Resonance Raman spectroscopy of polyene compounds (multimode systems). Polyacetylene synthesized from cyclooctatetraene

V. V. Berdyugin, P. P. Shorygin, K. Ya. Burshtein, Yu. V. Korshak, M. A. Tlenkopachev, and A. V. Orlov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

Specific features of the excitation spectra of resonance Raman (RR) lines in multimode systems were characterized. Based on this, the spectra, the structure, and the composition of polyacetylene (PA) synthesized by polymerization of cycloocta-1,3,5,7-tetraene in the presence of metathesis catalysts were investigated. A dependence of frequencies and intensities of the C—C and C=C stretching lines on the exciting light wavelength was found and explained by broad distribution of defect-free conjugated polymer segments in the PA samples studied on the number of double bonds incorporated in them. A procedure for the calculation of the distribution functions and of the shapes of RR lines was proposed. These functions are bimodal. A reversible *cis—trans*-transition was discovered in the PA samples not subjected to heat treatment, which was attributed to the presence of macrocyclic polyene structures.

Key words: resonance Raman effect, polyacetylene.

Resonance Raman (RR) spectroscopy is widely used in studies of poly-π-electronic conjugated polymers, for example, polyacetylene (PA),[1—4] substituted polydiacetylenes,[5—7] poly-*p*-phenylene,[8] polyaniline,[9] and carbyne.[10] A characteristic feature of the RR spectra of polyacetylenes is a substantial displacement of the observed C—C and C=C stretching vibration frequencies as a function of the exciting light wavelength λ_{excit}.[2,3] This is explained by the fact that the studied samples of PA contain conjugated subsystems of different effective lengths, which undergo selective resonance excitation at particular λ_{excit}. RR spectroscopy makes it possible to identify the distribution of conjugated subsystems over so-called "lengths of conjugation" (*i.e.*, over the numbers of bonds $n_{\text{C=C}}$ incorporated in them). This is very significant in the analysis of PA samples, since it is the length of conjugation rather than the conventionally used length of the polymeric chain and the molecular weight related to it that determines many physicochemical properties of PA. The cross-linkage of polymeric chains increases the mean molecular weight of PA and simultaneously decreases the lengths of conjugated segments by increasing the number of sp^3-hybridized carbon atoms.

In the present work, we used the RR method to study the structure and composition of polyacetylene, obtained by a new method, *viz.*, by polymerization of cycloocta-1,3,5,7-tetraene in the presence of catalysts of metathesis.[11,12]

Experimental

A polyacetylene film (PA sample **1**) was prepared at room temperature by condensation of cyclooctatetraene from the gas phase onto a solid layer of the $\text{W[OCH(CH}_2\text{Cl)}_2]_2\text{Cl}_4\text{—AlEt}_2\text{Cl}$ catalytic complex (Al/W = 2), which had been preliminarily deposited on the walls of a glass reactor. PA samples **2** and **3** were synthesized under similar conditions and, after the catalyst was washed out, they were subjected to heat treatment at 400—500 °C.

RR spectra were obtained on a Ramanor U1000 instrument; excitation was accomplished by an Ar^+/Kr^+-laser; the spectra of the PA samples deposited on the walls of the glass reactor were recorded according to the "reflection" scheme.

Results and Discussion

Spectra of all the samples studied (Figs. 1 and 2) exhibit characteristic intense lines due to ν(C—C) and ν(C=C) stretching vibrations (~1100 and ~1460 cm^{-1}, respectively), which indicates that *trans*-structures predominate in these polymers. Fragments with *cis*-structure (~5 %) characterized by a line at 1245 cm^{-1} were also detected in sample **1** (see Fig. 1).[4]

When the frequency of the light exciting the resonance scattering varied, changes in the frequencies of the lines corresponding to the vibrations of C—C bonds (see Figs 1 and 2), similar to those found previously in the spectra of other samples of *trans*-PA (**2**, **3**), were

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 2016—2020, August, 1996.

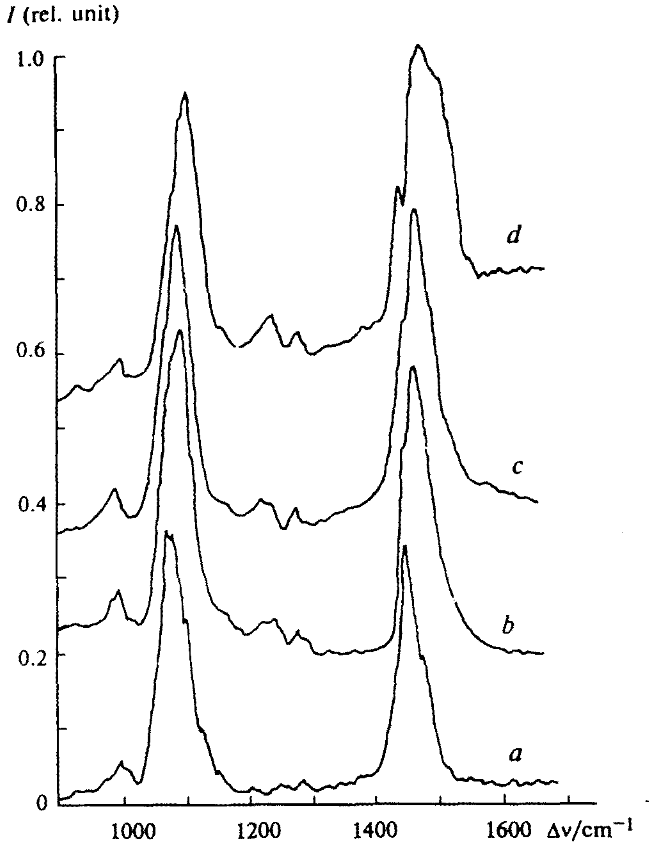

Fig. 1. RR spectra of PA sample **1**. λ_{excit} = 647.1 (*a*), 514.5 (*b*), 488 (*c*), and 457.9 (*d*) nm. P_{excit} = 1 mW.

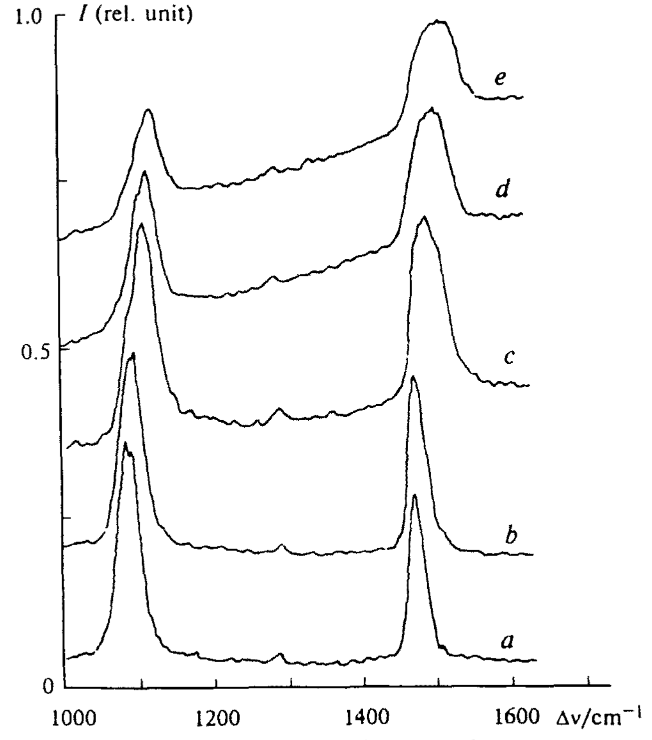

Fig. 2. RR spectra of PA sample **3** (*a*) and **2** (*b*—*e*). λ_{excit} = 647.1 (*a*, *b*), 514.5 (*c*), 488 (*d*), and 457.9 (*e*) nm. P_{excit} = 1 mW.

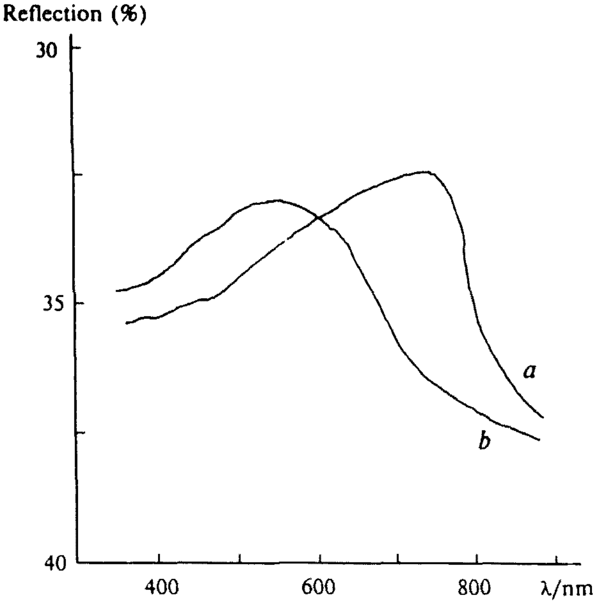

Fig. 3. Reflection spectra of PA samples **1** (*a*) and **2** (*b*).

observed in the spectra of all the PA samples studied. In terms of the concept of selective resonance excitation of conjugated subsystems of various effective lengths of conjugation, the experimental data show that as the excitation wavelength decreases from 647.1 to 457.9 nm (*i.e.*, as this wavelength moves away from the long-wavelength absorption boundary in the electronic absorption spectrum of the polymer, Fig. 3), the ν(C—C) frequency, for example, in PA sample **1** increases from 1076 to 1126 cm^{-1} (see Fig. 1) and the ν(C=C) frequency increases from 1436 to 1502 cm^{-1}, which corresponds to the transition to the resonance excitation of shorter conjugated subsystems.

Comparison of the spectra of samples **2** and **3** showed that they are very similar (see Fig. 2). Examination of the spectra of samples **1** and **2** indicates that sample **1** contains a relatively small number of short conjugated segments (with lengths of conjugation $n_{\text{C=C}}$ < 10) and contains long conjugated segments.

So far no reversible *cis*—*trans* transition in PA has been observed. The thermally induced *cis*—*trans* isomerization in a metastable *cis*-polymer, prepared, for example, by the Shirakawa method, is known to be caused by defects. This phase transition has been studied in detail by the RR method, since the spectra of *cis*- and *trans*-PA are markedly dissimilar, and the most typical bands at 1245 (*cis*) and 1100 cm^{-1} (*trans*) do not overlap.

When we studied the RR effect in PA sample **1**, we found, apparently for the first time, a reversible induced phase *cis*—*trans*-transition (Fig. 4). The line corresponding to *cis*-structures (1245 cm^{-1}) can be clearly seen in the RR spectrum of this sample in a sealed tube (in an oxygen-free medium), recorded at a low (probing) power of the laser excitation (~1 mW) (see Fig. 4, *a*). When the power of the exciting beam increases to 50 mW, this

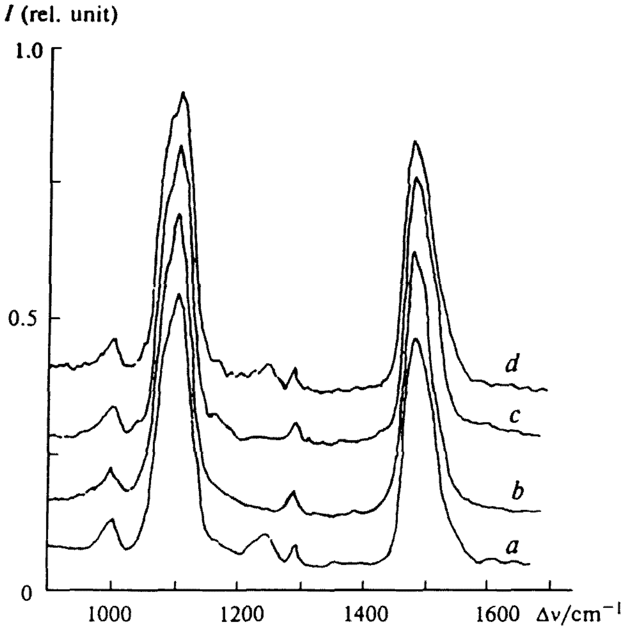

Fig. 4. Reversible *cis—trans* isomerization in the *cis*-fraction of PA **1**: RR spectra recorded at P_{excit} = 1 mW (*a*); 5 min after the beginning of irradiation with light of the increased power, 50 mW (*b*); at 1 mW, 10 min after irradiation with light of the increased power (*c*), and 1 h after the irradiation (*d*). λ_{excit} = 514.5 nm.

line disappears (see Fig. 4, *b*). Within 1 h after the high-power irradiation is terminated, the line corresponding to the *cis*-conformation is again exhibited (its intensity being virtually as high as initially) (see Fig. 4, *d*), which probably points to a reversible *cis—trans*-isomerization. This process is apparently associated with the presence of macrocyclic polyene structures in the PA sample **1**, which is accounted for by specific features of the synthesis of PA from cyclooctatetraene under the action of metathesis catalysts.[12]

To identify the statistics of the distribution of subsystems over different numbers of conjugated bonds, it is necessary to obtain data on the dependence of the C—C vibration frequencies and of the cross-section of Raman scattering, especially the resonance absolute differential cross-section (ADC), on the length of the polyene chain.

The ADC of the Raman line of the 0→*m* vibrational transition σ_{0m} for the excitation close to the resonance is determined from the formula

$$\sigma_{0m} = \mathrm{const}\ \nu_s^4 \sum_{\rho,\varphi} \left|(\alpha_{\rho\varphi})\right|^2, \qquad (1)$$

where ν_s is the frequency of the scattered light; $\alpha_{\rho\varphi}$ are components of the polarizability tensor; and ρ and φ are Cartesian coordinates. Near the resonance with the 0→*e* long-wavelength electron transition in polyenes, the contributions of the other excited states can be neglected; for the fully symmetrical vibrational modes, the dependence of the dipole moment of the electron transition on normal coordinates can also be neglected.[13] Hence, using the Born—Oppenheimer approximation for wave functions, similarly to a previously reported formula,[14] one can write

$$(\alpha_{\rho\varphi})_{0m} \propto \sum_{\upsilon,k} \frac{\mathrm{M}_{\rho}^{0\to e}\mathrm{M}_{\varphi}^{0\to e} < 0|\upsilon >< \upsilon|m >< 0|k >< k|0 >}{E_{000\to ek\upsilon} - h\nu_{\mathrm{excit}} - \mathrm{i}h\Gamma_{ek\upsilon}}, \qquad (2)$$

$$E_{000\to e\upsilon k} = E_{00\to e0} + E_k + E_\upsilon, \qquad (3)$$

where υ is the quantum number of its "own" vibrational mode in the electron-excited state, *i.e.*, the mode for which the line intensity is calculated, *k* are quantum numbers of another ("alien") vibrational mode, $\mathrm{M}^{0\to e}$ is a matrix element of the dipole moment of the electron transition constructed from the electronic wave functions; $E_{00\to e0}$ is the energy of the 00→*e*0 electron transition (from the zero to the zero vibrational sublevel); E_k and E_υ are the energies of the vibrational states with quantum numbers *k* and υ; ν_{excit} is the frequency of the exciting light; and $\Gamma_{ek\upsilon}$ is the half-width of the corresponding line in the absorption spectrum. If contributions of several "alien" modes are to be taken into account, integrals of the <0|*k*> and <*k*|0> type are additionally introduced into formula (2) for all the other "alien" modes.

If even one "alien" mode and *evk* vibrational sublevels are involved, the maxima at some components *ev* of the vibrational structure of the absorption band in the RR lines exitation spectra should "blur" toward higher frequencies, *i.e.*, extend to the *evk* region, where *k* = 0, 1, 2.... In addition, the RR excitation spectra of polyene derivatives are affected by: (1) partial overlap of the π→π* absorption bands corresponding to defect-free conjugated sections with different numbers (*n*) of double bonds; (2) the multiplicity of π-electron excitation levels (even for one particular *n*); (3) imperfection (and its variants) of the autonomy of the electron excitations in defect-free sections of the chain; (4) the presence of several fully symmetrical modes of the C=C vibrations, whose frequencies ν(C=C) differ only slightly from one another.

If f_n is the distribution function of defect-free conjugated subsystems with various numbers (*n*) of C=C bonds in PA, the shape of the 0→*m* line in the Raman spectrum of this sample, $I_{0m}(\nu_s)$, can be calculated from the following formula

$$I_{0m}(\nu_s) = \sum_n f_n I_{0m}(\nu_{sn}), \qquad (4)$$

where $I_{0m}(\nu_{sn})$ is the shape of the line of the corresponding vibrational mode for a segment with *n* conjugated C=C bonds. $I_{0m}(\nu_{sn})$ was specified by the Gaussian function

$$I_{0m}(\nu_{sn}) = \mathrm{const}\ \sigma_{0m}(n) \exp\{-[(\nu_s - \nu_n)/\nu_0]^2\}, \qquad (5)$$

where ν_n is the mean frequency of the 0→*m* vibrational transition in the spectrum of a polyene with *n* conju-

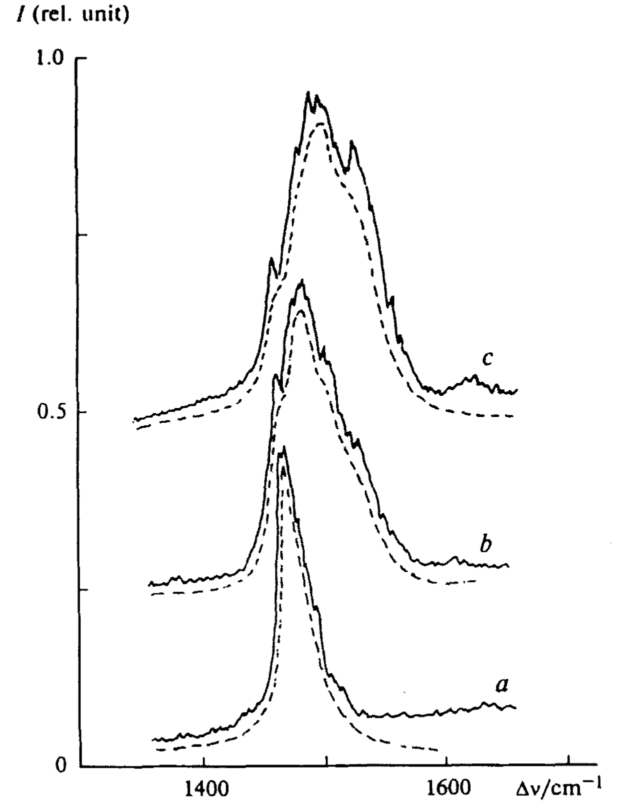

Fig. 5. RR spectra of PA sample **1** in the region of ν(C=C) vibrations (the continuous line shows the experimental results, and the dashed line corresponds to calculations). λ_{excit} = 647.1 (*a*), 514.5 (*b*), and 457.9 (*c*) nm.

gated bonds, ν_0 is the half-width of the corresponding Raman line. The ν_n value for the fully symmetrical stretching vibration of the C=C bonds was calculated from the empirical formula

$$\nu_n = A + B\exp(-Cn). \tag{6}$$

A, *B*, and *C* were selected from published data.[15] This formula reflects implicitly a certain participation of the fully symmetrical vibrations of the polyene chain, whose frequencies are similar to that of the coherent fully symmetrical vibration of C=C bonds. The $M^{0\to e}$, $<0|\upsilon>$, $<\upsilon|m>$, and $<0|k>$ values needed for the calculation of $(\alpha_{\rho\varphi})_{0m}$ according to formula (2) were determined previously,[13,16] and the Γ and ν_0 values were obtained from the experimental spectra of polyenes with a fixed number *n*.[17]

The above-presented formulae were used to design a computer program. By varying the function f_n, a distribution was selected for which the calculated shape of the RR spectral line is close to the experimental shape (Fig. 5).

The numerical experiments, in which the function f_n was specified either as one Gaussian

$$f_n = C_0\exp\{-[(n - n_{\max})/\Delta_n]^2\}, \tag{7}$$

or as the sum of two Gaussians

$$f_n = C_1\exp\{-[(n - n_{\max,1})/\Delta_{n,1}]^2\} + C_2\exp\{-[(n - n_{\max,2})/\Delta_{n,2}]^2\}, \tag{8}$$

where C_i are constants normalizing the sum Σf_n, gave the following results for the C=C bond vibrations: (1) if f_n is specified as one Gaussian, the shape of the Raman line varies only slightly as the frequency of the exciting light varies; (2) if f_n is specified as the sum of two Gaussians, then, for a relatively large difference between the $n_{\max,1}$ and $n_{\max,2}$ values ($|n_{\max,1} - n_{\max,2}| > 20$), the ν(C=C) line shifts more substantially, the shape of the line markedly changes, and better agreement with the experimental data is observed.

Figure 5 shows the calculated and experimental shapes of the line due to the C=C bond vibrations in PA sample **1** for the excitation of the RR effect with light with different λ_{excit}. The following parameters were used for the calculation: Γ = 800 cm^{-1}; ν_0 = 15 cm^{-1}; $n_{\max,1}$ = 65; $\Delta_{n,1}$ = 25; $n_{\max,2}$ = 18; $\Delta_{n,2}$ = 12.

When the excitation is carried out at λ_{excit} = 647.1 nm, the calculated spectrum is almost entirely determined by the contribution of long conjugated subsystems (ν(C=C) = 1462 cm^{-1}). For λ_{excit} = 457.9 nm, the contribution of short subsystems is more substantial and, according to the model used, the frequency at the maximum of the ν(C=C) line increases, due to the fact that the frequency of the incident light falls within the region of resonance with electron transitions in shorter conjugated subsystems.

Distribution functions for PA samples subjected to heat treatment (PA **2** and PA **3**) were also obtained. The following parameters were used: for sample **2**, $n_{\max,1}$ = 35; $\Delta_{n,1}$ = 15; $n_{\max,2}$ = 14; $\Delta_{n,2}$ = 10; for sample **3**, $n_{\max,1}$ = 40; $\Delta_{n,1}$ = 20; $n_{\max,2}$ = 14; $\Delta_{n,2}$ = 10.

Thus, it can be seen that the shifts of the ν(C=C) line following the variations of λ_{excit} are due to the fact that as the λ_{excit} varies, conditions for the resonance excitation in the conjugated subsystems of various lengths arise. Similar results were also obtained in the framework of the same model for the ν(C—C) line.

Comparison of our data on the distribution function of conjugated subsystems over *n* with the results of studies of the RR effect in other PA samples indicates that our model is commensurable with the model used previously[18] and leads to similar results. According to the data obtained in the present work, for samples of PA obtained from cycloocta-1,3,5,7-tetraene, distribution functions of defect-free conjugated subsystems over the number of units can be described by the sum of two Gaussian distributions; a specific feature of the PA synthesized from cyclooctatetraene is a larger mean length of short conjugated segments compared to the PA prepared over Ziegler—Natta catalysts. In the PA sample not subjected to heat treatment, reversible induced *cis—trans* isomerization of *cis*-segments is observed, which is probably due to the presence of macrocyclic structures.

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 93-03-5566) and the International Science Foundation (Grant No. 4895-0925).

References

1. V. V. Berdyugin, K. Ya. Burshtein, P. P. Shorygin, Yu. V. Korshak, A. V. Orlov, and M. A. Tlenkopachev, *Dokl. Akad. Nauk SSSR*, 1990, **312**, 379 [*Dokl. Chem.*, 1990, **312** (Engl. Transl.)].
2. H. Kuzmany, *Phys. Stat. Solidi*, 1980, **B97**, 521.
3. D. B. Fitchen, *Mol. Cryst. Liq. Cryst.*, 1982, **83**, 95.
4. L. S. Litchman, E. A. Imhoff, A. Sarhangi, and D. B. Fitchen, *J. Chem. Phys.*, 1984, **81**, 168.
5. D. Bloor, F. H. Preston, D. J. Ando, and D. N. Batchelder, in *Structural Studies of Macromolecules by Spectroscopic Methods*, Wiley, New York, 1976.
6. Y. Tokura, T. Koda, and A. Itsubo, *J. Chem. Phys.*, 1986, **85**, 99.
7. V. V. Berdyugin, A. I. Kuzaev, V. M. Misin, O. Yu. Os'kina, M. I. Cherkashin, and P. P. Shorygin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 809 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 722 (Engl. Transl.)].
8. V. V. Berdyugin, P. P. Shorygin, V. A. Sergeev, and S. A. Arnautov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2167 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 1977 (Engl. Transl.)].
9. N. S. Sariciftci and H. Kuzmany, *Synth. Metals*, 1987, **21**, 157.
10. V. V. Berdyugin, Yu. P. Kudryavtsev, Yu. V. Korshak, P. P. Shorygin, and V. V. Korshak, *Dokl. Akad. Nauk SSSR*, 1989, **305**, 362 [*Dokl. Chem.*, 1989, **305** (Engl. Transl.)].
11. Yu. V. Korshak, V. V. Korshak, G. Kanischka, and H. Hocker, *Macromol. Chem. Rapid Commun.*, 1985, **6**, 685.
12. M. A. Tlenkopachev, Yu. V. Korshak, A. V. Orlov, and V. V. Korshak, *Dokl. Akad. Nauk SSSR*, 1986, **291**, 409 [*Dokl. Chem.*, 1986, **291** (Engl. Transl.)].
13. V. V. Berdyugin, K. Ya. Burshtein, and P. P. Shorygin, *Optika i Spektroskopiya* [*Optics and Spectroscopy*], 1985, **58**, 1178 (in Russian).
14. P. P. Shorygin and L. L. Krushinskii, *Dokl. Akad. Nauk SSSR*, 1960, **133**, 337 [*Dokl. Chem.*, 1960, **133** (Engl. Transl.)].
15. V. V. Berdyugin, K. Ya. Burshtein, and P. P. Shorygin, *Dokl. Akad. Nauk SSSR*, 1985, **285**, 1397 [*Dokl. Chem.*, 1985, **285** (Engl. Transl.)].
16. P. Tsayi, R. P. Cooney, J. Heviside, and R. J. Hendra, *Chem. Phys. Lett.*, 1987, **59**, 510.
17. H. E. Schaffer, R. R. Chance, and R. J. Siebey, *J. Chem. Phys.*, 1991, **94**, 4161.
18. J. P. Brivio and E. Mulazzi, *Phys. Rev.*, 1984, **B30**, 876.

Received January 10, 1995;
in revised form January 4, 1996