

Polyacetylene

Kinetics of isomerization and doping of poly(t-butyl-acetylene)

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SUMMARY

The kinetics of doping with I_2 and isomerization of poly(t-butylacetylene) has been studied. A first-order reaction in polymer and iodine was observed during the doping process, as was found for unsubstituted polyacetylene. However, for the isomerization process, a reaction order of 0.5 in iodine and no simple order in poly(t-butylacetylene) were determined. These results can be explained using a free radical mechanism where the free radicals catalyze the isomerization. In contrast to unsubstituted polyacetylene, the isomerization and doping processes are not related; isomerization occurs first, within about 30 min, and it is followed by doping at much later times.

INTRODUCTION

Polyacetylene can be reacted with oxidizing or reducing agents ("doping") to give a conductive material (1). This reaction is accompanied by a cis-to-trans isomerization (2-6). Kinetic studies of oxygen doped polyacetylene have shown that doping is a first-order reaction with an energy of activation of 11.52 kcal/mol (7); the isomerization induced by doping is also first-order for both the oxygen and polymer with an energy of activation of 14.9 kcal/mole (8). Chien and Yang (9) have shown that the isomerization process can be divided into two steps: the doping reaction which occurs first is immediately followed by a cis-to-trans rearrangement.

Substituted polyacetylenes are soluble in common organic solvents and, in some cases, are stable in air (10); they can be used as models of polyacetylene which is insoluble, infusible and unstable in air. For some of these polymers, Simionescu et al. (11) have reported that the addition of chlorine causes a cis-to-trans isomerization with an increase of the rate with the chlorine content. However, the relative rates of doping and isomerization were not mentioned.

Preliminary measurements carried out in this laboratory seem to indicate that the doping and isomerization processes of substituted polyacetylenes are not directly related, although both are induced by iodine. To elucidate this question, we report studies on the kinetics of iodine doping and isomerization of poly(t-butylacetylene) followed by nuclear magnetic resonance (NMR) and ultra-violet (UV) spectroscopies in solution.

EXPERIMENTAL SECTION

The polymers used have been synthesized by metathesis polymerization using a carbene catalyst (12). Iodine doping has been carried out using CCl_4 or decalin solutions in a NMR tube under an argon atmosphere. The temperature of the reacting mixture was controlled with a precision of 0.1 °C. Cis isomer contents were determined by the NMR method described

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elsewhere (13), using a Varian 60 MHz (model EM-360A) apparatus.

For the UV measurements, solution aliquots were removed at appropriate times and diluted in CCl_4 to a concentration of about 5×10^{-4} M. A Hewlett-Packard (model 8450A) UV spectrophotometer was employed and the absorption of the solvent was subtracted from that of the solution to obtain the polymer contribution.

RESULTS

Addition of iodine at room temperature to polyphenylacetylene (PPhA), polypentylacetylene (PPA) and polymethylacetylene (PMA) leads to a cis-to-trans isomerization; but for poly(*t*-butylacetylene) (PTA), the direction of this reaction depends upon the solvent used. In CCl_4 and at room temperature, cis-to-trans isomerization is observed as usual but in decalin trans-to-cis isomerization occurs. Thermal isomerization of PTA (in the absence of iodine) also leads to different isomerization directions depending upon the solvent used (13). This peculiar behavior has been explained by the small difference in energy calculated between the two isomers of PTA (14); for other polyacetylenes with less bulky substituents, this difference is much larger and it always favors the trans isomer.

The question arises whether isomerization and doping are related or independent for substituted polyacetylenes. In a previous work (15), we have shown that only 0.12% of the repeat units of PTA are doped with I_3^- whereas it is shown in this study that 50% of the repeat units can be isomerized in the presence of I_2 . These numbers give a ratio of about 400 isomerized units per doped unit. For unsubstituted polyacetylene, a ratio between 7 and 11 has been suggested (16) and we believe that this number should not be very different for substituted polyacetylenes. On the basis of these values, it is tempting to assume that isomerization and doping proceed with different mechanisms. In order to verify this assumption, we have carried out kinetic measurements with PTA doped with iodine.

Figure 1 shows the isomerization of PTA in CCl_4 at 25, 35 and 45 °C upon iodine addition. Like for thermal isomerization, no simple order can be found for this reaction. The thermal isomerization of PTA has an energy of activation of 21 kcal/mole and is observed only above 60 °C (13). With iodine, isomerization occurs at much lower temperatures. Therefore, it appears that iodine catalyzes the isomerization which then shows an energy of activation of 11 kcal/mole. (This value was calculated using the data of Figure 1 and the Arrhenius equation).

In Figure 2, the isomerization of PTA is reported using CCl_4 at 25 °C at different iodine concentrations. From these results, using the initial rates of isomerization, a reaction order of 0.5 was calculated for iodine.

On the other hand, the kinetics of doping of PTA can be studied using UV measurements. We have already shown that iodine is found in the form of I_3^- in these complexes (15). This species absorbs at 290 and 365 nm (17) and, fortunately, PTA does not absorb above 340 nm. Therefore, the increase of the absorption peak at 365 nm can be directly related to the I_3^- concentration and to the doping.

Using this method and taking a maximum doping concentration of 0.12 mole %, the kinetics of doping of PTA was followed in CCl_4 as a function of time at different temperatures (Figure 3) and at different iodine concentrations (Figure 4). It is seen that the doping reaction is first-order for both polymer and iodine, with an energy of activation of 26 kcal/mole.

DISCUSSION

Table I compares the parameters calculated from the kinetic analysis of doping and isomerization of PTA. In view of the time scales of the two processes, it appears that these reactions are independent since the iso-

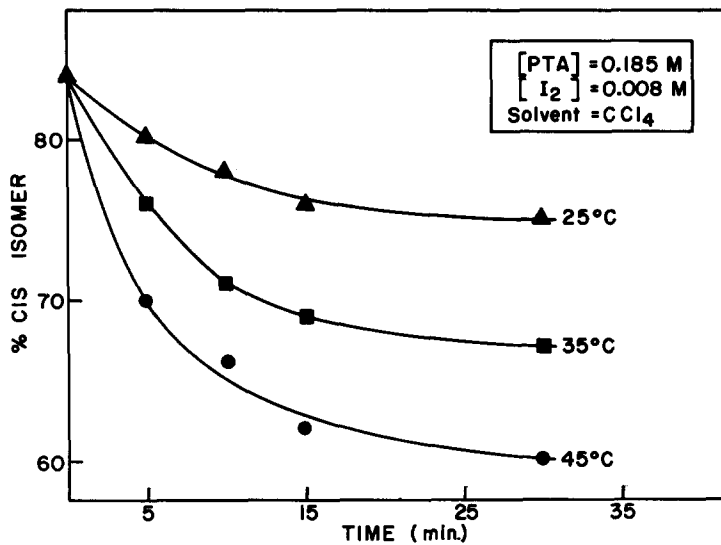


Figure 1: Rate of cis-trans isomerization of PTA in a 0.008 M iodine solution at 25, 35 and 45 °C.

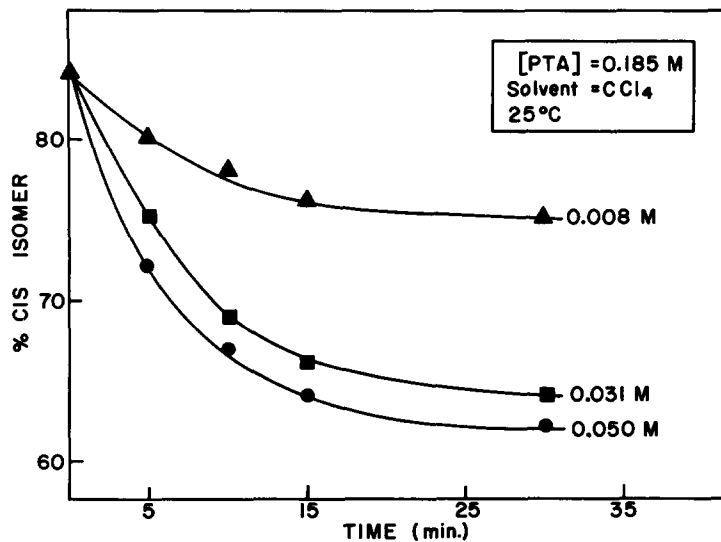


Figure 2: Rate of cis-trans isomerization of PTA at 25 °C in iodine solutions.

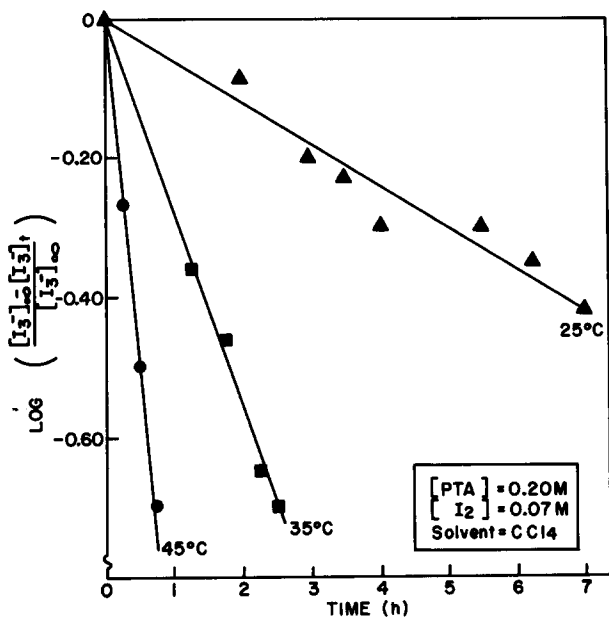


Figure 3: First order kinetic plot for doping of PTA in a 0.07M iodine solution at 25, 35 and 45 °C.

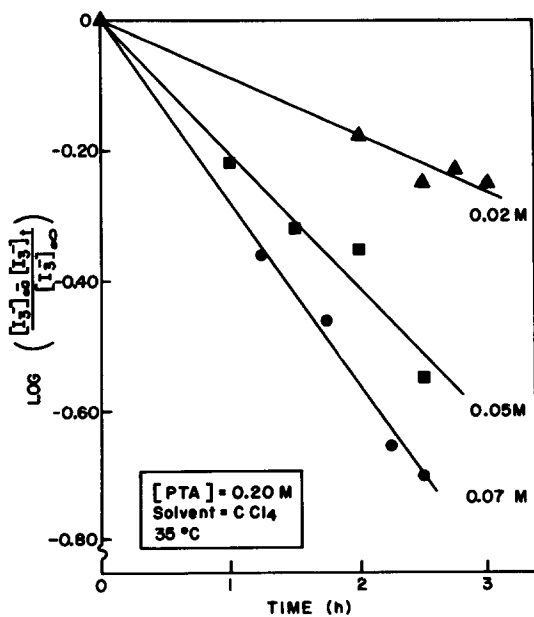


Figure 4: First order kinetic plot for doping of PTA at 35 °C in iodine solutions.

Table 1: Kinetic results of doping and isomerization of poly(*t*-butylacetylene).

	Isomerization	Doping
Reaction order in polymer	no simple order	1.0
Reaction order in iodine	0.5	1.0
Energy of activation (kcal/mole)	11	26
Time scale	30 min	7 h

merization is completed in about 30 minutes whereas the doping extends over a period of several hours. We must then search for a mechanism of isomerization in which doping is not included.

It is known that halogens catalyze the isomerization of double bonds by a free radical mechanism (18,19). This reaction is photosensitive owing to the presence of free radicals and it leads to a reaction order of 0.5 owing to the dismutation of iodine. In agreement with this mechanism, we have observed that the rate of isomerization of PTA in the presence of iodine decreases in the dark and the reaction order is 0.5. The addition of free radicals breaks up the double bonds and induces isomerization since these additions are reversible and the double bonds can be restored with the same or different geometries.

For the doping process, iodine and polymer obey first order kinetics as for polyacetylene, but with a higher energy of activation (8). For unsubstituted polyacetylene, doping occurs rapidly since its energy of activation is smaller than that of isomerization; thus doping occurs first and is followed immediately by a *cis*-to-*trans* rearrangement (9). Under these conditions, the same reaction order is observed for both processes (7,9). In contrast, PTA shows a completely different behavior which can be attributed to its bulky substituent and to its high energy of oxidation. In PTA, doping has a larger energy of activation than isomerization and the latter occurs first via a free radical mechanism. Under these conditions, different reaction orders are found for isomerization and doping.

For other substituted polyacetylenes i.e., with methyl, pentyl and phenyl substituents, it was impossible to follow the kinetics of doping with the method described in this article since these polymers absorb in the same UV region as I_3^- and since their absorption is a function of doping. In addition, these polymers are not available with a high *cis* content, contrary to PTA, and the study of their isomerization kinetics is not possible. It is then difficult to derive experimentally a mechanism of doping and isomerization for the substituted polyacetylenes, except of course for PTA. However, doping rates and free radical isomerization mechanisms similar to those found with PTA are also expected for polyacetylenes with bulky substituents; by decreasing the volume of the substituent, the doping rate should increase and isomerization induced by doping should become the dominant mechanism.

CONCLUSIONS

The isomerization and doping of PTA, which is used as a model for

polyacetylene, have been followed independently as a function of time. It has been shown that these two processes are independent since they exhibit different reaction orders for the polymer and for iodine, different activation energies, and different time scales. Isomerization occurs first, within about 30 min, and it is followed by doping at much later times.

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