of the mixture is mainly derived from the temporary network structure existing in a melt in the absence of silica.[10] The addition of silica does not greatly disturb the whole geometry of the network structure. It only subtracts degrees of freedom of the polymer system and induces more and more hindrances to monomeric motions. The net result is an improvement of elastic properties.

After free polymer chains are removed, some initial entanglements are eliminated; some others are trapped. However, when a random mixture reaches its thermodynamic equilibrium, new entanglements are formed to define a network structure. The existence of domains of dynamical correlations is clearly demonstrated by the present NMR approach. On the one hand, local high-frequency motions are independent of the silica concentration. Hence, silica particles do not cause correlation domains. These result from the intrinsic properties of polymer systems. Incidently, the high-frequency mechanical response of random mixtures should be insensitive to the presence of silica. On the other hand, local high-frequency motions are independent of the presence of swelling agent, for polymer concentrations smaller than about 0.5 (w/w). This is a common property of uncross-linked molten polymers.

Domains characterized by high-frequency dynamical properties screened from the presence of silica or solvents were also studied by observing the transverse nuclear relaxation instead of longitudinal relaxation.

Statistical properties of end-separation vectors joining junctions, whether these are temporary or not, were probed by adding solvent to mixtures to increase the fractal character of the domains. No affine property and no packing condition was found to apply to correlation domains. These two results are in strong contrast to properties observed in calibrated gels; they were assigned to the presence of numerous dangling chains in random mixtures. The result concerning the packing condition is easily accepted, whereas the behavior of end-separation vectors observed in some mixtures is more striking: end-separation distances correspond to average stretchings much larger than average distances corresponding to affine extensions.

A more quantitative approach will be given in a subsequent paper. The purpose of the present work was to give evidence for the presence of domains unaffected by variations of the silica concentration. Hence, the role of mineral particles is mainly to improve elastic properties and to shift viscoelastic terminal relaxation spectra toward lower frequencies.

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Transport Properties of Substituted Poly(acetylenes)

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ABSTRACT: Ac and dc conductivities of poly(*tert*-butylacetylene), poly(phenylacetylene), and poly(methylacetylene) have been investigated. Undoped polymers show dc conductivities smaller than 10^{-15} Ω^{-1} cm^{-1}, with a weak thermal dependence of ac conductivity which can be explained by a phonon-assisted hopping mechanism. Upon doping with iodine, dc conductivities in the 10^{-5}–10^{-3} range are obtained for all polymers. However, the values of conductivity decrease under a constant bias, indicating the presence of an ionic mechanism. These values stabilize to a reduced level which is a function of the size of the substituent, bulkier substituents giving lower values. This stable region is governed by two electronic mechanisms; at low temperatures, a phonon-assisted hopping mechanism is observed, whereas at higher temperatures, a thermally activated hopping mechanism becomes dominant. Different configurational structures of poly(*tert*-butylacetylene) have no effect on its electrical properties. The relative low conductivity values observed for substituted poly(acetylenes) as compared to unsubstituted poly(acetylene) can be explained by their nonplanar conformations and the presence of substituents which increase the distance between the chains.

Introduction

Poly(acetylene) is the simplest conjugated polymer. Pristine poly(acetylene) exhibits a low value of electrical conductivity which increases upon doping to reach values of about 1000 Ω^{-1} cm^{-1}.[1] Many studies have been devoted to the electrical properties of poly(acetylene) but its mechanisms of conduction are still incompletely resolved.[2–11]

For lightly doped poly(acetylenes) (concentrations lower than 0.01 dopants per carbon atom), an intersoliton electron hopping mechanism has been proposed by Kivelson; this theory leads to predictions which are in good agree-

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ment with most experiments.[2] Other models involving hopping among localized states[3] and polaron hopping[4] have also been proposed and applied to ac conductivity.

At higher dopant levels (concentrations of 0.01–0.04 dopants per carbon atom), the model of variable-range hopping among states near the Fermi level has been used to explain most of the experimental values.[5] Other models involving the diffusion of charged solitons[6] and bipolaron interchain hopping[7] have been recently proposed.

At high dopant concentrations (>0.05 dopants per carbon atom), the density of states increases considerably and the conductivity can be described as that of a disordered metal.[8] However, there is not yet a unique theory that can explain all the experimental facts that are presently known, whatever the dopant level of the material.

Unsubstituted poly(acetylene) is insoluble, infusible, and unstable in air. In contrast, substituted poly(acetylenes) are amorphous, soluble in common organic solvents, and more stable in air,[12] although their solubility and stability depend upon the nature and size of the substituent. The electrical conductivity of substituted poly(acetylenes) after doping is generally lower than $10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. This behavior has been explained by the twisted conformation of these polymers which reduces the interchain and intrachain transport of the charge carriers.[13,14] Indeed, a high conductivity value of about $0.1\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at room temperature was reached with poly(1,6-heptadiyne) which is planar.[15]

Very few studies have been carried out on the determination of the conduction mechanisms of substituted poly(acetylenes). However, for poly(phenylacetylene), photoconductivity[16] and ac[17] and dc measurements[18] have shown, upon doping with I_2 and AsF_5, a thermally activated electronic mechanism at low doping levels (<10 mol %) while an ionic mechanism was proposed at much higher doping levels.[19]

In previous publications,[14,20,21] we have characterized the configuration and the conformation of several substituted poly(acetylenes). We have followed the cis-trans kinetics of isomerization of these polymers and we have shown that poly(*tert*-butylacetylene) can undergo both cis–trans and trans–cis isomerization, depending upon the solvent used. We have also studied the nature of the doping species upon iodine addition. We have shown, by UV spectroscopy, that these polymers contain low I_3^- concentrations and that significant amounts of I_2 are required in order to increase significantly the conductivity.

The electrical conductivity of these polymers was also studied. At high doping levels, the maximum conductivity value reached by each conjugated polymer is nearly independent of the size of the substituent. However, the exact nature of the charge carriers and the mechanism of electrical transport were not elucidated.[14] In this article, we report a study of the electrical transport of several substituted poly(acetylenes) doped with iodine and the influence of the molecular structure on their electrical properties. More specifically, poly(*tert*-butylacetylene) (PTA), poly(phenylacetylene) (PPhA), and poly(methylacetylene) (PMA) are investigated.

Theory

Several theories have been developed to explain the charge-transport measurements of disordered materials.[22-27] An important point to note is that the concept of energy bands, initially developed for crystalline materials, is also applicable to noncrystalline solids. In amorphous polymers, there are still valence and conduction bands but the disorder leads to the formation of localized states near the conduction and valence bands and near the Fermi level.

Then conduction can be due to a thermal activation of the charge carriers from localized states in the band gap to extended states in the conduction band.[22-24] According to this model, the charge carriers have a high mobility in the conduction band and, therefore, high levels of conductivity are obtained. One important feature of this theory is that conductivity does not depend upon frequency, at least up to 10^{13} Hz.

With a smaller activation energy, the carriers can be excited into localized states in the band tails.[22,24] In these states, the mobility is at least 2 orders of magnitude lower than the mobility for conduction in the extended states. This transition in mobility of the charge carriers, between the extended states and the localized states, produces a mobility edge which is defined as the mobility gap. When the carriers are not in the extended states, in a disordered system, the conductivity at high frequencies is generally larger than the dc conductivity. Physically, this behavior is due to the fact that electrons can hop between neighboring structural defects at a greater rate than that which characterizes the hops necessary to cross the sample for dc conductivity. In addition, the conduction by activated hopping in band tails leads to identical activation energies in the ac and dc processes.

Conduction can also be due to a hopping in a manifold of states at the Fermi level.[24-27] In the Mott variable-range hopping model,[5,24] weakly temperature dependent dc and ac conductivities are expected. This model can be described as phonon-assisted tunneling of charge carriers between localized states. Using a similar model, Pike[25] has considered a thermally activated hopping between states. Pike's model can be related to Poole's theory which describes the dc conduction using similar assumptions.[26] Phonon-assisted or thermally activated processes show about the same frequency dependence but different thermal dependences.

Finally, the formation of small polarons by the charge carriers has been proposed.[4,23] This theory explains the conduction by a thermally activated hopping of the polarons.

Except for the thermal activation to extended states theory, all of these models propose a frequency dependence of the conductivity following the general relation

$$\sigma_{\mathrm{dc}} = A(T) \tag{1}$$

$$\sigma_{\mathrm{ac}} = B(T)f^{s} \tag{2}$$

where $s \sim 0.8$ and $A(T)$ and $B(T)$ are temperature-dependent coefficients. Table I gives the list of the most commonly applied models and their functional dependence upon temperature T for frequencies smaller than 10^6 Hz. In Table I, k_b is the Boltzmann constant, E_a, E_a', and E_a'' are activation energies, E_b is the polaron binding energy, and T_0 is a constant.

In dc measurements, it is seen that the phonon-assisted hopping model near the Fermi level is weakly affected by temperature: log (σ_{dc}) follows a $T^{-0.25}$ dependence. For the other models, a T^{-1} dependence is found. In ac measurements, the hopping models near the Fermi level are weakly dependent upon the temperature while polaron hopping and thermally activated hopping in band tails models lead to stronger thermal activation with log (σ_{ac}) following a T^{-1} dependence. A particular case is observed for the conduction in the extended-states model where $\sigma_{\mathrm{ac}} = 0$ leading to $B(T) = 0$.

Experimental Section

All solvents were kept on a drying agent (CaH_2 or Na) and distilled under argon before use. PTA and PPhA were synthesized

Table I
Temperature Dependence of Dc and Ac Conductivities of Different Models for Disordered Materials

model	$A(T)$	$B(T)$
thermal activation to extended states	$\exp(-E_a/kT)$	0
thermally activated hopping in band tails	$\exp(-E_a'/kT)$	$T\exp(-E_a'/kT)$
phonon-assisted hopping in the states near the Fermi level (Mott)	$\exp(-(T_0/T)^{0.25})$	T
thermally activated hopping in the states near the Fermi level	$T^2\exp(-E_a''/kT)$ (Poole)	T^n ($n > 1$) (Pike)
polaron hopping	$\exp(-E_b/2kT)$	$\exp(-E_b(1-s)/2kT)$

by using metal carbenes as initiators[28] and PMA was synthesized by using a Ziegler–Natta catalyst as described by Chien et al.[29] Polymers were precipitated several times in methanol in order to eliminate all residual traces of initiator. They were dried and stored under vacuum. They had number-average molecular weights of 4.0 (PMA), 11.0 (PPhA), and 120 (PTA) kg/mol and polydispersity indexes of 3.5.

The iodine doping of the polymers was performed in dry CCl_4 solutions, under an argon atmosphere. The polymers were reacted with the iodine for at least 24 h; the solvent was then slowly evaporated and stable polymer–I_3^- complexes were recovered (most of the unreacted iodine was evacuated with the solvent). This procedure was followed by vacuum drying until the complexes reached constant weight. Adsorption of iodine to the doped polymer films was carried out by leaving the samples under an iodine atmosphere. Measurements of I_3^- and I_2 contents were carried out by using UV spectroscopy with a Hewlett-Packard (Model 8450A) instrument, as described in a separate article.[14]

The structure of the polymers and their cis–trans content were determined by nuclear magnetic resonance and infrared spectroscopies by using methods previously described.[20] For this study, 75% trans PMA, 35% trans PPhA, and 15% trans PTA were used but iodine doping induces an isomerization which leads to 100% trans PMA and PPhA samples. The behavior of PTA is different: depending upon the solvent used for iodine doping, a 10% (in Decalin) or a 70% (in carbon tetrachloride) trans sample was obtained.

Conductivity measurements of doped and undoped polymers were performed on films for PTA and on pressed pellets for PPhA and PMA, under dry nitrogen. The PTA films were cast from CCl_4 and had a thickness ranging from 50 to 100 μm. The PPhA and PMA pellets were prepared from dried powders and usually had a thickness of 1 mm. For ac conductivity measurements, the samples were held between two electrodes with a guard ring (Balsbaugh Model LD-3). For dc measurements, similar results were obtained by using the Balsbaugh electrodes or the four-point probe method.[30] The four electrodes were set on a single line.

The dc conductivity measurements as a function of time of doping and the electrolysis measurements were performed in a vacuum-tight cell fitted with platinum wires.[31] Connections between the sample and the platinum wires were realized with the aid of a conducting glue (Electrodag no. 502, Acheson Co.). Owing to the low conductivity values of all polymers, it was not necessary to use a four-probe method. Ohm's law was always verified in the 1–30-V range and no significant polarization was observed. For electrolysis experiments, great care has been taken to limit iodine desorption. An environmental chamber was constructed to regulate the temperature of the cell. Heating and cooling rates were always close to 0.5 K/min and the temperature stability was better than 0.5 K.

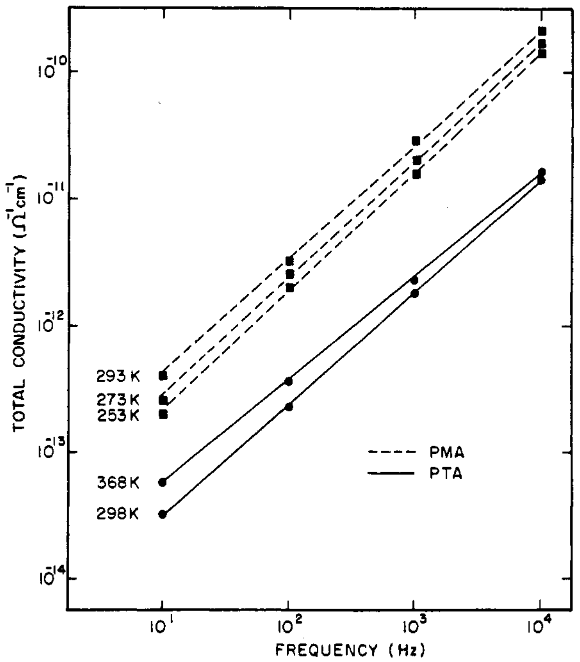

Figure 1. Total conductivity of poly(methylacetylene) (PMA) and poly(*tert*-butylacetylene) (PTA) as a function of frequency at several temperatures.

Table II
Dc Electrical Properties of Iodine Complexed Polymers

polymer	σ_{max}, Ω^{-1} cm^{-1}	σ_{stable}, Ω^{-1} cm^{-1}	E_a, eV
PMA	10^{-3}	10^{-4}	0.60
PPhA	10^{-5}	10^{-6}	0.76
PTA	10^{-5}	10^{-8}	0.60

The dc measuring circuit was made of a power supply and a Keithley ammeter (Model 480). The ac measurements were performed with a General Radio 1621 Precision Capacitance System in a frequency range of 0.01–100 kHz. The conductivity values thus obtained (σ_{tot}) could be decomposed into two contributions:

$$\sigma_{tot} = \sigma_{ac} + \sigma_{dc} \quad (3)$$

where σ_{ac} is the ac conductivity and σ_{dc} the dc conductivity.

Results

Poly(*tert*-butylacetylene). Figure 1 shows the total conductivity of undoped poly(*tert*-butylacetylene) (PTA) as a function of frequency. The conductivity dependence is linear in the frequency range investigated (logarithmic scales) and it depends slightly upon temperature, the activation energy calculated with the Arrhenius equation being lower than 0.01 eV. These results can be analyzed with eq 2 and it is then found that the frequency exponent s decreases from 0.90 to 0.81 as the temperature is raised from 298 to 368 K. The dc conductivity of undoped PTA is low with a value smaller than 10^{-15} Ω^{-1} cm^{-1}; it is at least 1 order of magnitude lower than the ac contribution. Therefore, the total conductivity can be equated to the ac conductivity.

PTA was subsequently doped with iodine in solution. It had an I_3^- content of 0.12%. Iodine doping has little effect on the dc conductivity which increases only to 10^{-15} Ω^{-1} cm^{-1} (Table II). The ac conductivity and its frequency dependence are also similar in doped and undoped samples, but doping causes an increase of the thermal dependence as shown in Figure 2. The activation energy calculated (~0.05 eV at room temperature) increases slightly with the temperature.

In previous studies,[14,32] it has been shown that substituted poly(acetylenes) are generally isomerized doping with iodine into a complete trans structure. The behavior of

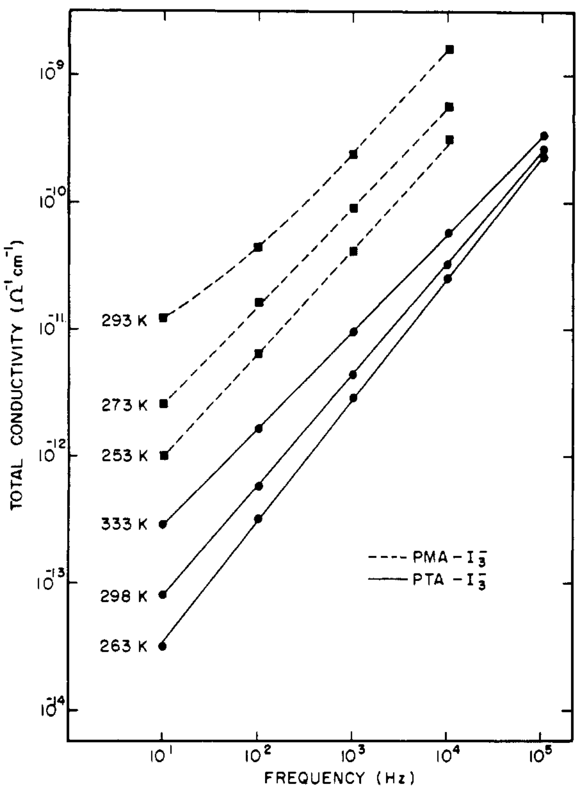

Figure 2. Total conductivity of poly(methylacetylene)–I_3^- and poly(*tert*-butylacetylene)–I_3^- complexes as a function of frequency at several temperatures.

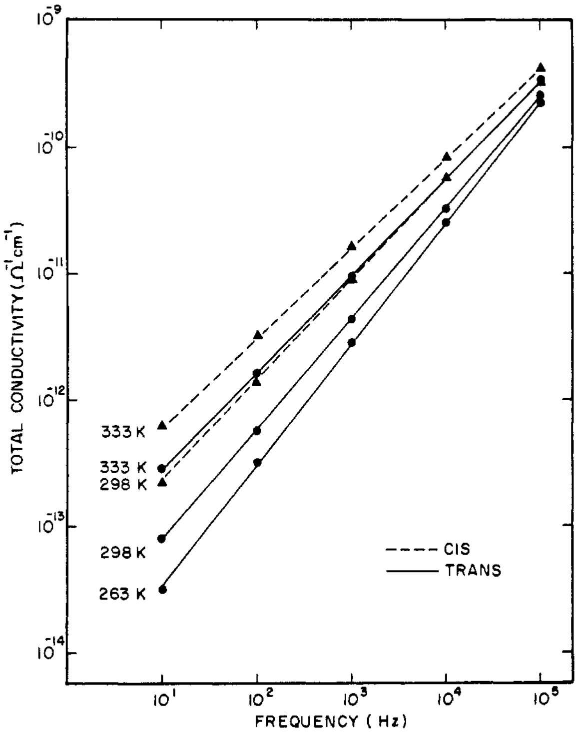

Figure 3. Total conductivity of poly(*tert*-butylacetylene) in the cis and trans geometric structure as a function of frequency at several temperatures.

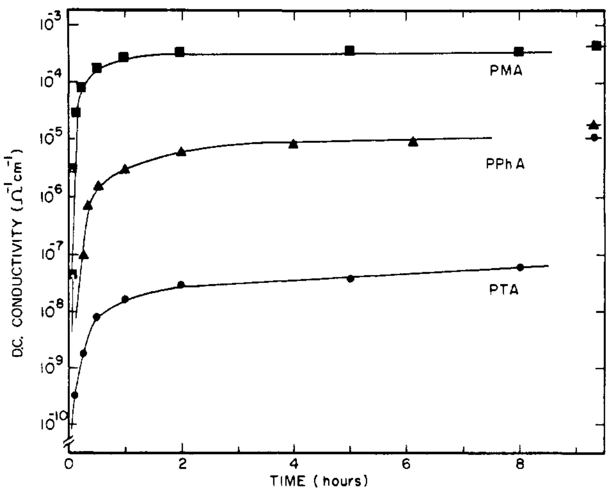

Figure 4. Dc conductivity of poly(methylacetylene) (PMA), poly(phenylacetylene) (PPhA), and poly(*tert*-butylacetylene) (PTA) complexed with I_3^- as a function of time in the presence of iodine.

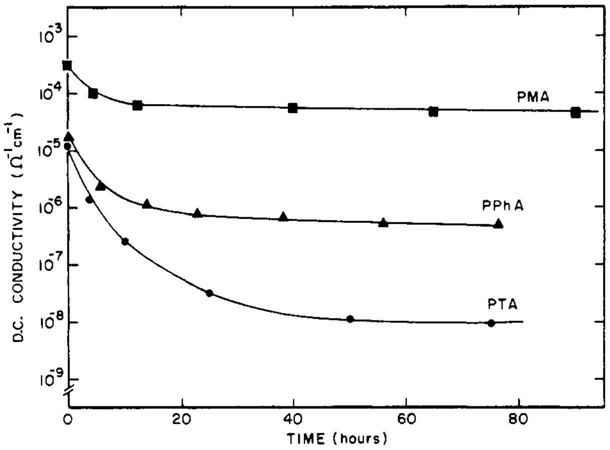

Figure 5. Dc conductivity of poly(methylacetylene) (PMA), poly(phenylacetylene) (PPhA), and poly(*tert*-butylacetylene) (PTA) as a function of time under a constant voltage.

PTA is, however, different. This polymer can be isomerized reversibly depending upon the solvent used; for example, it can be isomerized into a 70% trans form in CCl_4 or into a 90% cis form in decalin. In this study, PTA was doped in CCl_4 (*trans*-PTA) and decalin (*cis*-PTA) solutions to investigate the influence of the geometric structure upon conductivity. Figure 3 shows that these two samples exhibit similar frequency and thermal dependencies, with slightly different values of conductivities. This last point can be explained by slightly different I_3^- contents or by a small amount of free iodine adsorbed by one of the two samples.

As reported earlier[14] the presence of adsorbed iodine in a polymer does not create any additional charge carriers, but it increases significantly the electrical conductivity. As shown in Figure 4, the conductivity of PTA–I_3^- complexes (samples which were doped in solution and contain iodine in the I_3^- form only[14]) increases rapidly from 10^{-15} to 10^{-8} Ω^{-1} cm^{-1} when a sample is left in an iodine atmosphere where it can absorb free iodine; it is possible to obtain conductivities close to 10^{-5} Ω^{-1} cm^{-1} when PTA is kept several weeks in an iodine atmosphere. However, electrolysis experiments show that, above 10^{-8} Ω^{-1} cm^{-1}, the conductivity drops as a function of time to a stable value of about 10^{-8} Ω^{-1} cm^{-1} (Figure 5). Therefore, temperature-dependence measurements were performed only for conductivity values below 10^{-8} Ω^{-1} cm^{-1}, in the region where they are stable, i.e., at low doping levels (<10 mol %).

Figure 6 shows the total conductivity of PTA–I_3^- complexes with adsorbed iodine as a function frequency. At 263 K, the conductivity increases linearly with frequency. However, at higher temperatures, the curves show a plateau at low frequencies. This plateau is due to the dc contribution which increases and becomes of the same

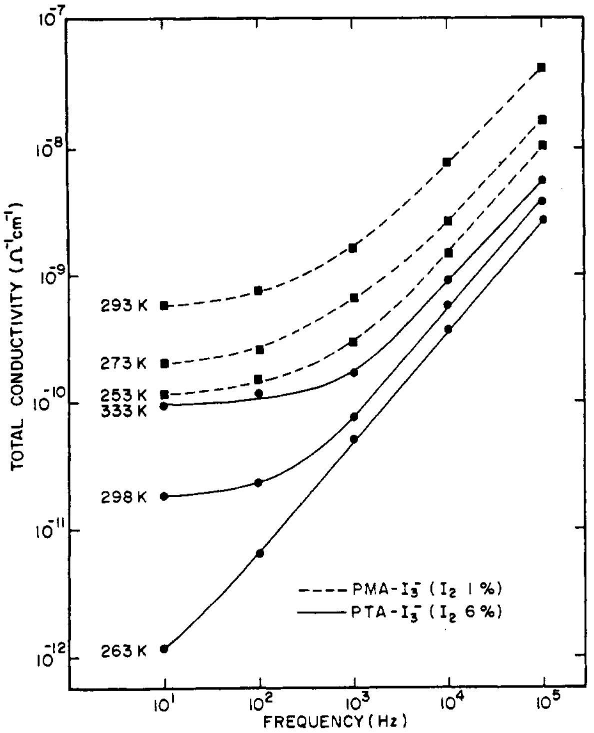

Figure 6. Total conductivity of poly(methylacetylene) (PMA) and poly(*tert*-butylacetylene) (PTA), complexed with I_3^- and containing additional iodine, as a function of frequency at several temperatures.

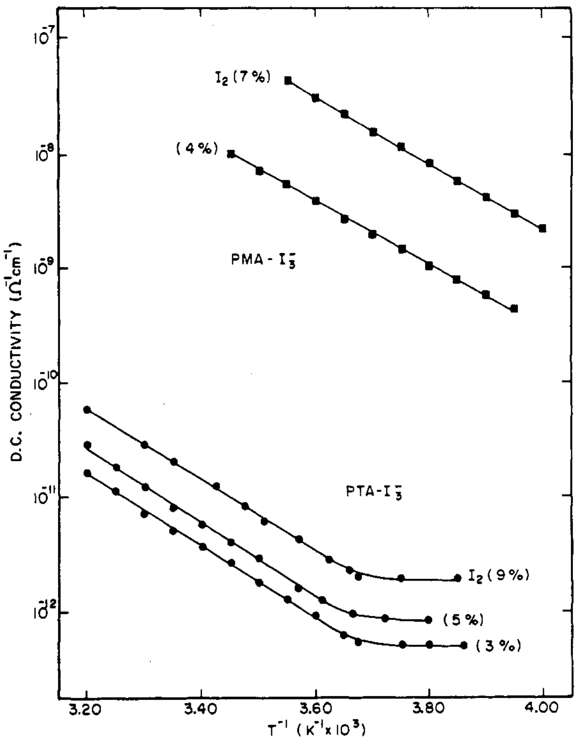

Figure 7. Dc conductivity of poly(methylacetylene) (PMA) and poly(*tert*-butylacetylene) (PTA), complexed with I_3^- and containing additional iodine, as a function of the inverse of temperature.

order of magnitude as the ac contribution. At frequencies over 10^3 Hz, the curves remain linear, and the ac contribution is isolated again with a slope and a thermal dependence similar to those observed for this complex without any adsorbed iodine.

Since the dc conductivity increases significantly with the adsorption of iodine, it was possible to study its thermal dependence for different iodine contents. From Figure 7, a transition temperature close to 273 K is seen: below this temperature, a very small thermal activation energy is observed, while above it, electrical transport becomes highly temperature dependent and, using an Arrhenius plot, an activation energy of 0.61 eV was calculated; a value which is independent of the amount of adsorbed iodine. Similar transitions have been reported for some poly(diacetylenes)[32] and for PPhA.[34]

Poly(methylacetylene). Similar measurements was performed with poly(methylacetylene) (PMA) samples. As for PTA, undoped PMA has a dc conductivity smaller than 10^{-15} Ω^{-1} cm^{-1}; its AC contribution varies linearly on a logarithm scale with frequency and a weak thermal activation is observed (Figure 1). The frequency exponent s of eq 2 varies from 0.96 to 0.90 as the temperature is increased from 253 to 293 K. The ac conductivity of PMA is larger than that of PTA under similar conditions (see Figures 1, 2, and 6).

Doping of PMA with iodine gives a charge-transfer complex containing 4% of I_3^-. As shown in Figure 2, the ac conductivity of PMA exhibits a larger thermal activation than the corresponding undoped polymer. In addition, there is a small dc contribution appearing at 293 K at low frequencies.

Figure 4 shows that the adsorption of iodine to the PMA–I_3^- complex increases the dc conductivity to a maximum of 10^{-3} Ω^{-1} cm^{-1}, in agreement with a value reported in the literature[29] but the conductivity stabilizes at about 10^{-4} Ω^{-1} cm^{-1} after applying a voltage for 20 h (Figure 5). Figure 6 shows the total conductivity of PMA–I_3^- complexes after adsorption of iodine as a function of frequency for several temperatures. The ac contribution can be isolated from the dc contribution at frequencies above 10^4 Hz and a comparison of Figures 2 and 6 shows that the thermal and frequency dependencies of PMA are not influenced by the adsorption of iodine. Again, the dc contribution shows up at low frequencies with the appearance of a plateau.

The thermal activation of dc conductivity of doped PMA was analyzed in Figure 7. There is no transition in the range investigated but, as reported for PTA, the activation energy (0.60 eV) calculated from an Arrhenius plot does not depend upon the amount of adsorbed iodine.

Poly(phenylacetylene). Ac and dc conductivities of doped and undoped poly(phenylacetylene) (PPhA) were also recorded but they are not reported in the figures for clarity. The conductivity behavior of PPhA is similar and always intermediate between those of PTA and PMA. Undoped PPhA has a dc conductivity smaller than 10^{-15} Ω^{-1} cm^{-1} and its ac conductivity varies linearly with frequency (s = 0.71–0.80) with a low thermal activation (~0.01 eV).

The charge-transfer PPhA–I_3^- complex contains 2.7% I_3^- and exhibits a larger thermal activation energy than undoped PPhA. It shows a dc conductivity value of 10^{-13} Ω^{-1} cm^{-1}, which increases to a maximum of 10^{-5} Ω^{-1} cm^{-1} with the adsorption of iodine (Figure 4) but decreases by nearly 1 order of magnitude after current has passed through the sample for approximately 20 h (Figure 5). The same behavior was reported previously for PPhA–AsF_5 complexes.[35] The thermal activation of ac and dc conductivities does not vary with iodine adsorption. A transition in the energies of activation of dc transport then occurs at 257 K, in agreement with a study of Bhatt et al.[34] Finally, as for PTA and PMA, the energy of activation of ac conductivity of PPhA after adsorption of iodine (~0.10 eV) is always smaller than that observed for dc conductivity (0.76 eV).

Discussion

At high doping levels, PMA, PPhA, and PTA show conductivities in the 10^{-5}–10^{-3} Ω^{-1} cm^{-1} range. These values decrease with time, under a constant voltage, to reach values which depend upon the size of the substituent of the polymer (Table II): the larger the substituent the smaller the value reached. This behavior is expected with an ionic conduction mechanism since the ionic charge carriers are purged from the system by bulk diffusion under the influence of the electric field. The ionic process can be due to the presence of iodide in iodine which is known to give high values of conductivity.[36,37] However, under a constant voltage, the conductivity levels off at a reduced value after a certain period of time and indicates the coexistence of an electronic conduction process. In contrast, at low doping levels, in a conductivity range smaller than 10^{-4} Ω^{-1} cm^{-1} for PMA, 10^{-6} Ω^{-1} cm^{-1} for PPhA, and 10^{-8} Ω^{-1} cm^{-1} for PTA, the conductivity values are stable and do not change upon an applied voltage indicating an electronic conduction mechanism.

The models of electronic conduction presented in Table I can be used to explain the behavior of substituted poly(acetylenes). For undoped polymers, a very weak dependence of ac conductivity is observed as a function of temperature (the dc conductivity is too low to be analyzed), and the best model to correctly describe this feature is Mott's variable-range hopping model.[22] Other models lead to a strong thermally activated ac conductivity whereas a phonon-assisted tunneling of charge carriers between localized states lead to activation energies in the 0.001–0.01-eV range. Mott's model also predicts that the ac conductivity should be linearly dependent upon the frequency with a slope of about 0.8, as it was found experimentally. This model was previously used to explain the conductivity behavior of PPhA samples by Diaconu et al.[38]

After doping, the thermal activation of ac conductivity increases considerably. Mott's theory cannot explain this behavior since it predicts that an increase of localized states in the band gap does not change the thermal dependence of ac conductivity. If it is considered that doping increases the density of states, as was observed for PPhA,[16] the Coulombic fields from two adjacent sites can overlap. Then, thermally activated hopping over these potential barriers can occur,[25-27] the activation energy of this process depending upon the height of the potentials and, therefore, upon the distance between the localized states.

Dc conductivity also gives more information about the mechanism of electrical transport of doped polymers. A transition temperature is observed at 257 K for PPhA and 273 K for PTA (Figure 7) and, therefore, DC conduction can be divided into two parts: a nonactivated region at low temperatures and a strong thermally activated region at higher temperatures—PMA might have a similar transition at a temperature lower than 250 K. The nonactivated process can be described by the variable-range hopping model since, at low temperatures, the energy of activation is low and the transport of the charge carriers results mainly from tunneling through the potentials. At the transition temperature, the energy becomes sufficient to allow hopping over the potentials and the thermally activated hopping mechanism may become dominant. To verify this possibility, log (σT^{-2}) was plotted vs. T^{-1} (Figure 8). This relation follows a straight line for the polymers investigated in agreement with the theory of thermally activated hopping near the Fermi level.[26] At low temperatures, it was impossible to discriminate between $T^{-0.25}$ or T^{-1} dependencies, because of the narrow temperature internal covered. However, the weak thermal activation observed is well explained by Mott's theory.[22]

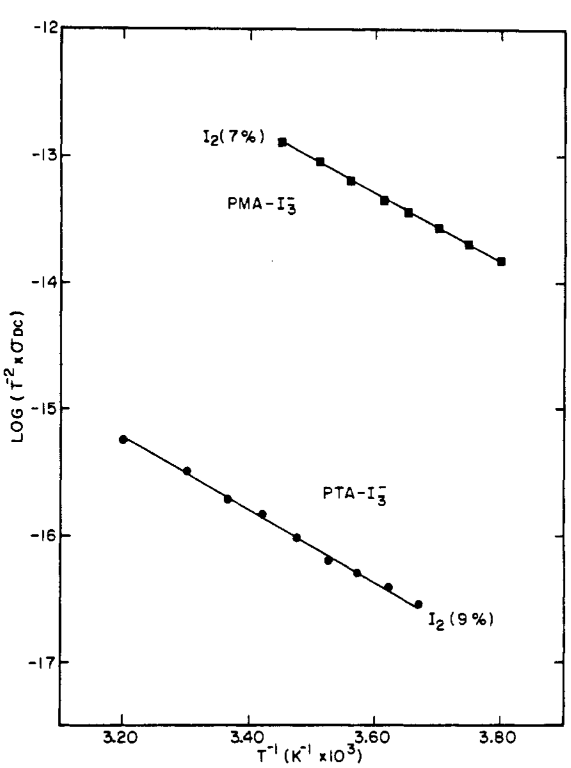

Figure 8. Variation of log ($T^{-2}\sigma$) as a function of T^{-1} of poly(methylacetylene) (PMA) and poly(*tert*-butylacetylene) (PTA), complexed with I_3^- and containing additional iodine. T is the temperature and σ the dc conductivity. Data taken above 273 K for PTA.

Hopping in band tails also leads to a strong thermal activation but, in addition, to similar energies of activation in the dc and ac transport. This behavior is not observed for the polymers investigated, the ac thermal activation being always smaller than the dc one. Bhatt[39] has also recently observed smaller energies of activation for the ac process of doped PPhA in disagreement with an earlier study.[17]

The strong temperature dependence of dc conductivity could also be described by the polaron hopping model. Using this model and experimentally observed activation energies, binding energies of 1–2 eV are calculated. These values are too large as compared to typical values of ~0.05–1.0 eV which are expected;[23] therefore, this model is ruled out.

Structural factors can influence electrical properties but, as shown in Figure 3, the cis and trans structures of PTA do not exhibit any significant difference in conductivity. This result is in agreement with many other studies which show the small influence of the intrachain transport on the bulk conductivity. For example, the conjugation along the polymer chain can be interrupted at about every seven repeat units by incorporating carbonyl[40] or sp$_3$ defects[41] without any major change in the electrical conductivity. Moreover, similar conductivity values are reached with poly(acetylenes) having molecular weights ranging from 400 to 870 000.[42] All these measurements, as well as those presented in this study, indicate the weak dependence of the conductivity upon intrachain transport.

Another important parameter to consider is the polymer conformation. Nonplanar N-substituted poly(pyrroles) exhibit, in the best cases, conductivities of about 5 orders of magnitude lower than those reported for unsubstituted poly(pyrrole) which has a planar chain conformation.[43] Similarly, polymers such as poly(*p*-phenylene)[44] and poly(*p*-phenylene sulfide)[45] show excellent dc conductivities because, as shown by recent calculations,[46] they can adopt a quasi-planar conformation in the doped state even if they exhibit a nonplanar conformation in the undoped state. Poly(acetylenes) behave in a similar manner. As shown in this article, substituted poly(acetylenes) exhibit a decrease in dc and ac conductivities of several orders of magnitude as compared to unsubstituted poly(acetylene). The larger the substituent on the polymer chain, the smaller the conductivity value reached because the chain conformation is less planar.[20] As mentioned above, the intrachain transport is not the dominant factor in terms of conductivity and we believe that the principal influence of the polymer conformation is to cause a reduction of the interchain interactions. Nonplanar conformations and bulky substituents lead to poor interchain contacts by keeping the chains away from one another, thereby reducing the probability of charge carrier hopping.

A high degree of crystallinity is not a prerequisite for obtaining highly conductive polymers, as reported with amorphous poly(*p*-phenylene sulfide)[45] and poly(1,6-heptadiyne)[15] but good interchain interactions are crucial.[47] A high degree of crystallinity might favor those.

The effect of adsorbed iodine is also important since it increases the conductivity without creating any additional charges. For example, the dc conductivity of PTA increases from 10^{-15} to 10^{-8} Ω^{-1} cm^{-1}, at 273 K, with the addition of free iodine. We believe that the additional iodine molecules decrease the pinning potential of the charge carriers by forming large delocalized anions. The formation of these large anions (polyiodide species[48] increases the mobility of the charge carriers since the latter can hop between localized states and stay under the electric field of the counterion.

Conclusions

In conclusion, studies of the electrical transport of undoped poly(acetylene) derivatives have shown an electronic mechanism which exhibits a weak thermal dependence. This behavior can be explained by the variable-range hopping theory. At low doping levels (<10 mol %), substituted poly(acetylenes) show a large thermal activation; a transition temperature for dc conduction is also observed at 257 K for PPhA and 273 K for PTA. The conduction mechanism of these polymers is electronic and Mott's theory can be applied to the nonactivated process.

For thermally activated regions, Poole's and Pike's models describe better the observed properties. At high doping levels, the conductivity increases to 10^{-5}–10^{-3} Ω^{-1} cm^{-1} and the conduction mechanism is ionic since the current decreases with time to reach a stable value of 10^{-8} Ω^{-1} cm^{-1} for PTA, 10^{-6} Ω^{-1} cm^{-1}, for PPhA and 10^{-4} Ω^{-1} cm^{-1} for PMA. The geometric structure of these polymers does not influence their electrical properties but their nonplanar conformation and the bulkiness of the substituents reduce significantly the conductivity by decreasing interchain interactions, hence interchain conductivity.

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Registry No. *cis*-PTA, 109244-73-7; *trans*-PTA, 109244-72-6; PPhA, 25038-69-1; PMA, 28391-48-2.

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