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# Molecular structure of "*trans*"-polyacetylene: The presence of remnant *cis* units and their influence on soliton formation and diffusion

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We report the infrared spectra of "*trans*"-polyacetylene that has been prepared by thermal isomerization of Shirakawa *cis*-$(CH)_x$. The minimum of $\sim 5\%$ residual 740-$cm^{-1}$ absorption observed for all cases studied is suggested to be due to isolated remnant *cis* linkages. It is shown that these remnant *cis* linkages may confine the neutral soliton and hence affect the neutral-soliton diffusion coefficient. Implications for the soliton-generation mechanism and for conjugation lengths derived from Raman spectra are pointed out.

## I. INTRODUCTION

Recently, there has been intense experimental and theoretical interest in the two isomers of polyacetylene, *trans*-$(CH)_x$ and *cis*-$(CH)_x$.[1] According to the soliton model,[2,3] both undoped isomers are semiconductors due to a commensurate Peierls distortion. For the ideal *trans* isomer, the two possible phases of the dimerization are degenerate in energy, and a soliton is the boundary between regions of the two phases, Fig. 1(a). When singly occupied, the soliton is neutral with spin $\frac{1}{2}$. If the soliton level is doubly occupied or empty, the soliton is charged, although spinless. In contrast, the *cis-transoid* [Fig. 1(b)] and *trans-cisoid* [Fig. 1(c)] structures are not degenerate in energy.[4] Hence, solitons remain bound in pairs, forming polarons and bipolarons in this system.[5] Photoinduced absorption, magnetic, infrared, and conductivity studies[1] have been interpreted as evidence for the presence of solitons in the *trans* structure and the absence of free solitons in the *cis* structure.

Since both phases of the dimerization in ideal *trans*-$(CH)_x$ have the same energy, the neutral soliton can, in principle, freely diffuse along the chain.[6,7] A large number of experiments have been undertaken to establish the diffusion coefficient of these solitons.[8-15] Several authors have analyzed magnetic resonance data and concluded that the solitons are (1) highly mobile, (2) thermally activated, or (3) confined to small regions of the sample or all three simultaneously. Similarly, there has been considerable disagreement concerning the interpretation of resonance Raman scattering data for *trans*-$(CH)_x$, including interpretation of the asymmetric line shapes as a ramification of a limited distribution of chain lengths ("short" and "long" chains) or as the energy dependence of relaxation pathways.[16-21]

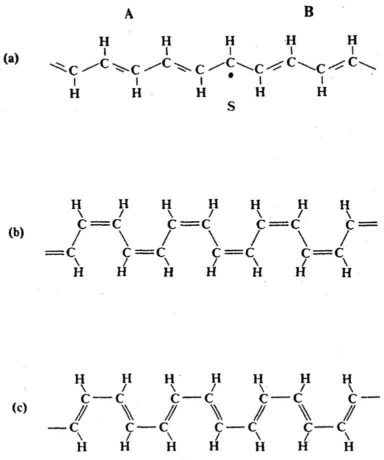

FIG. 1. Idealized polyacetylene structures: (a) *trans*-$(CH)_x$ with a soliton separating two regions ($A$ and $B$) of bond alternation with opposite phase (schematic). The soliton is actually spread over $\sim 15$ carbon atoms; (b) *cis*-$(CH)_x$ (*cis-transoid*); (c) *trans-cisoid* configuration.

Here, we present the results of our experimental study of the remnant *cis* content that remains in "*trans*"-polyacetylene. These data show that there is always residual 740-$cm^{-1}$ absorption normally assigned to *cis* linkages in the final isomerized polymer and when analyzed as being the *cis* isomer, it comprises a minimum of 5% of the sample. It is shown that these *cis* linkages form a low-energy barrier to neutral-soliton motion and lead to a macroscopic diffusion coefficient much smaller than the microscopic one characteristic of the region in which the soliton is confined. Implications of this result for the interpretation of both spin-relaxation results, Raman studies, and models of soliton generation are pointed out.

## II. EXPERIMENTAL TECHNIQUES

Thin ($< 10$ $\mu m$) $(CH)_x$ films on KBr discs were produced using a modified Shirakawa technique.[22] The films were composed of $\sim 500$-Å-diameter fibrils and were highly crystalline. Isomerization changed neither the fibril diameter, crystallite size ($\sim 100$ Å), nor percent crystallinity.[23] The *cis* to *trans* ratio was measured[24,25] by the ratio of the integrated intensities of specific ir modes of *cis* (740 $cm^{-1}$) *trans* (1010 $cm^{-1}$).

## III. EXPERIMENTAL RESULTS

Figure 2 shows typical infrared-absorption data for thin-film polyacetylene before isomerization (92% *cis*). The *cis* and *trans* vibrational modes are labeled with the

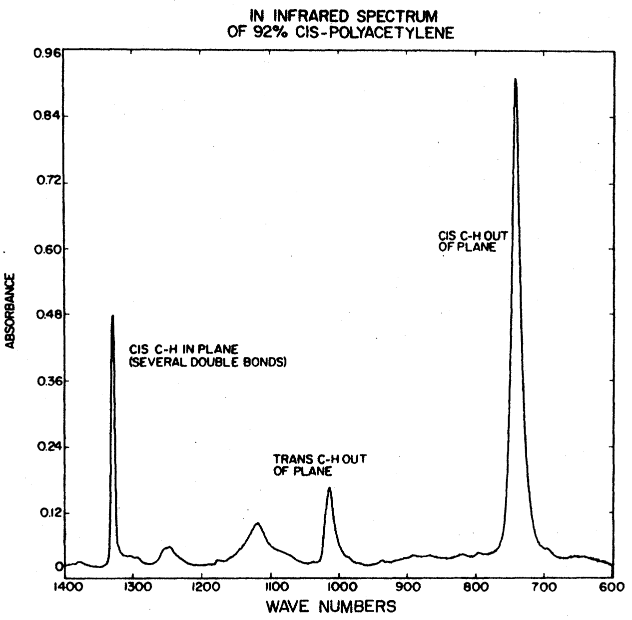

FIG. 2. Infrared-absorption spectrum of thin 91.9% *cis*-polyacetylene film. Assignments indicated are from the literature (Ref. 26).

literature assignments.[26] Figure 3(a) shows the spectrum resulting after isomerization at 180 °C for 17 min, while Fig. 3(b) shows the same sample after an additional 51 min at 180 °C. Figure 3(c) shows the spectrum of a second film after isomerization of *cis*-$(CH)_x$ at 100 °C for 142 h, and Fig. 3(d) at 100 °C for 552 h. Comparing the integrated intensities for the 740 and 1010 $cm^{-1}$ lines and using the calibration factor ratio for the *cis* versus *trans* olefin absorptions[24,25] indicates remnant *cis* contents of 5—7 %.

## IV. DISCUSSION

On the basis of the Fourier-transform infrared (FTIR) studies, we conclude[25] that the isomerization process *always* leaves a significant number ($\sim$5%) of isolated *cis* linkages in an otherwise *trans* chain of polyacetylene. The presence of these *cis* linkages has implications for the understanding of neutral-soliton diffusion as well as determination of *trans*-$(CH)_x$ bonding and conjugation length from Raman spectroscopy.

Figure 4 illustrates the *trans* chain sequence in the presence of isolated *cis* linkages. The remnant *cis* segments may be in either the *cis-transoid* (double bond parallel to chain axis) or *trans-cisoid* configuration (single bond parallel to chain axis). Both forms are expected[26,27] to

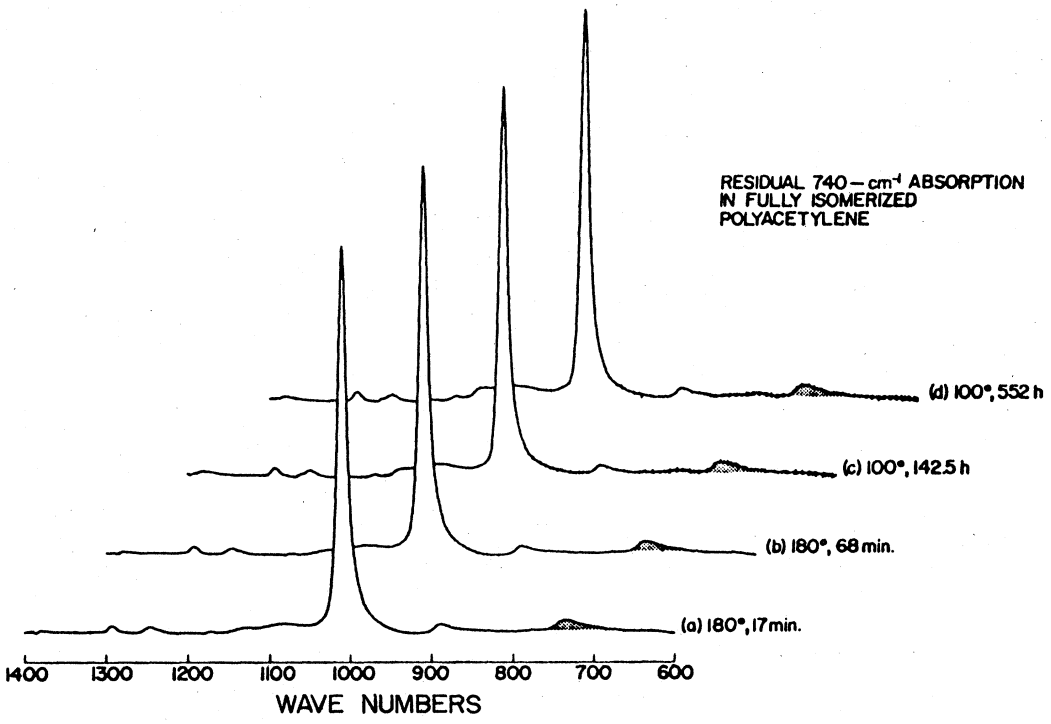

FIG. 3. Infrared-absorption spectra for thin $(CH)_x$ films. Film I: (a) film of Fig. 2 after isomerization at 180 °C for 17 min (5.2% "*cis*"); (b) after isomerization at 180 °C for 68 min (5.6% "*cis*"). Film II: (c) after isomerization at 100 °C for 142.5 h (6.8% "*cis*"); (d) after isomerization at 100 °C for 552 h (6.7% "*cis*"). The *trans* absorbances of the two films have been normalized. The absolute absorbances of the *trans* peaks are 1.4 and 0.75 for films I and II, respectively.

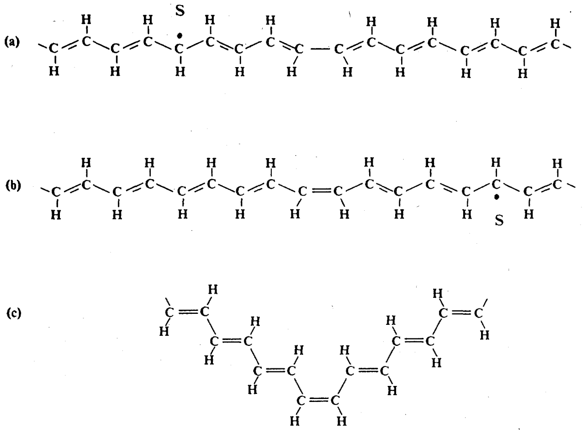

FIG. 4. *Trans*-$(CH)_x$ chain with remnant *cis* linkage in it: (a) soliton to the left of the *trans-cisoid* linkage; (b) soliton moves to the right of the remnant *cis* linkage transforming it to *cis-transoid*; (c) bent chain configuration for *trans*-$(CH)_x$ with remnant *cis* linkage in the absence of crystal lattice constraint.

display C—H out-of-plane vibrations at $\sim 740\ \mathrm{cm}^{-1}$ and are therefore indistinguishable on that basis. The *trans-cisoid* form is assumed to be the lower-energy configuration because of the larger strain imposed on the *cis-transoid* form [which in the unconstrained state would constitute a bend in the chain, Fig. 4(c)] by the crystal structure. Note that the phase of the dimerization does not reverse upon going through the remnant *cis* linkages. Hence, soliton propagation is still required to achieve the scrambling of the bond order found in *trans*-polyacetylene by nutation NMR.[10]

In Fig. 4(a), a neutral soliton is shown schematically on the left-hand side of the *cis* link. In Fig. 4(b), the soliton is shown having moved to the right. This causes a reversal of the bonds at the *cis* linkage, forming a *cis-transoid* configuration, which is higher in energy than the *trans-cisoid* by an amount $\Delta E$. The exact value of $\Delta E$ is uncertain, although calculations[4] suggest a value of $\Delta E \sim 0.01$ eV in the absence of lattice strain. The contribution of the difference in lattice strain energy between the *cis-transoid* and *trans-cisoid* configurations is as yet uncertain. The presence of a remnant *cis* linkage in its low-energy state then presents a barrier to soliton motion. (A soliton, however, may readily move through a *cis* linkage in its higher-energy configuration, converting it to its low-energy structure.) Hence, a neutral soliton will reside in a *trans* segment between *trans-cisoid* linkages unless it has sufficient energy to reverse one of the linkages by passing through it.

The intrachain diffusion rate may then by approximated as the product of the diffusion rate for an uninterrupted *trans* segment $(D_0)$ times the probability of the soliton having sufficient energy to reverse $n$ *trans-cisoid* linkages in an average chain:

$$D \sim D_0[\exp(-\Delta E/K_B T)]^n \ . \tag{1}$$

Assuming $\Delta E = 0.01$ eV,[4] a chain length of 500 $C_2$ units[28] and 6% remnant *cis*, half of which are *trans-cisoid*, $n = 15$ and

$$D \sim D_0\{\exp[(0.01\ \mathrm{eV})/k_B T]\}^{15}$$
$$= D_0 \exp[(-0.15\ \mathrm{eV})/k_B T] \ .$$

A distribution of chain lengths and/or remnant *cis* bond concentration will result in a distribution of apparent activation energies. If the isolated remnant *cis* bonds in an individual chain alternate in *cis-transoid* and *trans-cisoid* configurations, then the soliton has only a single (thermal) activation energy, and $D \sim D_0 \exp(-\Delta E/k_B T)$.[29]

The inclusion of the remnant *cis* "barriers" has implications for the models previously developed for nuclear spin relaxation and soliton diffusion in "*trans*"-$(CH)_x$. In almost all cases, neither the *cis* content nor final crystal structure are reported so we will assume that all samples studied had the minimum $c = 0.05$ and the same crystal structure.[23] Dynamic nuclear polarization experiments have shown a pure solid-state effect (implying localized spins) for a temperature of 4 K, changing to a pure Overhauser effect (implying mobile spins) at room temperature.[8,9,13] Two models were suggested.

(a) Highly one-dimensional diffusive spins (neutral solitons) which can be trapped in the presence of impurities or defects, in particular, traps connected with oxygen contamination. A distribution of trapping energies was found with a maximum value of $E_0 = 0.06$ eV. The diffusing untrapped spins were believed to relax the nuclear spins.[9] However, later double-resonance and proton relaxation experiments showed that stationary spins played an important role in the nuclear relaxation rate below 50 K.[13]

(b) The three-dimensional nuclear-spin diffusion to localized paramagnetic centers provides a very good fit to the data for $T < 100$ K but does not account for the Overhauser effect at room temperature.[13]

Alternately, Mehring, *et al.* have on the basis of NMR and time-resolved ESR experiments proposed the concurrent existence of three types of spins: localized, distributed, and mobile.[15]

The presence of remnant *cis* linkages affects these models. As seen by Eq. (1), the probability of a soliton visiting a distant part of a chain falls off rapidly due to the cumulative effect of many small barriers. This is in agreement with a distribution of "trapping energies."[9] although the trap is not associated with oxygen contamination,[9] but rather with remnant *cis* linkages. As readily seen from Eq. (1), at low temperatures, the probability of reaching distant parts of the chain becomes very small, so that nuclear-spin diffusion to weakly confined soliton will dominate.[12,13]

On the basis of nutation NMR spectroscopy,[10] nuclear-spin lattice relaxation rates for $^1H$ and $^{13}C$ in $^{13}C$ and deuterium-enriched samples,[11] electron-nuclear double resonance (ENDOR) linewidths[14,15] and Raman profiles,[16,17] Scott and Clarke proposed[11] that only $\sim 3\%$ of the chains contain solitons, that spins on these chains are rapidly relaxed by moving solitons, and the rest slowly by nuclear-spin diffusion. From our data above, this $\sim 3\%$ may represent the soliton-containing *trans* chain segments between remnant *cis* linkages. Hence, the soliton may slowly diffuse through the *cis* link barrier only to be localized in the neighboring region for a relatively long time. Then the soliton may visit the entire chain but in a time scale too slow for the NMR technique to measure. This implies that the Kivelson intersoliton electron-hopping mechanism[30] is still applicable as a conduction mechanism,[31] since the neutral soliton can diffuse throughout the polymer for $T > 70$ K, for $\Delta E \sim 0.01$ eV.

As noted above, distributions of *trans* segment lengths between remnant *cis* barriers, numbers of *trans-cisoid* barriers, numbers of twisted *trans-cisoid* units (see below) and $\Delta E$ values (due to varying conformational or morphological sites) could lead to the three types of spins proposed by Mehring *et al.*[15] In contrast, the ENDOR data of Thomann *et al.*[14] show a very narrow distribution of segment lengths, such that the spectrum is not smeared due to a large fluctuation about the mean length of 50 carbon atoms. The difference in these conclusions may reflect differences in sample preparation. The presence of the remnant *cis* bond, Fig. 4(c) leads to considerable lattice strain, which may be minimized under certain isomerization conditions through uniform spacing of the defects.

There have been extensive studies of the Raman band profiles for "*trans*"-$(CH)_x$.[1,16–20] The asymmetric peak profiles reported have been well fit by a bimodal distribution of chain lengths. For example, Kuzmany[16] found that two log-normal distributions peaked at 4 and 40 double bonds reproduced the data, while Brivio *et al.* and Turbino *et al.*[18] found a good fit with two Gaussian distributions peaked at 30 and 100 carbon-carbon double bonds. Alternatively, Mele has proposed[21] that the second component of each Raman band could be the effect of a hot luminescence process induced by long chains; however, this proposal is in disagreement with recent Raman anti-Stokes scattering data.[32] In another approach, Vardeny *et al.*[33] proposed that the resonant Raman peak profiles are due to a narrow distribution of the effective electron-phonon coupling constant which results from inhomogeneity or disorder. It is suggested here that the remnant *cis* linkages may act to give effective short chains in Raman spectroscopy (number of *trans* C=C units between remnant *cis* linkages) and lead to a range of electron-phonon coupling constants.

The presence of the remnant *cis* bonds leads to a simple mechanism for the generation of neutral solitons during the isomerization process. The remnant *cis* linkages within the *trans* crystal structure experience considerable strain. At sufficiently high temperature, the central double bond of the *cis-transoid* configuration may open to form the diradical, followed by electronic rearrangement to the *trans-cisoid* form, in which the strain is more readily accommodated by a distortion of the central single bond. The individual radicals so formed may then diffuse away to form two isolated neutral solitons. This sequence is illustrated in Fig. 5. Cleavage of additional *cis-transoid* double bonds on the same chain would lead to little further increase in soliton population, because of annihilation of soliton-antisoliton pairs. This mechanism would result in the formation of approximately two neutral solitons per polyacetylene chain, in agreement with experiment.[34]

The bond-breaking process is expected to be thermally activated. At normal annealing temperatures, each remnant *cis* site may be considered independent. Using a two-energy-level scheme (higher energy being *cis-transoid* and the lower energy two solitons plus twisted *trans-cisoid*) with activation energy, $\delta$, then the number of neutral solitons created per unit time, $dN_s/dt$, is related to the number of remnant *cis* linkages, $N_c$, by

$$dN_s/dt = 2N_c \exp(-\delta/k_B T_a) ,$$

where $T_a$ is the annealing temperature.[35] For concentrations of more than two remnant *cis* linkages per chain, the equation overestimates the number of solitons because it does not take into account anihilation of soliton pairs. Available experimental data[36–38] are in accord with this picture, the rate of spin generation and the equilibrium value of spin concentration in *trans*-$(CH)_x$ increasing with increasing annealing temperature, although for temperatures $\sim 500$ K the spin concentration decreases[38] due to "degradation".

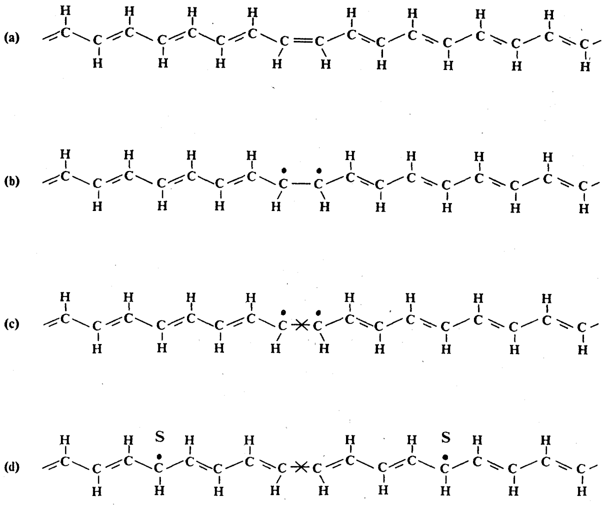

FIG. 5. (a) *Trans*-$(CH)_x$ chain with remnant *cis-transoid* linkage; (b) at high temperatures the *cis-transoid* double bond may form a diradical; (c) rotation primarily about the *cisoid* single bond leads to a linear chain compatible with the crystalline lattice; (d) the diradical separates to form two isolated neutral solitons. The symbol × on the center bond indicates a bond twist which inhibits diffusion of a soliton through this bond.

## V. SUMMARY

Analysis of infrared spectra of polyacetylene thermally isomerized from *cis* to *trans* has shown that there is always a remnant *cis* content of $\sim 0.05$ per carbon-carbon double bond. It is shown that the presence of isolated *cis* linkages in an otherwise *trans* chain has marked affects on the measured neutral-soliton diffusion coefficient, may effect the conjugation lengths measured in Raman spectroscopy, and leads to a simple mechanism for the creation of two neutral solitons per chain during isomerization.

[1] See, Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 9—14, 1981, edited by A. J. Epstein and E. M. Conwell [Mol. Cryst. Liq. Cryst. **77** (1981)]; *ibid.* **83** (1982); Proceedings of Conference International sur la Physique et la Chimie des Polymeres Conducteurs, Les Arcs, France, 11—15 December 1983, edited by R. Comes, P. Bernier, J. J. Andre, and J. Rouxel [J. Phys. (Paris) Colloq. **44**, C3 (1983)]; H. W. Gibson and J. M. Pochan, *Polyacetylene, Substituted Polyacetylenes and Analogs,* of *Encyclopedia of Polymer Science and Engineering* (Wiley, New York, in press); C. K. Chiang, A. J. Heeger, and A. J. MacDiarmid, Ber. Bunsenges. Phys. Chem. **83**, 407 (1979).

[2] M. J. Rice, Phys. Lett. **71A**, 152 (1979).

[3] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett **42**, 1698 (1979); Phys. Rev. B **22**, 2099 (1980).

[4] The total intrachain and interchain energy for the *trans-cisoid* configuration is calculated to be 0.01 to 0.03 eV lower in the orthorhombic structure than the *cis-transoid* [B. J. Orchard, S. K. Tripathy, A. J. Hopfinger, and P. L. Taylor, J. Appl. Phys. **52**, 5949 (1981)]; see also A. Karpfen and R. Holler, Solid State Commun. **37**, 179 (1981).

[5] A. R. Bishop, D. K. Campbell, and K. Fesser, J. Phys. (Paris) Colloq. **44**, C3-423 (1983).

[6] Y. Wada and J. R. Schrieffer, Phys. Rev. B **18**, 3897 (1978).

[7] K. Maki, J. Phys. (Paris) Colloq. **44**, C3-485 (1983).

[8] M. Nechtschein, F. Devreux, R. L. Greene, T. C. Clarke, and G. B. Street, Phys. Rev. Lett. **44**, 356 (1980).

[9] M. Nechtschein, F. Devreux, F. Genoud, M. Guglielmi, and K. Holczer, Phys. Rev. B **27**, 61 (1983).

[10] C. S. Yannoni and T. C. Clarke, Phys. Rev. Lett. **51**, 1191 (1983); T. C. Clarke, R. D. Kendrick, and C. S. Yannoni, J. Phys. (Paris) Colloq. **44**, C3-369 (1983).

[11] J. C. Scott and T. C. Clarke, J. Phys. (Paris) Colloq. **44**, C3-365 (1983).

[12] P. E. Sokol, J. R. Gaines, S. I. Cho, D. B. Tanner, H. W. Gibson, and A. J. Epstein, J. Phys. (Paris) Colloq. **44**, C3-349 (1983); Synth. Met. **10**, 43 (1984).

[13] W. G. Clark, K. Glover, G. Mozurkewich, C. T. Murayama, J. Sanny, S. Etemad, and M. Maxfield, J. Phys. (Paris) Colloq. **44**, C3-239 (1983).

[14] H. Thomann, L. R. Dalton, Y. Tomkiewicz, N. S. Shiren, and T. C. Clarke, Phys. Rev. Lett. **50**, 533 (1983); L. R. Dalton, H. Thomann, A. Morrobel-Sosa, C. Chiu, M. E. Galvin, G. E. Wnek, Y. Tomkiewicz, N. D. Shiren, B. H. Robinson, and A. L. Kwiram, J. Appl. Phys. **54**, 5583 (1983); H. Thomann, Ph.D. thesis, University of Southern California, 1982.

[15] M. Mehring, H. Seidel, W. Muller, and G. Wegner, Solid State Comm. **45**, 1075 (1983); M. Mehring, H. Seidel, H. Weber, and G. Wegner, J. Phys. (Paris) Colloq. **44**, C3-217 (1983); M. Mehring, H. Weber, W. Muller, and G. Wegner, Solid State Commun. **45**, 1079 (1983).

[16] H. Kuzmany, Phys. Status Solidi B **97**, 521 (1980); J. Phys. (Paris) Colloq. **44**, C3-255 (1983).

[17] L. S. Lichtmann, A. Sarhangi, and D. B. Fitchen, Chem. Scr. **17**, 149 (1981).

[18] G. P. Brivio and E. Mulazzi, J. Phys. (Paris) Colloq. **44**, C3-261 (1983); R. Turbino, L. Piseri, G. Dellepiane, and P. Piaggio, *ibid.* **44**, C3-329 (1983).

[19] S. Lefrant, E. Faulques, S. Krichene, and G. Sagan, Polymer **24**, 361 (1983); S. Lefrant, J. Phys. (Paris) Colloq. **44**, C3-247 (1983).

[20] D. C. Bott, C. K. Chai, D. A. Gerard, R. H. Weatherhead, D. White, and K. P. J. Williams, J. Phys. (Paris) Colloq. **44**, C3-45 (1983).

[21] E. J. Mele, J. Phys. (Paris) Colloq. **44**, C3-267 (1983).

[22] T. Ito, H. Shirakawa, and S. Ikeda, J. Polym. Sci. Polym. Chem. Ed. **12**, 11 (1974); **13**, 1942 (1975). Exposure time of catalyst (0.23 *M*Ti, 0.92 *M*Al) to acetylene gas was limited to control film thickness

[23] P. Robin, J. P. Pouget, R. Comes, H. W. Gibson, and A. J. Epstein, Phys. Rev. B **27**, 3938 (1983); J. Phys. (Paris) Colloq. **44**, C3-77 (1983).

[24] H. W. Gibson, W. M. Prest, Jr., R. A. Mosher, S. Kaplan, and R. J. Weagley, Polym. Prepr. (Am. Chem. Soc.) **24**, 153 (1983).

[25] H. W. Gibson, R. J. Weagley, W. M. Prest, Jr., R. Mosher, and S. Kaplan, J. Phys. (Paris) Colloq. **44**, C3-123 (1983).

[26] H. Shirakawa and S. Ikeda, Polym. J. **2**, 231 (1971).

[27] See for example, The Aldrich Library of Infrared Spectra, edited by C. J. Pouchert (unpublished). Spectra 21E, 1043E, 1047E, 1051J, and 1056G.

[28] J. W. C. Chien, J. D. Capistran, F. E. Karasz, L. C. Dickinson, and M. A. Schen, J. Polym. Sci. Polym. Lett. Ed. **21**, 93 (1983).

[29] S. Kivelson (private communication).

[30] S. Kivelson, Phys. Rev. B **25**, 3798 (1982).

[31] A. J. Epstein, H. Rommelmann, M. Abkowitz, and H. W. Gibson, Phys. Rev. Lett. **47**, 1549 (1981).

[32] R. R. Chance, H. Eckhardt, S. W. Steinhauser, M. Schott, and R. Silbey, Bull. Am. Phys. Soc. **29**, 218 (1984).

[33] Z. Vardeny, E. Ehrenfreund, O. Brafman, and B. Horovitz, Phys. Rev. Lett. **51**, 2326 (1983).

[34] A. J. Epstein, H. Rommelmann, M. A. Druy, A. J. Heeger, and A. G. MacDiarmid, Solid State Commun. **38**, 683 (1981).

[35] A similar model has been proposed for thermal generation of structural defects in chalcogenides: M. Abkowitz, Ann. N.Y. Acad. Sci. **371**, 170 (1981); M. Abkowitz and J. M. Markovics, Philos. Mag. B **49**, L31 (1984).

[36] P. Bernier, C. Linaya, M. Rolland, and M. Aldisi, J. Phys. (Paris) Lett. **42**, L295 (1981).

[37] H. Kuzmany, E. A. Imhoff, D. B. Fitchen, and A. Sarhangi, Mol. Cryst. Liq. Cryst. **77**, 197 (1981).

[38] A. Zanobi and L. D'Ilario, J. Phys. (Paris) Colloq. **44**, C3-309 (1983).