durham material has a photoconductivity decay even faster than Shirakawa material and is believed to have an even shorter conjugation length (implying more defects perhaps due to incomplete conversion of the precursor polymer[12]) than Shirakawa polyacetylene.[13,14]

The conjecture that the observed temperature-dependent photoconductivity tail in Naarmann-Theophilou polyacetylene is a result of low defect content is supported by the observation[15] that in single crystals of polydiacetylene the transient photoconductivity consists of a temperature-independent peak followed by a very-long-lived (10 ns) temperature-dependent tail. This suggests that the lifetime of the transient-photoconductivity tail may be inversely related to the defect content of the material.

The details of the subnanosecond room-temperature photoconductivity are shown in Fig. 3 together with the decay expected for a $t^{-0.50}$ process as observed with the time resolution of our system. In Shirakawa polyacetylene, photoinduced bleaching[1] of the interband transition has been reported to decay with this same power-law dependence for the first 50 ps. Similarly, photoinduced absorption in Shirakawa polyacetylene was reported[2] to decay as an error function erf[$(A /t)^{0.5}$] (with a decay constant $A =0.1$ ps at 300 K) for the first 100 ps. The asymptotic limit of such an error function is $t^{-0.5}$, which would be approached within a few picoseconds, well below our time resolution. This supports the assertion[16] that the photoconductivity and photoinduced-absorption experiments are probing the same charged entity. We believe that the primary charged carrier measured by the photoconductivity are solitons (S^+,S^-), whether they are directly produced or produced as a product of polaron-polaron[17] or polaron-S^0 interactions.[18] It should be noted that the convolution of $t^{-0.5}$ with a Gaussian (the decay constant determined by our instrumental resolution) is in good agreement with our data for times as long as 700 ps, whereas the photoinduced experiments on unoriented Shirakawa material[1,2] show this $t^{-0.50}$ behavior only out to 100 ps (with a sub-picosecond excitation pulse). For longer times, the photoinduced-absorption decay slows to $t^{-0.37}$. Since the $t^{-0.5}$ decay is consistent with a one-dimensional random walk,[2] one possible explanation is that the Naarmann-Theophilou material has a larger conjugation length than the unoriented Shirakawa material, as would be implied by the lower sp^3 content.

In such a photoconducting polymer, one-dimensional transport would be executed until the charge carrier reaches an sp^3 defect (e.g., chain end) which would serve as a deep trap or barrier to further transport. Specifically, when the photogenerated solitons reach
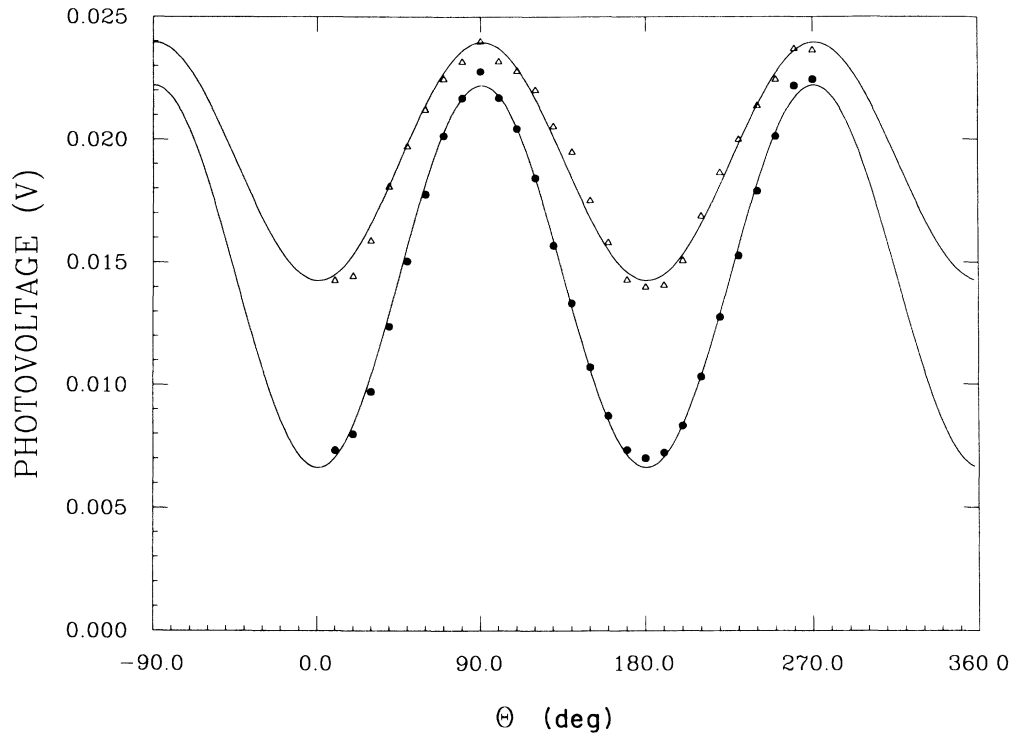
FIG. 5. Anisotropy of the peak photovoltage, $\theta=0°$, corresponds to optical polarization parallel to chain direction; ●, raw data; △, corrected for reflection dependence; ——, fit to data (corrected for reflectance, triangles) of form $A(1+B\sin^2\theta)$. $B=0.7$.

these traps, the decay rate of the photoconductivity signal would increase (i.e., faster than $t^{-0.50}$) because the trapped soliton would be immobile and could not contribute to the photoconductivity. The photoinduced-absorption decay rate, however, would be expected to decrease (i.e., slower than $t^{-0.50}$) once the solitons reach the sp^3 defects, because a trapped soliton does contribute to the photoinduced signal but is less likely to recombine than a mobile soliton. As previously discussed, the photoinduced decay rate does indeed slow from $t^{-0.50}$ to
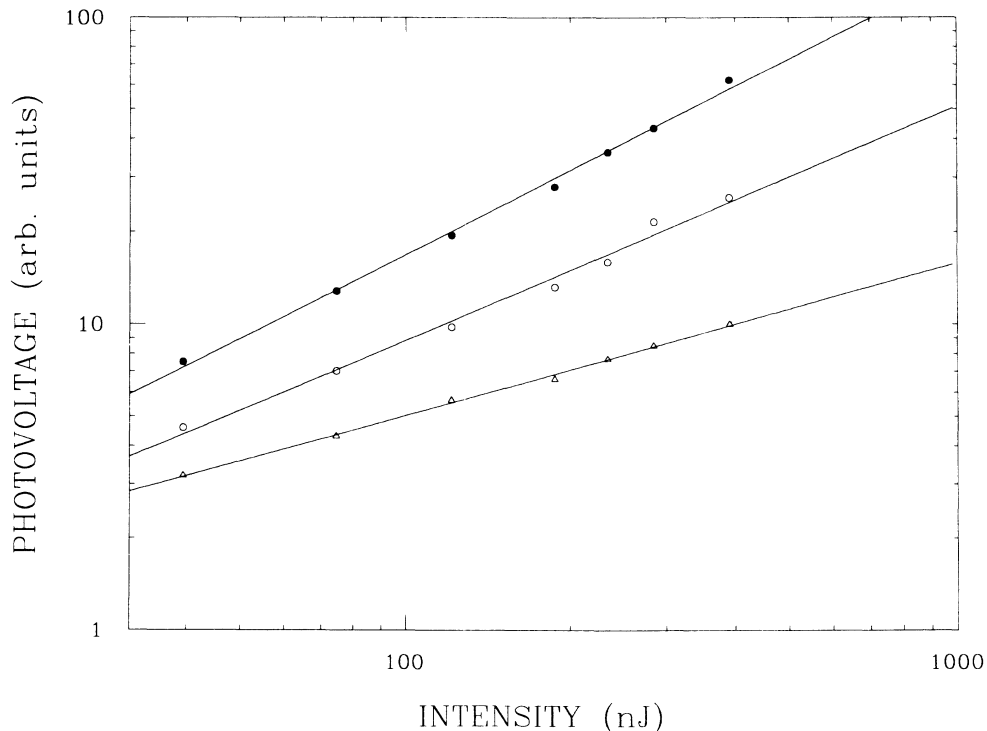

FIG. 6. Intensity dependence of photovoltage at three different times (300 K): ●, peak, $i_{ph}\sim I^{0.92}$; ○, 1.5 ns, $i_{ph}\sim I^{0.75}$; △, 4 ns, $i_{ph}\sim I^{0.50}$.

$t^{-0.37}$ within 100 ps for Shirakawa polyacetylene.

Figure 4 clearly shows the expected increase (from $t^{-0.50}$ to $t^{-1.0}$) in photocurrent decay rate when solitons become trapped at defect sites. Bleier *et al.*[8] have measured a t^{-1} dependence from 10 ns (the earliest time measured) to microseconds. At longer times, they find a $t^{-0.50}$ decay, in agreement with the results of Etemad and co-workers,[19] who concluded that it is a result of dispersive (hopping) transport from energetically equivalent sites.

Thus, there are three broad time regimes relative to photoconductivity: (i) the subnanosecond domain, which may provide information on intrinsic one-dimensional transport, (ii) the transitional regime from nanoseconds to microseconds where deep trapping is important, and, finally, (iii) the microsecond-to-seconds domain where dispersive transport dominates.

We turn now to the temperature dependence of the photoconductivity shown in Fig. 1. The close resemblance of the *low-temperature* photoconductivity curve of the Naarmann-Theophilou material to the *room-temperature* photoconductivity curve of Shirakawa material[6] is particularly interesting. Figure 2 shows the photocurrent measured at 1.5 ns. At this time, there is no temperature-independent contribution (as seen at earlier times). The activated temperature dependence appears to result from shallow (0.045 eV) trapping which may be due to oxygen traps or remaining *cis* segments in the polymer chain. At low temperature (80 K) these defects can trap charge carriers for long times. Thus, the resemblance of the low-temperature photoconductivity decay in Naarmann-Theophilou material to that of the room-temperature Shirakawa and Durham material occurs because, in both cases, the trap depth is large relative to the thermal energies available to the charge carriers. We again remark that the trapping mechanism responsible for decreasing the photoconductivity at low temperatures should increase the photoinduced signal at low temperatures by slowing recombination, which is in agreement with the increase in the photoinduced-absorption signal found at low temperature, as reported by Shank *et al.*[2]

If we assume the temperature dependence at times shorter than 1.5 ns to be due to the same shallow trapping mechanism, then by comparing the high- and low-temperature curves and assigning the difference to trapping a trap density can be found. The ratio of the 80-K photocurrent to the 300-K photocurrent drops to 0.5 by 175 ps after the peak, which, by our assumption, implies one-half the charge carriers are trapped by 175 ps at 80 K. The distance traveled by these charge carriers can be estimated by assuming either a random walk[2] with a jump time of 0.1 ps and a thermal velocity of $\sim 10^6$ cm/s or a uniform motion with a drift velocity $(v = \mu E)$ of 3×10^4 cm/s. Both lead to an average distance traveled before trapping of roughly 400 Å which corresponds to ~ 1 per 300 carbon atoms. These residual traps may be unrelated to sp^3 content, since they appear to be of the same energy (0.05 eV) and density ($\sim 1\%$) as oxygen-induced traps that have been calculated[20] and measured.[21]

The temperature independence of the transient photo-current reported in Shirakawa[6] and Durham[8] polyacetylene has been previously explained by considering the charge carriers produced to be "hot"[6,8] and, thus, their mobilities are independent of the thermal energy of the lattice. However, calculations[22] suggest that thermalization should occur within 1 ps. In addition, Shank[5] has observed anomalous photoinduced-absorption decay behavior in the subpicosecond domain and attributed this to thermalization of hot carriers with a thermalization time of 160 fs. This evidence has led to the suggestion[22] that the temperature-independent photoconductivity results are due to heating of the sample by the laser pulse. Our data on Naarmann-Theophilou polyacetylene demonstrate that it is possible to observe genuine temperature dependence when it is present, at least for times greater than 50 ps and temperatures above 80 K, providing evidence against the sample-heating hypothesis. Between 80 and 30 K the photoconductivity decay curve remains unchanged.

The anisotropy of the peak photocurrent is shown in Fig. 5; both the raw data and the data after correction for the polarization-dependent reflection are shown. The corrected data indicate a slight anisotropy, ≈ 1.7, in favor of the perpendicular polarization. The same value for the anisotropy was obtained in highly aligned Durham polyacetylene.[8] Two independent factors favor the photoconductivity generated by light with perpendicular polarization. First, it is expected that polarons on different chains should have a greater probability of escaping geminate recombination than an S^+, S^- pair confined to the same chain. Secondly, the absorption depth for the perpendicular case is more than an order of magnitude greater than the parallel case (a factor of 25 for highly aligned chains[11]). Thus, one initially expects that bimolecular recombination should be greatly reduced in the perpendicular case. The incident optical intensity used in our measurements was 5×10^{14} photons/pulse. Assuming an absorption depth of 500 Å (Ref. 11) for the parallel polarization yields 10^{20} excitation-pairs/cm^3 per pulse. Solitons have a reported lifetime[3] of less than 1 ps; this results in a steady-state excitation density (during illumination) of approximately 10^{18} soliton-pairs/cm^3. Since the density of carbon atoms is approximately 2×10^{22}, only one excitation pair exists per approximately 5000 carbon atoms, and this density decreases rapidly after the 20-ps illumination is completed. The perpendicular excitation density is an order of magnitude less, owing to its much smaller absorption coefficient. Thus, at the illumination levels considered, the excitation density is sufficiently low that the different absorption depths and, hence, bimolecular recombination, play a minimal role in affecting the peak photocurrent.

The perpendicular polarization does favor charge separation with the creation of electrons and holes (which rapidly pick up a lattice deformation and become polarons) on neighboring chains. These excitations are expected to have a lower probability of geminate recombination than intrachain excitations (solitons[23]) and should, therefore, make a greater contribution to the photoconductivity (per photon). A simple model for the

polarization dependence of the photoconductivity can be expressed by the following equation:

$$i_{\rm ph} = I_0 \{ (1 - R_\parallel)(\cos^2\theta)n_s\mu_s$$
$$+ (1 - R_\perp)(\sin^2\theta)[(1-f)\mu_p n_p + f\mu_s n_s] \} ,$$

where I_0 is the incident flux, θ is the angle between the polarization and the chains, $R_\parallel = 0.50$ and $R_\perp = 0.05$ are the polarization-dependent reflection coefficients, $n_{s,p}$ is the probability of solitons or polarons to escape early-time recombination, $\mu_{s,p}$ is the mobility for solitons and polarons, and f is the fraction of solitons generated during perpendicular-polarization illumination. This equation is of the form $A + B\sin^2\theta$, in agreement with the form of the anisotropy data.

Assuming all excitations created with the perpendicular polarization are polarons $(f = 0)$, then the ratio $\mu_p n_p / \mu_s n_s$ is 1.7. Since the mobility of polarons is estimated to be somewhat larger than that of solitons,[22] it is surprising that the observed ratio is so small. Either the probability of escaping recombination for polarons and solitons is similar, or only a fraction f of the charge carriers generated with the perpendicular polarization are polarons and the remaining fraction $(1 - f)$ are solitons. Recent calculations by Baeriswyl and Maki[24] imply that because of the zig-zag structure of the polyacetylene chain the intrachain absorption dominates, even for perpendicular polarization. Thus, for perpendicular polarization such intrachain absorption will lead to soliton pairs on the same chain. Based on their estimates, we conclude that perpendicular polarization will yield $f \sim \frac{2}{3}$, which results in the ratio $\mu_p n_p / \mu_s n_s = 3.1$. Thus, we attribute the observed intrinsic anisotropy to the enhanced creation of polarons for the perpendicular polarization. Similar conclusions have been reached in photoinduced-absorption experiments.[11]

Finally, we discuss the intensity dependence of the photoconductivity for the perpendicular polarization, as shown in Fig. 6. As discussed in the Experimental Results section, the peak is linear in intensity, as expected for this range of fluence from the excitation densities calculated above. The long-lived photocurrent tail provides us with the opportunity to measure the intensity dependence at later times. One possible explanation of the data is to assume that the photocarriers tend to saturate the traps. This would lead to the photocurrent becoming less intensity dependent (i.e., sublinear in the light intensity) for times beyond the characteristic trapping time. Trap-saturation effects have been reported to occur in the long-lived photoinduced-absorption signal.[25] The idea of trapping, furthermore, is consistent with the arguments presented above to explain the different decay rates of the photoconductivity and photoinduced absorption.

CONCLUSION

In summary, we have investigated the fast transient photoconductivity of oriented trans-polyacetylene prepared by the Naarmann-Theophilou method. The results are similar to those obtained in other forms of polyacetylene with the exception of a large temperature-dependent tail persisting for several nanoseconds. By comparison of the data to that obtained from high-quality single-crystals of polyacetylene, we conclude that the magnitude of this tail implies higher quality polyacetylene, consistent with the low sp^3 content reported by Naarmann and Theophilou. The temperature dependence of the tail results from shallow traps (0.045 eV) with a density estimated to be approximately 1 per 300 carbon atoms.

ACKNOWLEDGMENTS

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