## VOLUME 38, NUMBER 2

15 JULY 1988-I

## Nonlinear optical properties of linear chains and electron-correlation effects

J. R. Heflin, K. Y. Wong, O. Zamani-Khamiri, and A. F. Garito

Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania,

Philadelphia, Pennsylvania 19104

(Received 5 February 1988; revised manuscript received 29 April 1988)

The large third-order nonlinear optical properties  $\gamma_{ijkl}(-\omega_4;\omega_1,\omega_2,\omega_3)$  observed for conjugated organic linear chains, such as polyenes, are explained by strong electron-correlation behavior in virtual, two-photon  ${}^{1}A_{g}$  states. The dominant chain axis component  $\gamma_{xxxx}$  is found to possess a power-law dependence on the chain length with an exponent of  $4.6 \pm 0.2$ , independent of chain conformation. Good agreement in sign and magnitude is obtained between calculated and experimental gas-phase values of  $\gamma_{ijkl}(-2\omega;\omega,\omega,0)$ .

A principal focus of current nonlinear optics studies has been the origin and mechanism responsible for the unusually large microscopic second-order  $\beta_{ijk}(-\omega_3;\omega_1,\omega_2)$  and third-order  $\gamma_{ijkl}(-\omega_4;\omega_1,\omega_2,\omega_3)$  nonlinear optical susceptibilities observed for conjugated  $\pi$ -electron organic and polymer structures. Considerable progress has been achieved in many-electron microscopic descriptions of  $\beta_{ijk}$ in terms of electron-correlation effects. However, one major case still outstanding<sup>1-7</sup> is  $\gamma_{ijkl}$  of centrosymmetric conjugated linear chains such as polyenes and polyenynes which represent the finite-chain limit to the corresponding infinite-chain polymers polyacetylene and polydiacetylene. Current discussion of  $\gamma_{ijkl}(-\omega_4;\omega_1,\omega_2,\omega_3)$  has centered on the results of one-electron theories such as nearly free electron and tight-binding Hückel models which ignore electron-electron interactions and correlation.

Experimental and theoretical studies of  $\beta_{ijk}$  in conjugated structures<sup>7-12</sup> and of one-photon and two-photon resonant processes in finite polyenes<sup>13-19</sup> have demonstrated that the  $\pi$ -electron states are dominated by electron correlation and that, correspondingly, single-particle descriptions are inadequate. One principal result observed in polyenes, for example, is that below the first optically allowed, dominant singlet 1<sup>1</sup>B<sub>u</sub> state is located a twophoton singlet 2<sup>1</sup>A<sub>g</sub> state. Calculations based on Pariser-Parr-Pople (PPP) and Hubbard models have obtained the correct state ordering and have shown that the  $2^{1}A_{g}$  state is a highly correlated  $\pi$ -electron state that appears in the theoretical results only upon inclusion of at least doubly excited particle-hole configurations (DCI's).

In this paper, we report a symmetry-controlled electron-correlation mechanism that describes the properties and behavior of  $\gamma_{ijkl}(-\omega_4;\omega_1,\omega_2,\omega_3)$  of conjugated linear chains. The microscopic description is obtained from a direct summation method proven successful in the case of  $\beta_{ijk}(-\omega_3;\omega_1,\omega_2)$  for three major structural classes<sup>7-12</sup> in which each frequency-dependent susceptibility component is evaluated based on self-consistent-field configuration-interaction theory. We consider polyenes ranging in number of carbon sites N from 4 to 16 in both the all-*trans (trans)* and *cis-transoid (cis)* conformations shown schematically in Fig. 1. These finite-chain studies also provide important insight for the infinite-chain polymer limit.

The molecular third-harmonic susceptibility  $\gamma_{iikl}(-3\omega;\omega,\omega,\omega)$  is defined by the expression

$$p_i^{3\omega} = \gamma_{ijkl} (-3\omega; \omega, \omega, \omega) E_i^{\omega} E_k^{\omega} E_l^{\omega} , \qquad (1)$$

where  $p_i^{3\omega}$  is a component of the molecular polarization induced at a frequency of  $3\omega$  in response to the cube of an electromagnetic field  $E^{\omega}$  oscillating at  $\omega$ . The analytic expression for  $\gamma_{iikl}(-3\omega;\omega,\omega,\omega)$  is <sup>20</sup>

$$\gamma_{ijkl}(-3\omega;\omega,\omega,\omega) = \frac{1}{3!} \left( \frac{e^4}{4\hbar^3} \right) \sum_{n_1,n_2,n_3} \left( \frac{P_{jkl}(r_{gn_3}^i r_{n_3n_2}^j r_{n_2n_1}^k r_{n_1g}^l)}{(\omega_{n_3g} - 3\omega)(\omega_{n_2g} - 2\omega)(\omega_{n_1g} - \omega)} + \frac{P_{jkl}(r_{gn_3}^j r_{n_3n_2}^i r_{n_2n_1}^k r_{n_1g}^l)}{(\omega_{n_3g} + \omega)(\omega_{n_2g} + 2\omega)(\omega_{n_1g} - \omega)} + \frac{P_{jkl}(r_{gn_3}^j r_{n_3n_2}^k r_{n_2n_1}^l r_{n_1g}^l)}{(\omega_{n_3g} + \omega)(\omega_{n_2g} + 2\omega)(\omega_{n_1g} - \omega)} + \frac{P_{jkl}(r_{gn_3}^j r_{n_3n_2}^k r_{n_2n_1}^l r_{n_1g}^l)}{(\omega_{n_3g} + \omega)(\omega_{n_2g} + 2\omega)(\omega_{n_1g} - \omega)} + \frac{P_{jkl}(r_{gn_3}^j r_{n_3n_2}^k r_{n_2n_1}^l r_{n_1g}^l)}{(\omega_{n_3g} + \omega)(\omega_{n_2g} + 2\omega)(\omega_{n_1g} - \omega)} \right)$$

$$(2)$$

where  $r_{n_1n_2}^i$  is the matrix element  $\langle n_1 | r^i | n_2 \rangle$ ,  $\hbar \omega_{n_1g}$  is the excitation energy of state  $n_1$ , and  $P_{jkl}$  denotes the sum over all permutations of j, k, and l ensuring that  $\gamma_{ijkl}$  is independent of the ordering of those three indices. The convention has been chosen that the electric fields are represented as  $E^{\omega} \sin(\omega t - \mathbf{k} \cdot \mathbf{r})$ .



FIG. 1. Schematic diagrams of (a) *trans*-polyenes and (b) *cis*-polyenes.

© 1988 The American Physical Society

<u>38</u>

1573

1574

The individual terms of Eq. (2) were directly evaluated from the singlet-state excitation energies and transitiondipole moments obtained by configuration-interaction (CI) methods in which all singly (SCI) and doubly (DCI) excited  $\pi$ -electron configurations were included in order to describe properly electron correlations. (For example, the number of configurations for N = 12 are SCI: 36 and DCI: 666, and the total number of states: 703.) The CI  $\pi$ -electron basis sets were obtained by an all-valenceelectron self-consistent-field (SCF) molecular-orbital (MO) method in the standard, rigid lattice complete neglect of differential overlap/spectroscopic (CNDO/S) approximation.<sup>21</sup> Although the calculation of the ground state includes all of the valence-shell electrons for each atom in the molecule, CI theory needs only consider  $\pi$ electron orbitals since the low-lying excitations are  $\pi \rightarrow \pi^*$  transitions and for conjugated systems the  $\pi$ electron contributions to  $\gamma_{iikl}(-\omega_4;\omega_1,\omega_2,\omega_3)$  dominate those from  $\sigma$  electrons. Bond lengths and bond angles for the molecular configurations are experimentally determined values, and consequently, the bond alternation (carbon-carbon bond lengths of 1.34 and 1.46 Å)<sup>14</sup> is treated directly. The hopping interaction between all pairs of sites in included, and the electron-electron repulsion is accounted for via the Ohno potential.<sup>22</sup> The values calculated at the SDCI level of the excitation energies for both the one-photon allowed  $1^{1}B_{\mu}$  state and the twophoton allowed  $2^{1}A_{g}$  state are in good agreement with experimental values and with previously reported theoretical results.<sup>14,16,17</sup>

For all chain lengths and conformations studied, the  $\gamma_{xxxx}$  component of  $\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)$ , with all fields along the direction of conjugation, is far larger than the others, even as the input photon energy approaches the  $3\omega$ 

$$\rho_{nn'}(\mathbf{r}_1) = \int \psi_n^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_M) \psi_{n'}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_M) d\mathbf{r}_2 \cdots d\mathbf{r}_M; \ \langle \mu_{nn'} \rangle = -e \int \mathbf{r} \rho_{nn'}(\mathbf{r}) d\mathbf{r}, \tag{3}$$

where M is the number of valence electrons included in the state wave function. Contour diagrams for  $\rho_{nn'}$  of the ground,  $2 {}^{1}A_{g}$ , and  $6 {}^{1}A_{g}$  states with the  $1 {}^{1}B_{u}$  state are shown in Fig. 2 where solid and dashed lines correspond to increased and decreased charge density. Whereas the virtual transition  $2 {}^{1}A_{g} \rightarrow 1 {}^{1}B_{u}$  results in a modulated charge redistribution, the  $6 {}^{1}A_{g} \rightarrow 1 {}^{1}B_{u}$  transition, in sharp contrast, produces a large charge separation that spans the entire chain length and results in a large transition moment. The same characteristic features are found for all other chain lengths of both *trans* and *cis* conformations.

Gas phase third-order susceptibility measurements of  $\gamma_g(-2\omega;\omega,\omega,0)$  for polyenes have been obtained<sup>3</sup> using dc-induced second harmonic generation (DCSHG). At the nonresonant fundamental input of 1.787 eV ( $\lambda = 0.69 \mu m$ ), the values for butadiene (BD) with N = 4 and hexatriene (HT) with N = 6 are (Ref. 23)  $3.45 \pm 0.20$  and  $11.30 \pm 1.05 \times 10^{-36}$  esu, respectively. Although the BD gas was more than 99% *trans*-BD, the HT was believed to contain 40% *cis*-HT.<sup>3,24</sup> Based on the results of our calculations described above and the appropriate expression for  $\gamma_g(-2\omega;\omega,\omega,0)$  with isotropic averaging, we calculate

resonance with the 1  ${}^{1}B_{u}$  state. For example, the calculated values for the independent tensor components of  $\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)$  of *trans*-octatetraene (*trans*-OT) with N=8 at a nonresonant fundamental photon energy of 0.65 eV ( $\lambda = 1.907 \ \mu$ m) are  $\gamma_{xxxx} = 15.5$ ,  $\gamma_{xyyx} = 0.6$ ,  $\gamma_{yxxy} = 0.5$ , and  $\gamma_{yyyy} = 0.2 \times 10^{-36}$  esu.

For centrosymmetric conjugated chains, the  $\pi$ -electron states have definite parity of  $A_g$  or  $B_u$ , and the one-photon transition moment vanishes between states of like parity. Since the ground state is always  ${}^{1}A_{g}$ , it is evident from Eq. (2) that the  $\pi$  states in a third-order process must be connected in the series  $g \rightarrow {}^{1}B_{u} \rightarrow {}^{1}A_{g} \rightarrow {}^{1}B_{u} \rightarrow g$ . Virtual transitions to both one-photon  ${}^{1}B_{u}$  and two-photon  ${}^{1}A_{e}$  states are necessarily involved. In the summation over intermediate states for trans-OT there are two major terms which constitute 70% of  $\gamma_{xxxx}$ . In both of these terms, the only  ${}^{1}B_{u}$  state involved is the dominant lowlying one-photon  $1^{1}B_{u}$   $\pi$ -electron excited state. In addition to its low energy, the importance of this state lies in the value of its transition-dipole moment with the ground state of 7.8 D being the largest of all those that involve the ground state. For one of the two major terms, the intermediate  ${}^{1}A_{g}$  state is the ground state itself; but for the other, it is the  $6^{1}A_{g}$  state of OT calculated at 7.2 eV. Since this state has a transition moment with  $1^{1}B_{\mu}$  of 13.2 D, it is much more significant than the  $2^{1}A_{p}$  that has a corresponding transition moment of only 2.8 D.

Important major features of the microscopic descriptions of third-order virtual processes are contained in the transition density matrix  $\rho_{nn'}$ . The  $2 {}^{1}A_{g}$  and  $6 {}^{1}A_{g}$  states are both nearly 60% composed of doubly excited configurations, and the contributions to  $\gamma_{xxxx}$  of these two highly electron-correlated states are distinguished by  $\rho_{nn'}$ defined by

the  $\pi$ -electron contributions at the same frequency to be 2.1, 11.5, and  $9.1 \times 10^{-36}$  esu for BD, *trans*-HT, and *cis*-HT, respectively. Although the  $\sigma$ -electron contribution to  $\gamma_g$  is negligible for longer chains since it increases much more slowly with respect to chain length than the  $\pi$ -electron contribution, it is more significant for shorter chains and should be included in the cases of BD and HT. After adding in respective  $\sigma$  contributions of 1.5 and  $2.4 \times 10^{-36}$  esu as estimated in Ref. 3, we obtain values for  $\gamma_g(-2\omega;\omega,\omega,0)$  of 3.6 and  $12.9 \times 10^{-36}$  esu for BD and HT, respectively, in agreement with experiment both in sign and magnitude.

The calculated values of  $\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)$  far from resonance at 0.65 eV for the N=4 to 16 *trans*- and *cis*polyenes are plotted against N as the upper scale of Fig. 3. The good linear fit in both cases shows that the susceptibility has a power-law dependence on N:

$$\gamma_{xxxx} \mathbf{x} N^{\nu}, \qquad (4)$$

with  $v=5.4\pm0.2$  for *trans* and  $4.7\pm0.2$  for *cis*. There are several features common to both conformations that emerge from comparison of polyenes of different length. First, the lowest optical excitation energy decreases pro-



FIG. 2. Transition density matrix diagrams for (a) ground state, (b)  $2 {}^{1}A_{g}$  state, and (c)  $6 {}^{1}A_{g}$  state with  $1 {}^{1}B_{u}$  state. Corresponding transition-dipole moments have x components of 7.8, 2.8, and 13.2 D, respectively.

portionally to the inverse of the number of sites with a lowering from 5.9 eV in butadiene (N=4) to 3.7 eV in the case of dodecahexaene (N=12). Second, the magnitudes of transition-dipole moments along the chain axis increase steadily with the number of sites. Third, while for OT and the shorter chains the nonlinear susceptibility is almost entirely composed of the contributions from only a few states, longer chains have significant contributions from an increasingly larger number of both  ${}^{1}B_{\mu}$  and  ${}^{1}A_{g}$  states. All three of these factors are responsible for the very rapid growth that is observed in the nonresonant  $\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)$  with increased number of sites. Although various power-law behaviors for  $\gamma$  have been previously reported based on delocalized, noninteracting electron models,<sup>4,5</sup> these calculations are in strong disagreement with experiment in the magnitude and, in one case, even the sign of  $\gamma$ , and are, therefore incomplete descriptions of third-order properties. The apparent similarity in power-law behavior simply reflects the delocalized nature of the conjugated bonds in polyenes as compared to, for example, the linear dependence resulting from the bondadditivity rule for localized bonds.

The calculated values of the dominant tensor component of the nonresonant  $\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)$  for the *cis* conformations are smaller than the values for the *trans* of an equal number of sites for all of the chains considered.



FIG. 3. Log-log plot of  $\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)$  vs the number of carbon sites N (upper scale) and the length L (lower scale) for *cis*- and *trans*-polyenes.

In addition, there is a lesser rate of growth for  $\gamma_{xxxx}$  with increasing N for the *cis*. These apparent differences in the two conformations are well accounted for by plotting  $\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)$  against the actual length of the chain L rather than N as is shown on the lower scale of Fig. 3, where L is defined as the distance along the x direction between the two end carbon sites. This plot unifies the calculated values for the two conformations and yields a power-law dependence of  $\gamma_{xxxx}$  on L:

$$\gamma_{xxxx} \propto L^{4.6 \pm 0.2} \,. \tag{5}$$

Because of the different geometry, a given *cis* chain is always shorter than its corresponding *trans* form. The difference in  $\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)$  values for the two is simply due to this fact, and  $\gamma_{xxxx}$  is therefore, much more sensitive to the physical length of the chain than to the conformation.

Finally, from our calculated power-law dependence, we can draw several important results for polymers. A typical value of the nonresonant macroscopic third-order susceptibility  $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$  observed for polymers is  $10^{-10}$  esu.<sup>25,26</sup> For an isotropic distribution of chains considered as independent sources of nonlinear response with a single dominant tensor component  $\gamma_{xxxx}$ , we have  $\chi^{(3)} = \frac{1}{5} N(f^{\omega})^3 f^{3\omega} \gamma_{xxxx}$ , where N is the number density of chains and  $f^{\omega} = (2 + n_{\omega}^2)/3$  is the Lorentz-Lorenz local-field factor. Using typical values of  $N = 10^{20}$  molecules/cm<sup>3</sup> and 1.8 for the refractive index, we estimate a  $\gamma_{xxxx}$  of roughly  $2 \times 10^{-31}$  esu. From Eq. (5), this value would correspond to a chain of  $N \approx 50$  carbon sites, or a length of approximately 60 Å. Since these polymers consist of much longer chains, we infer that  $\gamma_{xxxx}$  must deviate from the power-law dependence and begin to saturate at some length shorter than 60 Å. This then suggests

1576

that large values of  $\gamma$ , and correspondingly  $\chi^{(3)}$ , require only chains of intermediate length of order 100 Å.

In summary, we have reported a symmetry-controlled correlation mechanism for  $\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)$  of polyenes ranging in chain length from N = 4 to 16 in both *trans* and *cis* conformations. After showing on general symmetry grounds that two-photon allowed states, as well as one-photon allowed states, must play a role in  $\gamma_{ijkl}$ , we have identified in detail the significant contributions, especially dominant terms from highly correlated two-photon  ${}^{1}A_{g}$  states, and demonstrated good agreement between our calculations and previous experimental measurements.

- <sup>1</sup>A. D. Buckingham, M. P. Bogaard, D. A. Dunmur, C. P. Hobbs, and B. I. Orr, Trans. Faraday Soc. 66, 1548 (1970).
- <sup>2</sup>J. P. Hermann, D. Ricard, and J. Ducuing, Appl. Phys. Lett. **23**, 178 (1973).
- <sup>3</sup>J. F. Ward and D. S. Elliott, J. Chem. Phys. 69, 5438 (1978).
- <sup>4</sup>G. P. Agrawal, C. Cojan, and C. Flytzanis, Phys. Rev. B 17, 776 (1978).
- <sup>5</sup>E. McIntyre and H. Hameka, J. Chem. Phys. **68**, 3481 (1978).
- <sup>6</sup>D. N. Beratan, J. N. Onuchic, and J. W. Perry, J. Phys. Chem. **91**, 2696 (1987).
- <sup>7</sup>A. F. Garito, C. C. Teng, K. Y. Wong, and O. Zamani-Khamiri, Mol. Cryst. Liq. Cryst. 106, 219 (1984).
- <sup>8</sup>S. J. Lalama and A. F. Garito, Phys. Rev. A 20, 1179 (1979).
- <sup>9</sup>C. C. Teng and A. F. Garito, Phys. Rev. Lett. **50**, 350 (1983); Phys. Rev. B **28**, 6766 (1983).
- <sup>10</sup>A. F. Garito, K. D. Singer, and C. C. Teng, in *Nonlinear Optical Properties of Organic and Polymeric Materials*, edited by D. J. Williams, ACS Symposium Series, Vol. 233 (American Chemical Society, Washington, DC, 1983), Chap. 1.
- <sup>11</sup>A. F. Garito, Y. M. Cai, H. T. Man, and O. Zamani-Khamiri, in *Crystallographically Ordered Polymers*, edited by D. J. Sandman, ACS Symposium Series, Vol. 337 (American Chemical Society, Washington, DC, 1987), Chap. 14.
- <sup>12</sup>A. F. Garito, K. Y. Wong, and O. Zamani-Khamiri, in Nonlinear Optical and Electroactive Polymers, edited by D. Ulrich and P. Prasad (Plenum, New York, 1987).
- <sup>13</sup>B. S. Hudson and B. E. Kohler, J. Chem. Phys. **59**, 4984 (1973).
- <sup>14</sup>See, for example, B. S. Hudson, B. E. Kohler, and K. Schulten, in *Excited States*, edited by E. C. Lim (Academic, New York, 1982), Vol. 6, p. 1, and references therein.
- <sup>15</sup>A. A. Ovchinnikov, I. I. Ukrainski, and G. V. Kuentsel, Usp. Fiz. Nauk **108**, 81 (1972) [Sov. Phys. Usp. **15**, 575 (1973)],

Finally, for both *trans* and *cis* conformations over the range of chain lengths we considered,  $\gamma_{xxxx}$  exhibits a power-law dependence on the chain length L with an exponent of  $4.6 \pm 0.2$ .

This research was generously supported by the U.S. Air Force Office of Scientific Research and the U.S. Defense Advanced Research Projects Agency Grant No. F49620-85-C-0105 and National Science Foundation/Materials Research Laboratories Program Grant No. DMR-85-19059. The calculations were performed on the Cray X-MP of the Pittsburgh Supercomputing Center.

and references therein.

- <sup>16</sup>K. Schulten, I. Ohmine, and M. Karplus, J. Chem. Phys. 64, 4422 (1976).
- <sup>17</sup>K. Schulten, U. Dinur, and B. Honig, J. Chem. Phys. **73**, 3927 (1980).
- <sup>18</sup>Z. G. Soos and S. Ramasesha, Phys. Rev. B 29, 5410 (1984).
- <sup>19</sup>P. Tavan and K. Schulten, Phys. Rev. B 36, 4337 (1987).
- <sup>20</sup>J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. 127, 1918 (1962).
- <sup>21</sup>The formalism is described in detail in Ref. 8. The input parameters are as follows: Slater exponents  $C:\zeta_{2s,2p} = 3.78$  Å<sup>-1</sup>,  $H:\zeta_{1s} = 2.30$  Å<sup>-1</sup>; valence-state ionization energies  $C:I_{2s} = 21.3$  eV,  $I_{2p} = 11.5$  eV,  $H:I_{1s} = 13.6$  eV; Coulomb repulsion integrals  $C:\gamma = 11.1$  eV,  $H:\gamma = 12.8$  eV; resonance integrals  $C:\beta_{2s} = 21.0$  eV,  $\beta_{2p} = 16.0$  eV,  $H:\beta_{1s} = 10.0$  eV.

<sup>22</sup>The Coulomb repulsion integral between sites A and B is

$$\gamma_{AB} = 14.397 \text{ eV } \text{\AA} \left[ \left( \frac{28.794 \text{ eV } \text{\AA}}{\gamma_{AA} + \gamma_{BB}} \right)^2 + [R_{AB} \text{ (Å)}]^2 \right]^{-1/2}$$

where  $\gamma_{AA}$  and  $\gamma_{BB}$  are intra-atomic repulsion integrals and  $R_{AB}$  is the interatomic distance.

<sup>23</sup>We have converted Ward's and Elliott's  $\chi^{(3)}$  to our notation by  $\gamma_g(2\omega;\omega,\omega,0) = \frac{3}{2}\chi^{(3)}$ . The subscript indicates gas-phase isotropic orientational averaging such that

$$\gamma_{g} = \frac{1}{5} \left( \sum_{i} \gamma_{iiii} + \frac{1}{3} \sum_{i \neq j} (\gamma_{iijj} + \gamma_{ijij} + \gamma_{ijji}) \right)$$

where i and j represent the Cartesian coordinates x, y, and z.

- <sup>24</sup>R. M. Gavin, Jr., S. Risemberg, and S. A. Rice, J. Chem. Phys. 58, 3160 (1983).
- <sup>25</sup>C. Sauteret et al., Phys. Rev. Lett. 36, 956 (1976).
- <sup>26</sup>F. Kajzar and J. Messier, Polym. J. 19, 275 (1987).