PHYSICAL REVIEW B VOLUME 30, NUMBER 11 1 DECEMBER 1984

Optical properties and photoexcitation of a novel liquid form of soluble polyacetylene

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(Received 10 April 1984)

Optical absorption, fluorescence emission, Raman scattering, and time-resolved emission experiments are reported on a new liquid form of soluble polyacetylene. This liquid consists of separate polyene chains, grown on activated sites of a polybutadiene chain. The depolarization ratios as well as the time-resolved spectrum of the secondary emission were measured. The relevant spectral features are discussed and analyzed in terms of the lack of interchain interactions which characterize the polymer in solution.

INTRODUCTION

In this paper we report on optical properties and photoexcitation effects obtained on a novel form of polyacetylene. In this material, because of the special preparation, we expect that interchain forces, as well as chain rigidity, are strongly reduced compared to the solid form. This permits us to study intrachain effects without interference from interchain interactions, cross-linking, etc.

Polyacetylene (PA) synthesized according to the traditional Shirakawa procedure[1] is an insoluble, infusible, and poorly stretchable polymer, which, in spite of its simple chemical formula $(CH)_x$, is difficult to characterize. Electronic micrography, x-ray and electron diffraction data[2] have shown that solid films of conventional polyacetylene consist of a fleece of loosely tangled fibrils with diameter of about 20 nm, randomly oriented. The films consist of several polyene chains held together by interchain forces; these forces together with the chain rigidity typical of the conjugated systems are responsible for the lack of solubility of the polymer as well as for its poor mechanical properties. The existence of relatively strong van der Waals interactions between the polyene chains makes it difficult to disentangle the interchain and intrachain contributions to the electrical, optical, and spectroscopical properties of the polymer, thus preventing a full understanding of its electrical transport mechanism. X-ray data[1] have also shown that the interchain spacings decrease when the pristine cis polymer is thermally isomerized to the thermodynamically stable trans isomer.

Single-chain effects could be observed in dilute polymer solutions. Attempts to obtain soluble conjugated polymers by polymerizing differently substituted acetylene monomers have been rather disappointing, mainly because of steric effects. The electronic properties of substituted soluble polymers bear very little similarity with those of the parent polyenic chain and the conductivity rapidly decreases as hydrogen atoms are substituted by side groups.[3]

Using the Shirakawa catalyst, and growing polyene chains into activated sites of polybutadiene, which acts as a soluble carrier, we have been able to obtain a novel form of polyacetylene partially soluble in conventional aromatic solvents. The synthetic details of this work will be published elsewhere.[4] Recently, a different synthetic route to obtain a soluble graft copolymer has been proposed by workers at Bell Laboratories[5] using polyisoprene or polystyrene as carrier polymers. Their product contains only one polyacetylene block per carrier chain and is quite different from our material which possesses a comblike structure owing to the presence of more than one polyene chain attached to the polybutadiene backbone. Moreover, with our method the polyene chain length can be controlled by varying the polymerization time.

The availability of the polyene chains in solution can contribute to solution of controversies regarding the structure and the properties of PA, namely the extent of interchain interaction, the cross-link formation, and the soliton dynamics in a truly one-dimensional system. The dynamics of the configurational and conformational isomerism could be properly studied by using conventional spectroscopic techniques in solution, such as NMR, infrared, Raman, and absorption spectroscopy, as well as the more recently developed ultrafast laser spectroscopy.

ABSORPTION SPECTRUM

The optical-absorption spectrum of the soluble PA is shown in Fig. 1. It consists of a broad and asymmetric

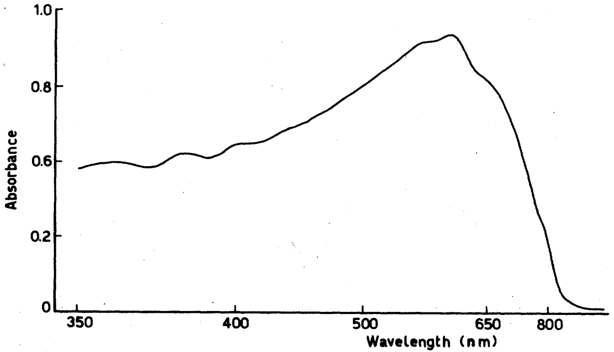

FIG. 1. Absorption spectrum (at room temperature) of soluble polyacetylene.

absorption band centered at 580 nm. The absorption maximum is blue-shifted by 90 nm with respect to the maximum exhibited by the optical-absorption spectrum of thin films[6] prepared by the conventional Shirakawa polymerization technique.

Two possible explanations might account for the observed shift.

(1) In the soluble PA the interchain interactions are probably far less effective than in the solid. It has been shown[7] that the introduction of three-dimensional (3D) interactions through transverse hopping integrals has the effect of reducing the energy gap of a strictly one-dimensional chain. As a matter of fact, it has been observed[7] that in the solid film an increase of the hydrostatic pressure lowers the absorption edge. Our observed shift between the solution and the solid can therefore monitor the reduction of the 3D interactions in the dissolved polymer (single-chain effects).

(2) It is well known that in polyenes the lowest optical absorption ($\pi \rightarrow \pi^*$) shifts towards lower energies with increasing chain length.[8] The observed blue shift could be related to a reduction of the average conjugation length in the solution with respect to the film. Because the totally symmetric vibrations are also sensitive to the conjugation length,[9] an analysis of the Raman band shapes as a function of the exciting laser frequency could provide further information on the distribution of the chain lengths in solution.

The absorption spectrum of the soluble *trans*-PA exhibits phonon-assisted side bands. Even though the spectrum is rather poorly resolved, nevertheless the underlying vibronic structure is quite apparent, the average separation between two consecutive peaks being about 1300 cm^{-1}, which is the average phonon frequency ($\bar{\omega}$) of the two Raman-active phonons. The shape of the absorption spectrum results from phonon replicas of the zero-phonon band; these map the electronic joint density of states between the valence and the conduction band[10] (inverse-square-root singularity for a strictly one-dimensional semiconductor). The intensity of the nth phonon-assisted transition centered at $\Omega = \Omega_0 + n\bar{\omega}$ (Ω_0 being the frequency of the purely electronic transition) is given by[11]

$$I_n \sim e^{-S} S^n / n! , \tag{1}$$

where $S = V_1^2/\omega_1^2 + V_2^2/\omega_2^2$ is the Huang-Rhys factor, and V_1 and V_2 are the electron-phonon coupling constants, which are responsible for the broadening of the absorption band and for the resonant enhancement of the two totally symmetric phonons observed in the Raman scattering ($\omega_1 = 1121$ cm^{-1} and $\omega_2 = 1521$ cm^{-1}). Owing to the lack of the resolution in the absorption spectrum, individual *e-p* coupling constants cannot be evaluated. However, a rough estimate of the overall Huang-Rhys factor S can be obtained by fitting the absorption spectrum [using Eq. (1)] and a proper joint density of states, namely an inverse-square-root singularity rounded off by lifetime- and inhomogeneous-broadening effects.

Assuming the peak at 660 nm is the zero-phonon line, a value of about 1.5 is obtained for the Huang-Rhys factor. If, on the other hand, the peak at 600 nm is assumed to be the origin of the vibronic progression, a somewhat smaller coupling constant ($S = 0.8$) is obtained. This value is consistent with the trend observed in polyenes of various lengths: The electron-phonon interaction inferred from the absorption spectrum slowly decreases with the increasing conjugation length, reflecting the increasing delocalization of the electronic excitation. As a matter of fact, an extensive analysis of the absorption spectrum and excitation profile of β-carotene[12] ($n = 9$ double bonds) yield $S = 1.16$ for this molecule.

Unlike the solution, the absorption spectrum of *trans*-PA films does not exhibit any resolved vibronic structure even at 7 K.[13] Merging individual phonon-assisted processes into a continuum might be due to various effects, namely short excitation lifetimes (homogeneous broadening), transverse bandwidth (interchain interactions),[7] and inhomogeneous broadening of the vibronic levels.[14] This latter effect arises from a distribution of the electronic energies due to inequivalent absorbing sites related to sample inhomogeneity. The presence of a resolved vibronic structure in the absorption spectrum of the dissolved polymer (at room temperature) seems to indicate a sharper distribution of chain lengths and, or a reduction of the interchain interactions, as expected.[15] These conclusions are also supported by the fact that, under controlled isomerization conditions, even the reflectivity spectrum of thick films of *trans*-PA exhibits a well-resolved vibronic structure,[16] the zero-phonon line having been observed at 833 nm. It has been inferred that such films are composed largely of chains of infinite conjugation length, as a distribution of shorter conjugation lengths would obliterate the vibrational structure. An alternative expansion for the presence of the vibronic structure in the electronic absorption spectrum of soluble *trans*-PA is that the two peaks at 635 and 600 nm might be due to the residual cis content in the polymer. If this is the case, the considerations previously reported to provide a rough estimate of the Huang-Rhys factor S are still correct, since, within the framework of the Su-Schreiffer-Heeger Hamiltonian, which assumes only transfer integrals between nearest neighbors, the two isomers are identical from the electronic point of view.

RESONANT RAMAN SPECTRUM

The emission spectrum of the soluble PA taken with the 488-nm exciting line is shown in Fig. 2. The spectrum consists of two fundamental Raman vibrations centered at

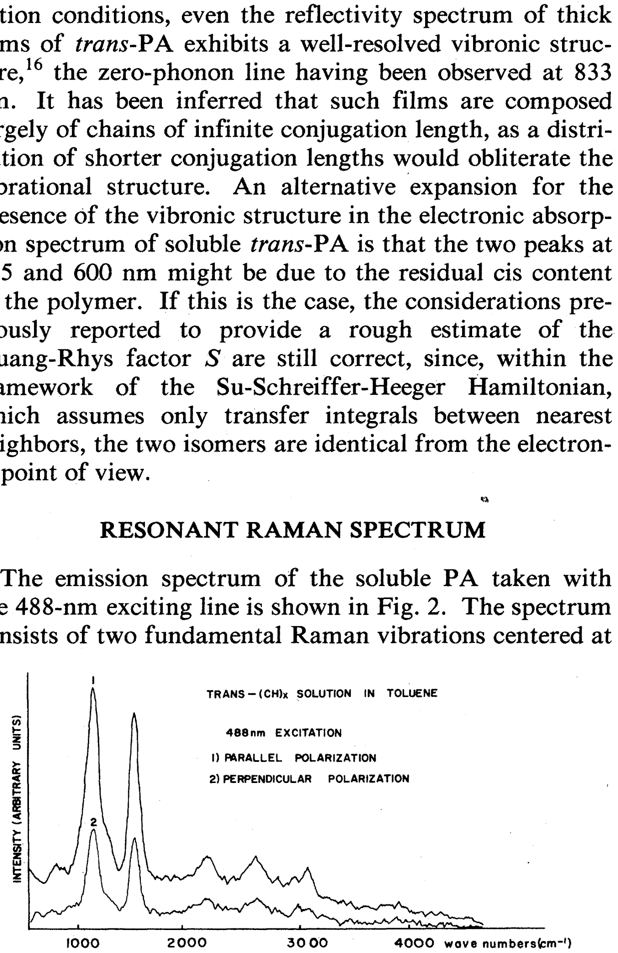

FIG. 2. Emission spectrum of soluble polyacetylene, excitation 488 nm. (1) Analyzer parallel to the polarization of the laser beam. (2) Analyzer perpendicular to the polarization of the laser beam.

1110 and 1490 cm^{-1}, followed by a weak second-order scattering. A broad background underlies the Raman spectrum, but no clear luminescence peaks are detected. The spectrum of the solution is consistent with the emission spectrum of films of *trans*-PA reported by various authors.[17,18] Therefore, we believe that our soluble PA consists of polyene chains mainly in the trans form, as might be expected from thermodynamic considerations on the polymerization temperature.

The two strong Raman lines observed at 1110 and 1490 cm^{-1} are easily assigned to the C—C and C=C A_g stretching vibrations, respectively. As the spectrum is resonantly enhanced, no Raman lines of the carrier polymer are observed. Availability of soluble PA offers the unique opportunity of measuring the polarization properties of the scattered radiation in order to confirm the assignment. The observed depolarization ratio for both the observed Raman lines (see Fig. 2) is $P_s = 0.4$, in agreement with the expected value for A_g modes under noncubic symmetry (C_{2h} point group). Overtone modes, also expected of A_g symmetry, exhibit similar depolarization ratios.

A rather strong polarization is also exhibited by the luminescence background, which is considerably lower in the perpendicular polarization. Even though the emission spectrum of neat toluene also exhibits some background scattering, its baseline does not appreciably change with the polarization. The polarized emission appears to be intrinsic of the dissolved polymer, but presently it cannot be unambiguously established whether it comes from impurities (traces of the catalyst) or from a radiative recombination of the photogenerated states of the polyene chain.

The measure of the ratio between the Raman intensity of the two A_g phonons (roughly 1.5) can provide an estimate of the relative electron-phonon coupling constant. Neglecting temperature effects, which are irrelevant for high-energy phonons, one has[19]

$$\frac{I_1}{I_2} = \frac{V_1^2/\omega_1^2}{V_2^2/\omega_2^2} \frac{|S(\Omega_L) - S(\Omega_L - \omega_1)|^2}{|S(\Omega_L) - S(\Omega_L - \omega_2)|^2} , \tag{2}$$

where

$$S(\Omega_L) = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \left[\frac{V_1^2}{\omega_1^2} \right]^{n_1} \left[\frac{V_2^2}{\omega_2^2} \right]^{n_2} \frac{1}{n_1! n_2!} \frac{\gamma + i(\Omega_L - \Omega_0 - n_1\omega_1 - n_2\omega_2)}{(\Omega_L - \Omega_0 - n_1\omega_1 - n_2\omega)^2 + \gamma^2} , \tag{3}$$

where γ is the inverse lifetime of the vibronic resonant states and Ω_L is the exciting wavelength. As the frequencies of the two Raman lines are not drastically different, and the absorption spectrum is a rather smooth function of the frequency, one obtains

$$I_1/I_2 \cong (V_1^2/\omega_1^2)(V_2^2/\omega_2^2) , \tag{4}$$

which yields $V_1/V_2 = 0.90$.

Combining this result with the value for the overall Huang-Rhys factor S obtained from the previous analysis of the absorption spectrum, it is then possible to derive the individual electron-phonon coupling constants for the isolated *trans*-PA chain ($V_1 \simeq 775$ cm^{-1} and $V_2 \simeq 860$ cm^{-1}). An attempt to interpret these data in terms of a simple Hückel (tight-binding) theory for the electronic states[20] and a proper lattice-dynamical model[21] for the phonon displacements is in progress and will be reported elsewhere.

Generally, the resonant secondary emission of the dissolved PA bears a very close similarity with the corresponding spectrum of the solid *trans*-PA. In this latter system the lack of a distinctive band-edge recombination luminescence peak and a strong multiphonon Raman activity has been taken as evidence of the soliton formation due to an intrinsic instability of the photogenerated electron-hole pair.[22] Our results seem to imply that PA should be able to support solitons even in solution. Experiments on the photoinduced infrared spectrum of the solution are presently being carried out to check this point.

TIME-RESOLVED EMISSION SPECTRUM

The time dependence of the secondary emission of the solution of PA measured using a picosecond streak camera spectrometer is shown in Fig. 3. The spectrum consists of a sharp peak whose decay time is faster than the temporal resolution ($\tau_f \approx 20$ ps) followed by a long-time tail, which decays with a time constant of about 200 ps

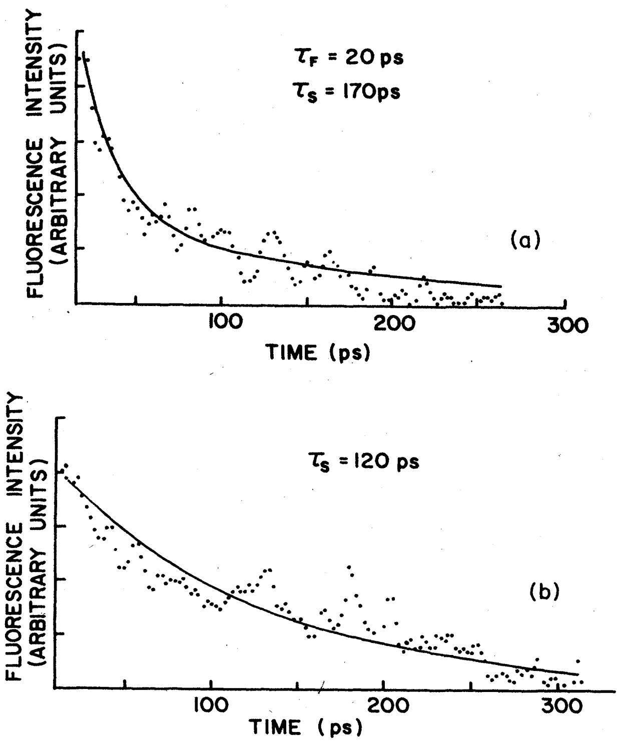

FIG. 3. Time-resolved emission spectrum of soluble polyacetylene, excitation 530 nm. (a) Emission for wavelengths > 540 nm. (b) Emission for wavelengths > 580 nm.

($\tau_s \approx 170$ ps). The main features of the time-resolved spectrum are very similar to those observed by Andrews *et al.*[23] in the corresponding spectrum of *trans*-PA films. In order to clarify the nature of the long-time tail, we have also recorded the time-resolved spectrum [Fig. 3(b)] using a filter which passes the emitted wavelength above 580 nm, thus excluding the Raman lines. Only the slow component ($\tau_s \approx 120$ ps) was present in the spectrum. Further work is in progress on the details of the temporal profile.

These observations combined with the polarization properties of the emission background observed in the cw scattering provide a possible explanation for the mechanism of secondary emission in dissolved PA. Following Pellegrino *et al.*,[24] we define an order parameter which characterizes the polarized emission in terms of the intensity measured parallel and perpendicular to the incident polarization direction $I_{\|}(t)$ and $I_{\perp}(t)$, respectively. It is $r(t)$, the emission polarization anisotropy, defined as

$$r(t)=\frac{I_{\|}(t)-I_{\perp}(t)}{I_{\|}(t)+2I_{\perp}(t)} . \tag{5}$$

If the molecule excited by the light rotates or otherwise transfers its energy prior to emission, the resulting emission will depolarize and $r(t)$ will decrease. From Fig. 2 it is apparent that for the observed Raman lines ($t \to 0$), $r(0)=0.4$. However, the order parameter for the background luminescence emission is considerably lower, ranging from $r(t)=0.25$ for emitted frequencies near the exciting line to $r(t)\to 0$ (total randomization) for the low-frequency tail of the emission. These data suggest that as the light is absorbed, an instantaneous (coherent) $t=0$ scattering occurs, giving rise to the two polarized Raman lines in the cw spectrum and to the short-lived peak in the time-resolved emission. However, due to nonradiative energy transfer, via various possible decay routes (collisions, multiphonon emission, etc.), dephasing of the optical transition also occurs, yielding the observed background scattering in the cw spectrum and the long-time tail in the picosecond spectrum. As the dephasing increases with the energy loss of the excited state, the polarization of the scattered radiation is expected to decrease, which is consistent with observation.

SUMMARY

The optical properties of the soluble PA in solution seem to indicate both a reduction of the interchain interactions and of the conjugation length with respect to the polymer obtained in the solid form. The electronic absorption spectrum and the position of the two Raman lines yield a rough estimate of the average conjugation length of 20—25 double bonds. This value has been obtained using an empirical relationship, between $\omega_{C=C}$ and the number of double bonds, derived[25] from the observed vibrational frequencies of short trans polyenes. Preliminary data[26] on films obtained by evaporating the solution on a quartz plate show that, upon doping with iodine vapor, three new dopant-induced infrared bands appear. In the case of the conventional Shirakawa films some authors have interpreted the bands as evidence for the soliton formation. These results could have two different implications: (1) The polyene chain in solution possesses a certain degree of flexibility which reduces the planarity of the carbon backbone and therefore the conjugation length. Upon crystallization, the chain flexibility is lost and a higher conjugation able to support soliton-formation length is resumed. (2) The conjugation length in the films obtained by evaporation is the same as in solution (namely, 20—25 double bonds). If this is the case, soliton excitations can exist even in relatively short conjugated segments. Work is presently in progress to distinguish the possibilities.

ACKNOWLEDGMENTS

We thank Mr. H. Zarrabi and Mr. M. Junnarkar for technical assistance. This work was partially supported by U.S.A.—Italy Binational Program, National Aeronautics and Space Administration, and U.S. Air Force, Office of Scientific Research, National Science Foundation, U.S. Army Research Office, and grants from the Board of Higher Education Professional Staff Congress Faculty Research Award Program at the City College of New York.

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