

# PHYSICAL REVIEW B

## CONDENSED MATTER

THIRD SERIES, VOLUME 32, NUMBER 6

15 SEPTEMBER 1985

### Infrared-photoinduced-absorption studies in soluble *trans*-polyacetylene

R. Dorsinville, R. Tubino, S. Krimchansky, R. R. Alfano, and Joseph L. Birman

*Institute for Ultrafast Spectroscopy and Lasers, Physics Department and Electrical Engineering Department,  
The City College of New York, New York, New York 10031*

A. Bolognesi, S. Destri, M. Castellani, and W. Porzio

*Istituto di Chimica delle Macromolecole, Consiglio Nazionale delle Ricerche, Milano, Italy*

(Received 5 April 1985)

We report on the observation of photoinduced excitations in *trans*-polyacetylene in its liquid form in the frequency range from 2000 to 6000  $\text{cm}^{-1}$ . These measurements strongly suggest that *trans*-polyacetylene is capable of supporting charged solitons even in solution.

#### INTRODUCTION

Most recently, absorption, fluorescence, Raman scattering, and time-resolved emission spectroscopy were measured<sup>1</sup> in a new liquid form of soluble polyacetylene (PA) consisting of polyene chains grown on activated sites of polybutadiene which acts as a soluble carrier.<sup>2</sup> These measurements have shown that the liquid form has similar absorption and emission properties to that of the solid form. The blue shift of the absorption peak and the polarization properties of the emission spectrum of the soluble form indicate a reduction of the interchain interactions and of the conjugation length compared to the solid form.<sup>1</sup> The question of whether or not *trans*-PA is able to support "solitons" in its liquid form was left open. In this paper we report on the observation of photoinduced excitations in *trans*-PA in its liquid form. These measurements imply that the soluble *trans*-PA should be able to support free solitons even in solution.

According to Su and Schrieffer<sup>3</sup> a photoinduced electron-hole pair evolves to a soliton-antisoliton pair in about 100 fsec. The pair is coupled to nonbonding localized states at the center of the gap and an important test of the existence of solitons in the soluble *trans*-PA should be the observation of photoinduced absorption below the interband threshold. Recently, infrared optical absorption due to photogenerated carriers has been reported<sup>4-7</sup> in solid, insoluble *trans*-PA. We were able to observe the photoinduced-absorption spectrum of the soluble *trans*-PA in the energy range from 2000 to 6000  $\text{cm}^{-1}$ .

#### METHODS

Two different samples were used in the experiments: a solution of *trans*-PA in toluene (concentration 1  $\text{mg}/\text{cm}^3$ )

in a 1-mm-thick quartz cell and a solid sample prepared from the solution by evaporating it on a sapphire plate. These samples were mounted on the cold finger of a nitrogen Dewar. The photoexcitation was produced by a 100-mw cw argon-ion laser ( $h\nu=2.4$  eV) modulated at 90 Hz. The ir emission of a glowing silicon resistor was focused into the sample and the transmission analyzed with an ir spectrometer coupled to a InSb detector. The photoinduced-absorption changes were recorded by lock-in detection and displayed on a recorder.

#### RESULTS AND DISCUSSION

In Fig. 1 the photoinduced absorption of the evaporated soluble *trans*-PA at 77 K is plotted versus photon energy. This spectrum is similar to the photoinduced spectra of nonsoluble solid *trans*-PA.<sup>5</sup> The main feature is a broad asymmetric band peaking at about 0.49 eV with full width at half maximum of 0.3 eV. The ir photoinduced-absorption spectrum of a toluene solution of *trans*-PA at 180 K just above the freezing temperature of toluene is also displayed in Fig. 1. Below this temperature crystallization of the solvent occurs which increases the scattering and causes the signal to disappear. Although the detected signal from the solution at 180 K was about an order of magnitude weaker than the signal from the evaporated film, we were able to measure the photoinduced spectrum and found it similar to the spectrum of the film or of standard solid *trans*-PA.

We have also measured the magnitude of the photoinduced absorption as a function of temperature for both samples. In Fig. 2, the induced absorption at 0.49 eV is plotted versus temperature. These curves are similar to the one measured for the nonsoluble polyacetylene.<sup>5</sup> The amplitude of the photoinduced change in absorption decreases with increasing temperature, becoming unobserv-

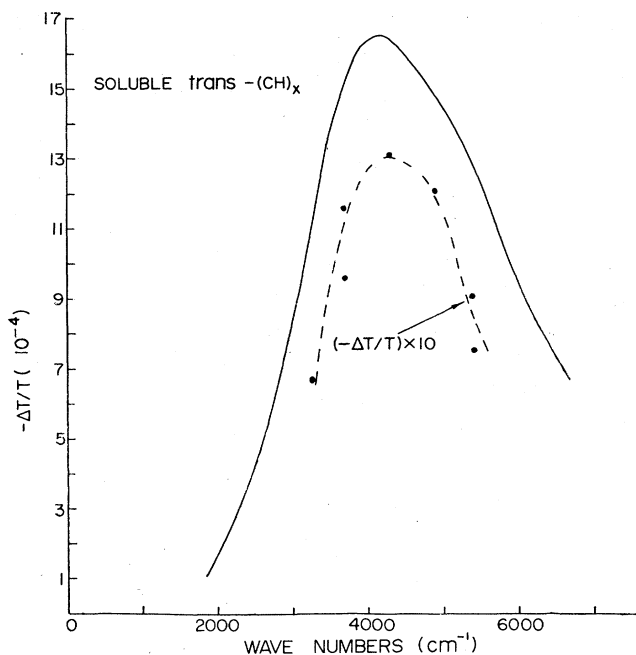


FIG. 1. Photoinduced absorption spectra of soluble *trans*-PA. Solid line, film at 77 K. Broken line, solution at 180 K.

able above 220 K. The experimental curve displayed in Fig. 2 for the evaporated film of the soluble PA shows the characteristic "knee" around 150 K attributed to the unbinding of the pinned soliton pairs with temperature.<sup>7</sup> Figure 3 shows the magnitude of the photoinduced-absorption change at 0.49 eV for the evaporated film of soluble polyacetylene as a function of the laser intensity. The dependence upon laser intensity is similar to previ-

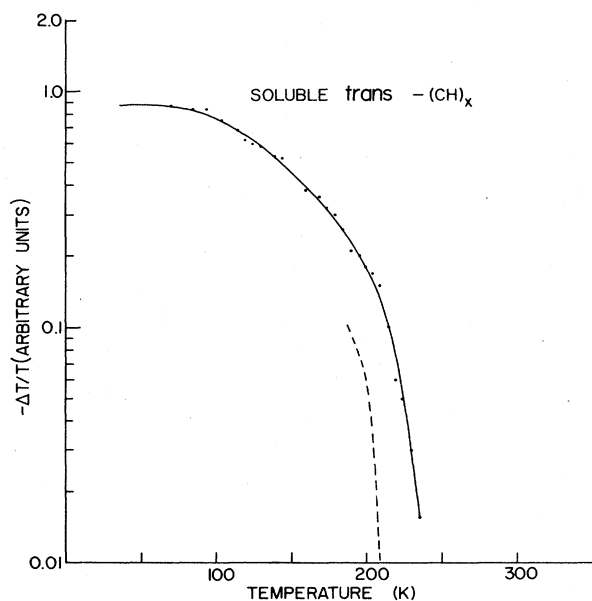


FIG. 2. Temperature dependence of the induced absorption at 0.49 eV in soluble *trans*-PA. Solid line, film. Broken line, solution in toluene.

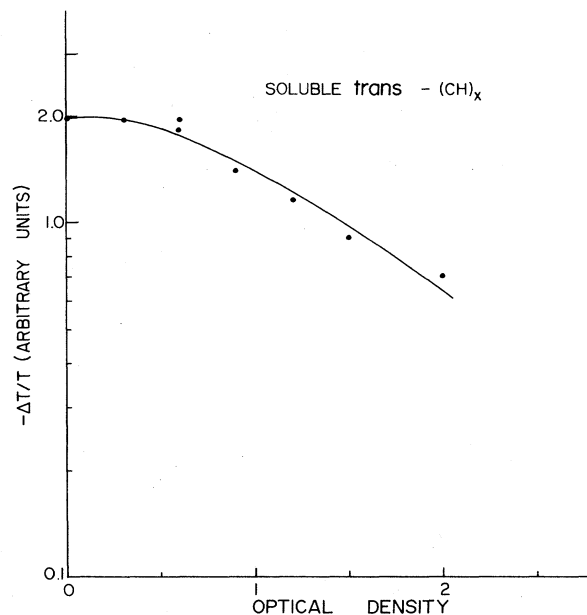


FIG. 3. Photoinduced absorption at 0.49 eV, as a function of the attenuation of the laser pump, of an evaporated film of soluble *trans*-PA.

ously reported results for nonsoluble *trans*-PA<sup>5,6</sup> where the peak intensity increases as  $\sqrt{I}$  for  $I < 20$  mw/cm<sup>2</sup> and saturates above this low value. According to Ref. 6 the square-root dependence suggests that photoexcitations in *trans*-PA must decay in pairs and the low saturation level implies the existence of a photoinduced mode of decay.

## DISCUSSION

The purpose of preparing grafted soluble polyacetylene has been the expectation of being able to study isolated polyenic chains in which the contribution to the optical and transport properties arising from interchain effects could be possibly separated from the intrachain effects.<sup>8</sup> However, there is evidence that the grafted forms of polyacetylene prepared so far<sup>2,9</sup> do not form a true solution but rather tend to cluster into micellar aggregates, whose size and shape depend on the solvent and on the polymerization conditions.<sup>10,11</sup> Even though there is no definitive structural data available on (CH)<sub>x</sub> in solution and the extent of molecular aggregation is not fully understood, it is our opinion that the soluble material used in the present study differs from the conventional Shirakawa films in two significant ways.

(1) Conjugation length. A rough estimate of the conjugation length in solution has been obtained from an analysis of the resonant Raman band shapes and of the excitation profiles.<sup>12,13</sup> These indicate that most of the scattering intensity in solution comes from sequences whose conjugation length ranges from 20 to 40 conjugated double bonds. The reduction in conjugation length with respect to that estimated for conventional Shirakawa insoluble films is also supported by the blue shift observed in the electronic absorption maximum of the *trans* component in solution.<sup>14</sup> As noted in Ref. 1 a residual *cis*

content is probably present in the sample and could contribute to the reduction in conjugation length.

(2) Chain aggregation. No direct structural information of the polymer in solution has been so far obtained from the nuclear magnetic resonance (NMR) spectra. A preliminary characterization of the soluble  $(\text{CH})_x$  used in the present study has been attempted both in solution (inelastic light scattering) and on films cast from the solution [transmission electron microscopy (TEM), electron diffraction spectra]. Light scattering data<sup>11</sup> rule out an extended conformation of the copolymer molecule in solution and indicate the presence of micellar aggregates whose average radius is approximately 200 Å for the toluene solutions. A probable model for these aggregates is a core of polyacetylene surrounded by the polybutadiene matrix, which shields the polyenic chains from the solvent thus preventing the observation of the NMR signal. Figure 4 shows a typical TEM of cast films obtained from a solution containing 50% of  $(\text{CH})_x$ . The difference in morphology between our copolymer and Shirakawa films is apparent. No fibrillar morphology is detected and the ultimate microdomains (indicated by arrows), in which polyacetylene preferentially segregates, do not exceed 100 Å perpendicularly to the chain axis. This size is considerably lower than the corresponding value found for the Shirakawa films. Within these microdomains a reduced degree of order is detected by the width of the diffraction peaks.<sup>15</sup>

All these data indicate that even though some aggregation in solution appears to exist, the environment experienced by the polyenic chain changes quite significantly from the insoluble Shirakawa films to the solution. Raman data seem to support this picture. As a matter of fact, the value for the inhomogeneous broadening parameter ( $\Delta = 650 \text{ cm}^{-1}$ ) obtained from an analysis of the sliced Raman excitation profiles of our soluble  $(\text{CH})_x$  indicates a spread of the electronic energies for a chain of given conjugation length larger than the value observed for a true solution ( $\Delta = 50 \text{ cm}^{-1}$ ) for carotene in isopentane but significantly smaller than the value observed for the insoluble films (a few thousand wave numbers; this substantial change could be attributed to the internal strains during isomerization which are greater for the solid than for the solution).

In conclusion, the measurements reported in the present paper strongly suggest that even in solution *trans*-polyacetylene is capable of supporting solitons. Using the conjugation length of our soluble  $(\text{CH})_x$  inferred from the optical and Raman data, the present results show that soliton excitations can exist even in relatively short conjugated segments. Further experimental work on the photoinduced infrared spectra of oligomers of various length is

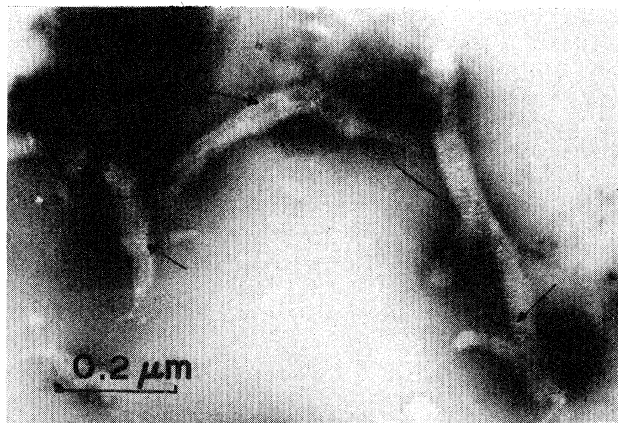


FIG. 4. TEM of  $\text{OsO}_4$  vapor-stained  $(\text{CH})_x$  copolymer film. The arrows indicate the ultimate  $(\text{CH})_x$  microdomains.

required to determine the shortest conjugation length capable of supporting solitonic excitations. This information would provide a better understanding of the role played by solitons as charge carriers in conjugated polymers.

The second point to be stressed is the close similarity (peak position and shape) between the near-infrared photoinduced absorption observed in our polyacetylene in solution at 0.49 eV and that in Shirakawa films (reported at 0.43 eV by Vardeny *et al.*<sup>5</sup> and at 0.48 eV by Blanchet *et al.*<sup>6</sup>). Some authors have interpreted<sup>16,17</sup> this peak as originating from an optical transition involving the charged solitons created by the absorption of the light quanta. If this is the case, the large shift of about 0.9 eV between the absorption peak of neutral (observed as an absorption dip at 1.4 eV in Shirakawa films<sup>17</sup>) versus the charged solitons appears to be maintained even in solution. This implies that the Coulomb correlation is only slightly changed by the modified environment experienced by the polyenic chain in solution.

#### ACKNOWLEDGMENTS

This research is supported in part by the U.S. National Aeronautics and Space Administration (NASA) and by the U.S. Air Force of Scientific Research (AFOSR) at the Institute of Ultrafast Spectroscopy and Lasers (IUSL). It is also supported in part by the United States—Italy Binational Program of the National Science Foundation, under Grant No. NSF-DMR-83-03981, and by PSC-BHE (Professional Staff Congress—Board of Higher Education) CUNY grants at the City College.

<sup>1</sup>R. Tubino, R. Dorsinville, W. Lam, R. R. Alfano, J. L. Birman, A. Bolognesi, S. Destri, M. Catellani, and W. Porzio, *Phys. Rev. B* **30**, 6601 (1984).

<sup>2</sup>S. Destri, M. Catellani, and A. Bolognesi, *Macromol. Chem. Rapid Commun.* **5**, 353 (1984).

<sup>3</sup>W. P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. Lett.* **42**, 1698 (1979).

<sup>4</sup>Z. Vardeny, J. Strait, D. Moses, T. C. Chung, and A. J. Heeger, *Phys. Rev. Lett.* **49**, 1657 (1982).

<sup>5</sup>Z. Vardeny, J. Orenstein, and G. L. Baker, *Phys. Rev. Lett.* **50**, 2032 (1983).

<sup>6</sup>G. Graciela, B. Blanchet, C. R. Fincher, and A. J. Heeger, *Phys. Rev. Lett.* **50**, 1938 (1983).

<sup>7</sup>G. Graciela, B. Blanchet, C. R. Fincher, and A. J. Heeger,

- Phys. Rev. Lett. **51**, 2132 (1983).
- <sup>8</sup>P. Calvert, *Nature (London)* **304**, 487 (1983).
- <sup>9</sup>G. L. Baker and F. S. Bates, *Macromolecules* **17**, 2619 (1984).
- <sup>10</sup>F. L. VanNice, F. S. Bates, G. L. Baker, P. J. Carroll, and G. D. Patterson, *Macromolecules* (to be published).
- <sup>11</sup>C. Cuniberti, P. Piaggio, G. Dellepiane, M. Catellani, L. Piseri, W. Porzio, and R. Tubino, in *Proceedings of the International Workshop on Polymer Trends, Capri, 1984* (unpublished).
- <sup>12</sup>A. Bolognesi, R. S. Cataliotti, G. Dellepiane, G. Paliani, L. Piseri, and R. Tubino, in *Proceedings of the IXth International Conference on Raman Spectroscopy, Tokyo, 1984* (unpublished), p. 414.
- ed), p. 414.
- <sup>13</sup>R. S. Cataliotti, G. Paliani, G. Dellepiane, S. Fuso, S. Destri, L. Piseri, and R. Tubino, *J. Chem. Phys.* **82**, 2223 (1985).
- <sup>14</sup>A. Bolognesi, M. Catellani, S. Destri, W. Porzio, and R. Tubino, in *Proceedings of International Workshop on Polymer Trends, Capri, 1984* (unpublished).
- <sup>15</sup>A. Bolognesi, M. Catellani, S. Destri, W. Porzio, S. V. Meille, and E. Pedemonte, *Mol. Cryst. Liq. Cryst. A* **118**, 76 (1985).
- <sup>16</sup>J. Orenstein, Z. Vardeny, G. L. Baker, C. Eagle, and S. Etemad, *Phys. Rev. B* **30**, 786 (1984).
- <sup>17</sup>S. Etemad, G. L. Baker, G. B. Roxlo, B. R. Weinberger, and J. Orenstein, *Mol. Cryst. Liq. Cryst.* (to be published).

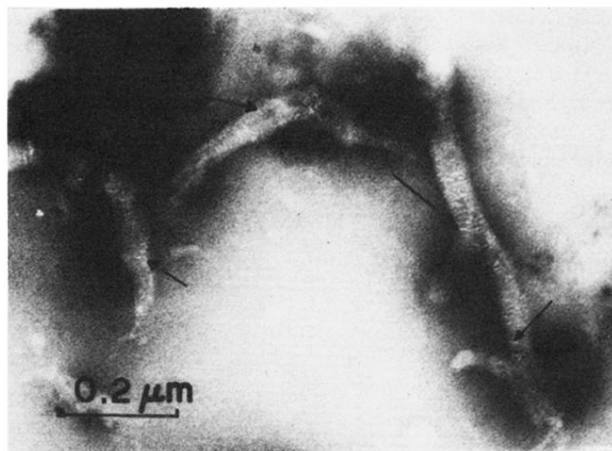


FIG. 4. TEM of OsO<sub>4</sub> vapor-stained (CH)<sub>x</sub> copolymer film. The arrows indicate the ultimate (CH)<sub>x</sub> microdomains.