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C. I. Simionescu^a; I. I. Negulescu^a

^a "P. Poni" Institute of Macromolecular Chemistry, Jassy, Romania

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Geometrical Changes in Conjugated Polyenes

CRISTOFOR I. SIMIONESCU and IOAN I. NEGULESCU

"P. Poni" Institute of Macromolecular Chemistry
6600 Jassy, Romania

ABSTRACT

The activation energy and the threshold temperature of isomerization are determined for the cis-trans conversion of polyacetylene (26.5 kJ/mol and 236 K) and poly(phenyl acetylene) (42.5 kJ/mol and 373 K) in the solid state. Based on the low activation energy of conversion, a mechanism is proposed for the isomerization of cis-rich polyacetylene, which involves the delocalization of electrons in the first step followed by formation of trans geometries through their relocation in the cisoidal form and rotation around single bonds to form stable transoidal sequences. No threshold temperature and activation energy could be defined in the case of poly(β -ethynyl naphthalene) where it is suggested that the driving force of isomerization lies in the constrained character of the cis-cisoidal helix.

INTRODUCTION

The discovery in 1973 by Walatka et al. [1] that polymeric $(SN)_x$ crystals were metallic, rather than semiconducting as previously believed, renewed the interest of scientists in low-dimensional conducting materials. When in 1977 [2, 3] it was shown that a variety of halogens, most notably bromine, could be incorporated into the $(SN)_x$ lattice, causing its room temperature conductivity to increase

without destroying the superconductivity transition, a new stage in the development of conducting polymers was inaugurated. Thus, just later in that year [4, 5], it was demonstrated that polyacetylene films could be made to exhibit metallic and semiconducting properties by means of chemical modification with electron acceptors and donors.

Doped polyacetylene is a material on which many laboratories now focus their research, and various experiments concerning its transport and magnetic properties have been performed. Much less work has been done, however, on pristine samples. The morphology and the crystal structure of polyacetylene are rather well defined, and at the molecular level the molecular weight of this insoluble polymer was elegantly shown to range from 500 to 120,000 [6, 7]. However, the irreversible process of isomerization of polyacetylene from the as-formed *cis* isomer to the thermodynamically more stable *trans* geometry is still insufficiently understood. Moreover, the change of isomeric composition with the temperature of synthesis [8] implies the existence of a thermal barrier under which the *trans* isomer does not arise. Therefore, the present work was undertaken with two objectives:

1. To find out if there exists a threshold temperature of isomerization of conjugated polyenes.
2. To elucidate the irreversible character of isomerization of these polymers.

To this aim, besides polyacetylene, $(\text{CH})_n$, two other conjugated polyenes with aromatic substituents of increasing bulkiness were considered, i.e., poly(phenyl acetylene) (PPA) and poly(β -ethynyl naphthalene) (PbEN).

EXPERIMENTAL

Silvery films of *cis*-rich $(\text{CH})_n$ were synthesized according to the method reported by Shirakawa et al. [8]. PPA and PbEn were synthesized and fractionated as reported elsewhere [9].

Two kinds of $(\text{CH})_n$ samples were considered for this investigation, with 90 and 5% *cis*, respectively; the latter was obtained by heating the *cis*-rich polymer in vacuum at 118°C for 3 h. The isomeric content of $(\text{CH})_n$ was determined according to Ito et al. [8] from IR absorptions peculiar to *cis* (740 cm^{-1}) and *trans* (1014 cm^{-1}) bands.

As regards the PPA samples, only the insoluble *cis*-*cisoidal* fraction with ~90% *cis* units was considered for DSC measurements. The relative *cis* content was determined from IR data by the following equation, useful in the case of insoluble PPA [10]:

$$\% \text{ cis} = 100(aA_{740})/(aA_{740} + A_{760}) \quad (1)$$

where A_{740} and A_{760} are the absorptions at 740 cm^{-1} (cis) and 760 cm^{-1} , respectively, and a is a constant determined from the NMR spectra of soluble cis-transoidal fractions, $a = 5.5$.

In the case of PbEN, only the red fraction which was insoluble in benzene and assumed to have a cis-cisoidal structure [11], was taken into consideration.

Infrared spectra were recorded on a Perkin-Elmer 577 spectrometer.

Thermal data were obtained using a Du Pont DSC-990 Calorimeter.

RESULTS AND DISCUSSION

Polyacetylene

It is well established that the chains of acetylenic polymers can adopt, at least theoretically, four geometries: two cis and two trans, i.e., cis-cisoidal, cis-transoidal, trans-cisoidal, and trans-transoidal configurations [12, 13].

Wetmore et al. [14] showed that the first excited state of acetylene is the cis 3B_2 state, predicted to lie 3.43 eV above the ground state, while the lowest trans triplet state is 3B_u (3.78 eV). Consequently, polyacetylene should always be obtained as cis- $(CH)_n$ unless different forms of energy determine the appearance of the thermodynamically more stable trans isomer. Furthermore, Chien et al. [7] concluded with the polymerization of acetylene by a $Ti(OBu)_4/AlEt_3$ catalyst that the monomer, after being activated on π -complexation, undergoes cis opening of the triple bond with a Mobius transition state that leads to addition to the Ti-C bond (insertion of acetylene into the Ti-C bond of the complex catalyst).

However, the change of the isomeric composition at different synthesis temperatures [8], i.e., 98% cis at -78°C , 95% cis at -18°C , 75% cis at 18°C , 7.5% cis at 100°C , and 0.0% cis at 150°C , suggests the existence of a barrier temperature under which the trans geometries are not formed unless other energetic factors are present, e.g., electromagnetic radiation. At higher temperatures it is believed [7] that propagation by cis insertion is followed by isomerization before the chain segment has a chance to crystallize in the cis form. This supposition correlates very well with our observations [15] of the polymerization of acetylenes with lamellar graphite compounds $C_{30}MoCl_5$ and $C_{10}FeCl_3$ that: a) due to the almost matrix-type sterical hindrances

imposed by the lamellar structure of the catalytic complex, the initial configuration of polyenic chains, i.e., *cis*, is preserved even at a relatively high synthesis temperature (50°C), at least until the chain segments come out of the matrix and can move freely into solution, b) insoluble polyacetylene continues to precipitate from the clear solution after repeated filtrations, showing that the process of crystallization follows polymerization and is not simultaneous with it [7]; and c) thermally activated isomerization can easily take place in solution since the slower the reaction rate or the longer the resting time of the reaction mixture, the lower the content of *cis* sequences.

In order to detect the threshold temperature of the *cis*-*trans* conversion, the exothermic flux associated with this process was isothermally followed by DSC [16] based on a kinetic model derived from topoenergetic considerations [17]:

$$\ln(t_m T) = -E/RT + K \quad (2)$$

where t_m represents the time required by the maximum intensity of the conversion process to be reached, T is the transformation temperature in degrees Kelvin, E represents the activation energy of the process, R is the gas constant, and K is a parameter proportional to E and the amount of inert component in the sample. This equation was verified for certain thermally driven processes specific to macromolecular systems such as polymer synthesis [18] or crystallization from the melt [19].

The data obtained at the isomerization of *cis*-(CH)_n are presented in Fig. 1. By linear regression the temperature at which the *cis*-*trans* conversion can start was found to be $T_0^1 = 236 \pm 2^\circ \text{K}$ ($-37 \pm 2^\circ \text{C}$), i.e., under this temperature polyacetylene exists in the *cis* form only (the small percentage of *trans* units reported for polyacetylene obtained at temperatures lower than -37°C , e.g., 2% for -78°C [8], appeared undoubtedly during recording of the IR spectra since careful EPR measurements established that there are no unpaired electrons in the pristine polyacetylene prepared at this temperature [20, 21]). It should be mentioned at this point that Wegner [22] reported that polyacetylene synthesized by the method of Shirakawa gives rise by chlorination to insoluble materials except if the polymerization is carried out in petroleum ether at temperatures below -30°C , when ~50% soluble fraction of chlorinated product is obtained. These findings support the existence of a threshold temperature since, as shown by the same author, the process of intramolecular conversion of *cis* chains can be accompanied by intermolecular crosslinking.

Moreover, a transition at -37°C was recently reported by Fontanille et al. [23] as the glass transition temperature for poly(1-heptyne).

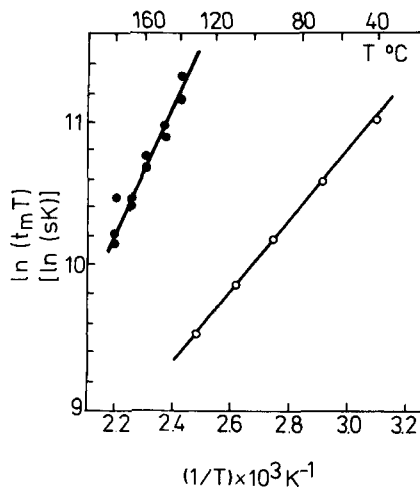


FIG. 1. Kinetics of isomerization of cis-transoidal polyacetylene (\circ) and cis-cisoidal poly(phenyl acetylene) (\bullet).

This temperature seems to represent, as a matter of fact, the lowest value at which the delocalization of π -electrons from the polyenic chain can occur (vide infra).

Using the data plotted in Fig. 1, the activation energy for isomerization of cis-(CH)_n was calculated as 26.5 kJ/mol (6.3 kcal/mol).

The low value of the apparent activation energy (the isomerization of polyacetylene in the solid state is a complex phenomenon including, besides the exothermic conversion, an endothermic in-plane disordering of molecular chains and an exothermic rearrangement of the new structure [24]) should be taken for the pure cis species since it usually depends on the degree of conversion [7], i.e., the barrier energy increases with the content of trans units in polyacetylene from 71 kJ/mol (17 kcal/mol) for 88% cis to about 159 kJ/mol (38 kcal/mol) for 80% trans polymer. When these data were extrapolated for 100% cis polyacetylene, an activation energy close to 6.5 kcal/mol (27 kJ/mol) was obtained [25].

Both this dependence and the low activation energy can be explained if the intimate mechanism of isomerization is closely examined. On the one hand, the usual pathway of isomerization of a double bond involves: a) breaking of the π -bond, b) rotation around the single bond bearing the two unpaired electrons, and c) reformation of the π -bond. Energetically, this means for conjugated bonds more than 110 kJ/mol (26 kcal/mol) for π -bond breaking [26] and almost 12.5 kJ/mol (3 kcal/mol) for rotation [27], which makes a total close to 125 kJ/mol (30 kcal/mol). This value is, however, much higher than any energy

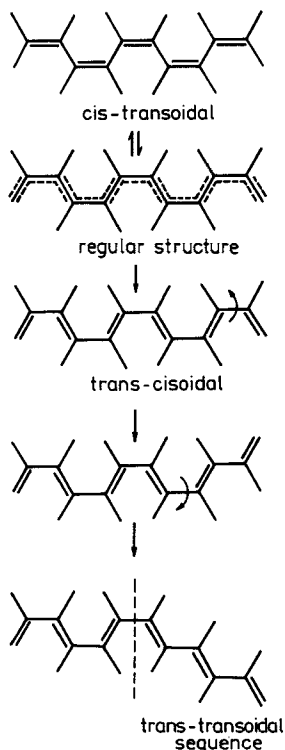


FIG. 2. Mechanism for thermal isomerization of polyacetylene.

barrier experimentally observed for a cis-rich polyacetylene, e.g., 70-90 kJ/mol (17-22 kcal/mol) for 90-80% cis content [8].

On the other hand, if one considers the regular and alternating models of polyacetylene, i.e., with delocalized and localized π -electrons, respectively, a calculated difference in energy close to 40 kJ/mol (9.5 kcal/mol) [28] between these two models is found, the regular structure being less stable. Consequently, it is reasonable to consider that for cis-rich polyacetylene the mechanism of isomerization involves the delocalization of π -electrons in the first step followed in the second step by their localization in a new geometry, i.e., the trans-cisoidal form (Fig. 2). Furthermore, the trans-cisoidal form may easily afford some transoidal structures in the polyenic chain through internal rotation around two carbon-carbon single bonds of two adjacent double bonds as suggested by Yamabe et al. [29] for the rapid isomerization of cis-(CH)_n after doping, or of a longer sequence as illustrated in Fig. 2 (only one single bond involved is shown).

Yamabe et al. [29] concluded that the internal rotation in the trans-cisoidal form is characterized by the irreversible motion that stabilizes the polymer by virtue of the strengthening of the electrostatic nature in the polyene chain, i.e., the attractions between nuclei and electrons are increased and simultaneously the repulsions between electrons are enlarged.

On the basis of the residual cis content observed in the thermal isomerization of polyacetylene films, Gibson et al. [30] suggested that the trans sequences were limited to 15 bonds on the average and that the isolated cis bands are, as a matter of fact, trans-cisoidal bonds which are responsible for the residual absorption at 740 cm^{-1} observed in the thermally isomerized polyacetylene.

Such a process of thermal isomerization of polyacetylene as described in the present paper would allow the cis-trans conversion to proceed within the constraints of the crystalline matrix of the pristine polyacetylene, in agreement with recent x-ray measurements [31]. As the trans content in the polymer increases and the cis sequences become shorter and shorter, this mechanism is gradually replaced by the usual pathway of conversion (i.e., the breaking of π -bonds and rotation around single bonds joining the two radicals), and hence the barrier energy will be higher and higher. For example, the activation energy jumped to 125 kJ/mol for 70% trans content, and higher energies are required for isomerization of $(\text{CH})_n$ of lower cis contents [8, 23].

If two delocalized segments of different chains are close enough, the relocalization process could lead to crosslinked structures (defects of conjugation) instead of converted bonds [22, 32].

Poly(Phenyl Acetylene)

It is well established that the geometrical structure of cis-cisoidal or cis-transoidal PPA isomerized in the solid state is identical with that of a trans configuration obtained by isomerization in solution of the cis-transoidal polymer [33]. However, the thermal isomerization of cis geometries, if carried out at temperatures higher than 120°C , is accompanied by cyclization, aromatization, and chain scission reactions [33, 34]. At the same time, it was suggested that the cyclization reactions are responsible for the low value of activation energy registered in the case of solution isomerization of this polymer [35].

The thermally activated reactions of transformation undergone by poly(phenyl acetylene) in the solid state were recently reinvestigated on the basis of topoenergetic principles [36]. Since the cis content of the sample changes significantly in the solid state over 140°C (the highest rate of transformations are registered between 150 and 180°C [10]), the kinetics of the exothermic flux were investigated in the 140 to 180°C range (Fig. 1). The lowest temperature at which the thermal isomerization of PPA in the solid state is not inhibited was found by

TABLE 1. Threshold Temperature, Enthalpy Change, and Activation Energy for the Isomerization of Conjugated Polyenes in the Solid State

Conjugated polyene	T_0^i , °K	ΔH , kJ/mol ^a	E_a , kJ/mol
Polyacetylene	236	7.75	26.5
Poly(phenyl acetylene)	373	10.50	42.5
Poly(β -ethynyl naphthalene)	None	24.50	None

^aRef. 35.

linear regression of Eq. (2) to be around 373 K (100°C) and the activated energy of this process was determined to be 42.5 kJ/mol (10.2 kcal/mol), very close to the theoretical figure cited above for delocalization of π -electrons from a defectless conjugated polyenic chain.

A value close to this threshold temperature was graphically observed [10, 25, 37] as the temperature at which the slope of the curve expressing the dependence between conductivity and temperature changed dramatically and the transformations were irreversible, i.e., the activation energy of electrical conduction increased each time this value was exceeded following cooling; at the same time, due to side reactions which gave rise to major structural defects, the conductivity of the sample measured at the same temperature was lower and lower after each heating-cooling cycle (in a similar experiment carried out with cis-(CH)_n [16], the electrical conductivity was higher and higher since trans sequences are more conductive and the isomerized polymer is practically defectless if the upper limit of the thermal cycle does not exceed 150°C [32, 38]).

Poly(β -Ethynyl Naphthalene)

By considering the enthalpy changes associated with exothermic phenomena at the isomerization of (CH)_n, PPA, and PbEn (Table 1), it was expected that the barrier energy would also increase with the bulkiness of the substituent. However, when the isomerization of PbEN was analyzed topologically [36], no definite threshold temperature or activation energy could be determined. Therefore, these results can be interpreted for the time being only in terms of steric hindrances, i.e., the cis geometry can afford exclusively a strained cisoidal arrangement stabilized by voluminous naphthyl groups settled in the incommodious β -position (as compared with the α -position where the enthalpy change does not exceed 10 kJ/mol [35]).

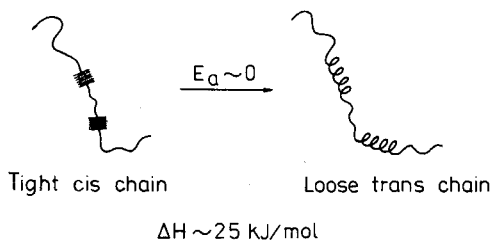


FIG. 3. Isomerization of poly(β -ethynyl naphthalene).

The driving force of isomerization consequently lies in this constrained character of the cis-cisoidal configuration of PbEN, i.e., a tight helix which distends like a spring to a loose trans structure (Fig. 3).

CONCLUSIONS

The activation energy and the threshold temperature for thermal isomerization in the solid state, under which the conversion of cis structures to trans geometry is inhibited, were determined for polyacetylene (26.5 kJ/mol and 236 K) and poly(phenyl acetylene) (42.5 kJ/mol and 373 K). Based on the low activation energy for the conversion of cis-(CH)_n, a mechanism for thermal isomerization was suggested which involves the delocalization of π -electrons in the first step followed by the formation of trans geometries through their localization (trans-cisoidal form) and rotation around single bonds (trans-transoidal form, the stable geometry).

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