Crystallizable Polyphenylacetylene-Preparation and Solution Properties

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ABSTRACT

The molecular weight distribution (MWD) of crystallizable polyphenylacetylene prepared near room temperature in the presence of ferric acetylacetonate and triethylaluminum was determined through use of fractions characterized by vapor pressure osmometry and gel permeation chromatography (GPC). The number- and weight-average molecular weights ($\overline{M}_n$ and $\overline{M}_w$) are both less than the molecular weight corresponding to the maximum of the weight distribution function, which lacks a high molecular weight tail. $\overline{M}_w/\overline{M}_n$ is less than is consistent with models allowing for chain termination characteristic of vinyl polymers. GPC elution volumes are much less than those characteristic of polystyrene of similar molecular weight, and the Mark-Houwink exponent is high (2.4 for $\overline{M}_v$ 4800 to 6800). These data indicate more rodlike behavior than for polystyrene of equivalent molecular weight. The MWD and other data suggest intramolecular chain termination, possibly associated with the molecule's tendency to form paramagnetic defect states.

INTRODUCTION

Phenylacetylene (PPA) is known to be polymerizable thermally and in the presence of several types of initiators. Kern has described differences in physical properties in polyphenylacetylenes obtained with different initiators, and it was shown that a crystallizable polymer of number-average molecular weight of about 5000 (PPA-C) was readily obtainable in the presence of transition metal acetyl-acetonates and triethylaluminum [1, 2]. This polymer provided initial samples for studies of electron spin resonance (ESR) [3] and dc conductivity [4]. In subsequent research, designed to relate electronic structure and electron transport in PPA to its chemical structure, it became necessary to study in greater detail and to scale-up the preparation of PPA in the presence of transition metal catalysts as carried out by Kern [1] and to determine its molecular weight distribution and other solution properties. This report deals in greater detail with the preparation of PPA-C, its molecular weight distribution, and some of its solution properties.

EXPERIMENTAL

Polymer Preparation and Work-Up

The exploratory experiments of Kern [1] had been performed in glass flasks with spin bars. To minimize nonreproducible effects resulting from gel formation and to facilitate bench-scale operation with more reliable agitation, a special reactor was built [5]. It was a 1000-ml, cylindrical SS-136 vessel, 3.5 in. i.d. × 7 in., flanged on top with a Viton O-ring seal. This reactor provided a means for high speed agitation with the help of a Magne-drive unit, for reliable evacuation, purging, and operation under superatmospheric nitrogen and for monitoring the course and rate of the reaction (which, in general, did not proceed isothermally) with a thermocouple.

Since the polymer-diluent (Tetralin) interaction was appreciable, the polymer formed as a gel-like mass, swollen by Tetralin, and motion of the agitator throughout the reaction did not preclude the possibility that the course of the reaction might have been affected by variable nonequilibrium conditions in the neighborhood of the growing site.

Under the conditions of these studies, the reaction ceased at moderately low conversion (< 50% of monomer convertible to methanol-insoluble polymer). Somewhat higher conversion could be obtained by a second injection of the catalyst mixture. Upon the start of the reaction and the second injection of catalyst, the contents

of the reactor warmed up to temperatures beyond ambient, and a rough monitoring of the course of reaction became possible. All polymerizations were carried out in the range of 25 to 35°C.

The reactor had been baked at 150°C prior to reaction, cooled under nitrogen, and evacuated and repurged with nitrogen repeatedly. Components of the reaction mixture were added under flowing nitrogen in the following order: ferric acetylacetonate [$Fe(OAcAc)_3$], followed by part of the diluent and triethylaluminum. The slurry was then agitated for 10 min. This was followed by addition of the monomer and the rest of the diluent. Typical reaction conditions were monomer, 50 ml (0.455 mole); Tetralin, 250 ml; Fe $(OAcAc)_3$, 2.5 mmole; $Al(C_2H_5)_3$, 6.25 mmole.

Phenylacetylene was obtained from Chemical Samples Co., Columbus, Ohio, at 99+% purity and redistilled under reduced pressure before use. Triethylaluminum was obtained at 25% solution in toluene from Texas Alkyls, Inc., Eastman practical grade Tetralin was re-distilled under reduced pressure and dried over Linde molecular sieves 4A, packed into a 1-in. i.d., 4-ft long column prior to use.

The swollen polymer recovered from the reactor was allowed to stand and shrink in methanol for at least 1 day, treated with 1.0 N HCl in methanol, and shredded for 1 to 3 min in a Waring blender. The polymer was filtered and washing was continued in the HCl methanol mixture until no color due to iron could be detected upon testing with a KCNS solution in methanol. The polymer was then washed with water, then methanol, and dried in a vacuum oven near 50°C. The color of this polymer is orange to dark red.

Fractionation and Preparation of Room Temperature Soluble Polymer [6, 7]

The polymer, purified as described, is insoluble at room temperature. It was dissolved in o-dichlorobenzene at 145°C under nitrogen to give an approximately 3% solution. This solution, which contained 2.0 g PPA, was added to a slurry containing 42 g of Fisher Celite No. 545 in 200 cc methanol. The PPA-coated celite was removed by filtration and packed on top of 100 g uncoated Celite into a jacketed column 1-1/4 in. i.d. × 34 in. in length. The polymer was eluted with 15 toluene (solvent)-methanol (nonsolvent) mixtures, each approximately 250 cc in volume.

The same procedure of dissolution of the native polymer in o-dichlorobenzene at 145°C under nitrogen and precipitation in methanol was followed to obtain samples of whole polymer for study of solution properties at or near room temperature. The color of this polymer is yellow, it displays no readily detectable crystallinity, and it dissolves in benzene at room temperature. The solutions are stable over long periods of time.

Gel Permeation Chromatography

Measurements were performed on a Waters GPC Model 200. The sample column set consisted of four 4-ft columns with maximum pore sizes of 10^3, 10^3, 10^4, and 10^6 Å, the reference set of two 4-ft columns with maximum pore sizes of 100 and 500 Å. The eluting solvent was Fisher Scientific grade toluene. The solvent flow rate was 1 ml/min, the polymer concentration 0.5 wt%, and the injection time 2 min.

Vapor Phase Osmometry

Number-average molecular weights were measured on a Hitachi-Perkin-Elmer Model 115 vapor pressure osmometer in benzene with the main and suboven assemblies set at 42.5 and 38°C, respectively. Benzil was used as molecular weight standard.

Intrinsic Viscosity

The intrinsic viscosity was measured in a specially designed dilution viscometer, operable under nitrogen, using benzene as solvent at 35°C.

RESULTS

Yields, Purity, and Characteristics of Molecular Weight Distribution

Maximum yields are obtained at molar ratios of Al/Fe in the range of 2 to 4. Typical yields of polymer, insoluble in excess methanol, were in the range of 40 to 50% where the technique of catalyst reinjection was not employed. A typical GPC chromatogram is shown in Fig. 1. The peaks near counts of 39 and 41 are attributable to cyclic trimer, with possible traces of $Fe(OAcAc)_3$ and to o-dichlorobenzene, respectively, the peak between 25 and 35 to polymer. The peak near 39 and the shoulder at about 37 to 30 can be removed upon washing with a 50/50 THF/methanol solution. The shape in the region of the shoulder (low end of the molecular weight range) is also sensitive to details of the preparative procedure.

The sharp drop in the chromatogram in the region of 27.5 to 25 is remarkable, testifying to a highly asymmetric molecular weight distribution (MWD) and virtual absence of the usual high molecular weight tail. The latter feature was also apparent in earlier work performed with columns of maximum pore size 10^4 Å. A column of
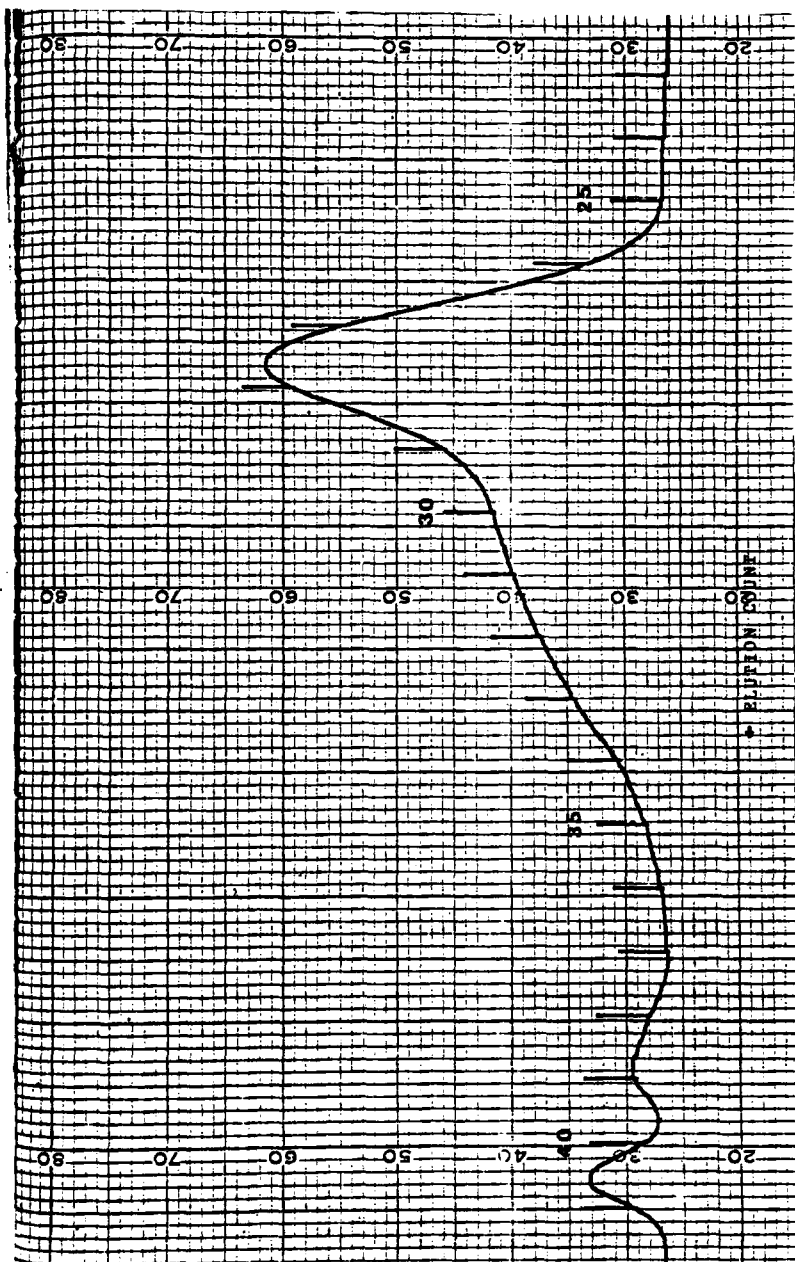
FIG. 1. Typical GPC chromatogram of PPA-C.

larger pore size (10^6 Å) was substituted in the present work to make certain that the apparent sharp cut-off in the MWD at the high end was not an artefact caused by poor resolving power of the columns.

Attempts were made to reduce the levels of iron, derived from the catalyst, to as low levels as possible. Analysis by x-ray fluorescence indicated iron contents of about 0.3 wt% in the crystalline polymer which had been washed exhaustively in acid and methanol. Dissolution of the polymer in o-dichlorobenzene and reprecipitation in methanol lowered the iron content to 0.08 wt%. Although the possibility that some $Fe(OAcAc)_3$ remained occluded in the polymer cannot be ruled out, the presence of residual iron after exhaustive washing suggests that it was chemically bound. Chemically-bound iron (0.08%) corresponds to 6% of the polymer chains at a number-average molecular weight ($\overline{M}_n$) of 4000.

Attempts to measure the aluminum content of the polymer by x-ray fluorescence failed due to low and irreproducible counts.

Numerical Determination of the Molecular Weight Distribution

Molecular weight averages and the MWD were calculated from the GPC chromatograms through use of fractions of known molecular weight determined by vapor pressure osmometry (VPO).

Using the fractionation procedure described, 15 fractions were obtained. Very little fractionation (and extraction) occurred at solvent (toluene) concentrations of less than 50%, and most of the polymer was concentrated in the last fraction (No. 15), extracted with 100% toluene. Fractions 7 to 15 showed a sufficient spread in molecular weights to allow their use in calibrating the GPC data. The quality of the fractions differed; the average value of $\overline{M}_w/\overline{M}_n$ was 1.21.

Figure 2 is a plot of the VPO data obtained for one of the fractions (No. 14). The slope of the plot is zero within experimental error. Figure 3 is a plot of $\overline{M}_n$ vs the position of the peak on the GPC chromatogram for Fractions 7 to 15. The considerable scatter and the limited range in molecular weights justify representation of the data by a straight line. In any case, the data points cannot be said to be convex to the abscissa over the entire range in molecular weight and do not call for the usual representation of log M vs elution count. If $\overline{M}_n$ for Fractions 7-15 is now calculated from their GPC chromatograms, assuming that the points in Fig. 3 represent perfect fractions, the calculated values fall below those measured experimentally on the VPO. This is to be expected, since the GPC peak count represents more nearly a weight-average than a number-average molecular weight
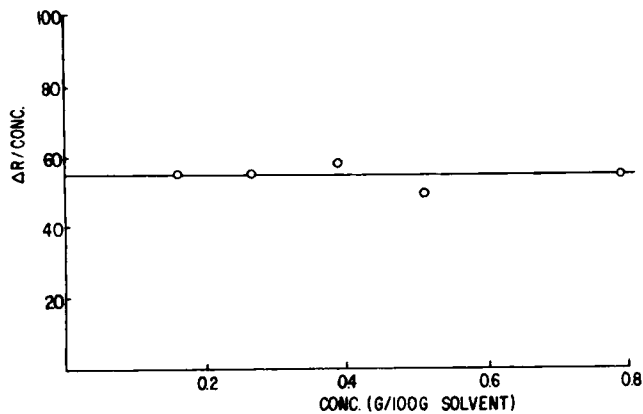
FIG. 2. VPO data for Fraction 14. ΔR is given in scale units, proportional to the osmotic pressure.
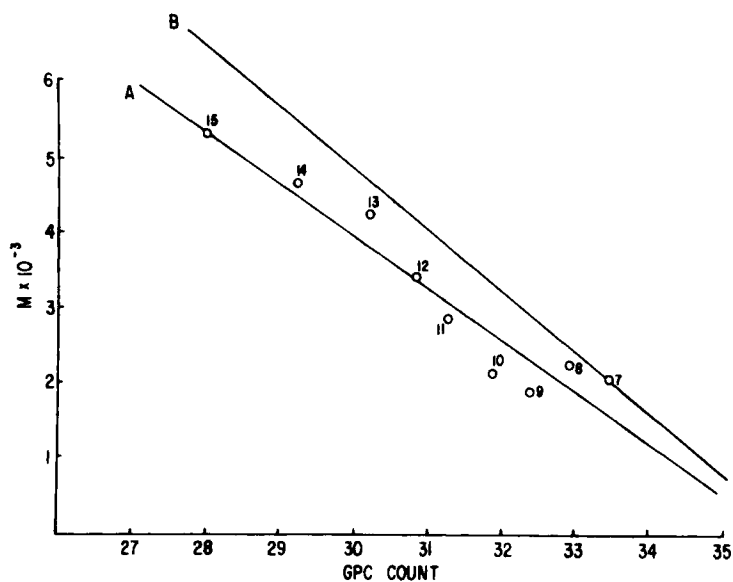

FIG. 3. Molecular weight vs elution count for fractions. Ordinate represents $\overline{M}_n$ measured on VPO (A); M of perfect fractions after correction for polydispersity (B).

for samples other than perfect fractions. Assuming an identical MWD
for all fractions, and that the peak count represents $\overline{M}_w$, the correct
calibration plot would be obtained from Fig. 3 by multiplying the
values of all ordinates by the value of $\overline{M}_w/\overline{M}_n$. The average value of
$\overline{M}_w/\overline{M}_n$ of the fractions is 1.21, and the suggested calibration plot—
Line B in Fig. 3—is obtained in that manner. This procedure is
considered adequate, since the scatter in individual points does not
seem to justify a point by point recalibration or any more sophisticated
optimization procedure. The new calibration plot may be expressed
numerically in the form

$$M = 29,400 - 822 \, c \tag{1}$$

where M is the molecular weight and c the GPC count.
   The MWD for the sample fractionated and calculated by means of
Eq. (1), using the standard methods of summing sections of the
chromatogram, is shown in Fig. 4, expressed as normalized weight
distribution, $w(M)$. The unusual features of the MWD, referred to
earlier, can be seen quantitatively here. Note that both $\overline{M}_n$ (4070)
and $\overline{M}_w$ (4980) are less than the most probable value of M (6000) and
that no measurable amounts of polymer of M > 8000 are present.
$\overline{M}_w/\overline{M}_n$ is therefore only 1.22, a typical value for polymer batches in
which catalyst was not reinjected during polymerization. The
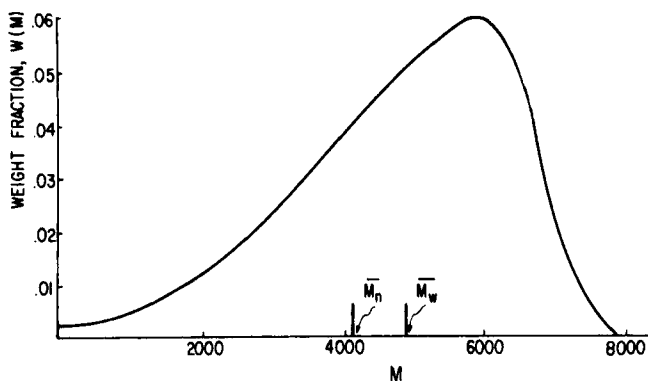magnitude of $\overline{M}_w/\overline{M}_n$ provides, of course, an insufficient description

FIG. 4. Normalized weight distribution $w(M)$ of sample
fractionated.

of the MWD which is highly asymmetric and whose most interesting characteristic is the absence of a high molecular weight tail. No polymerization mechanism can be considered adequate which fails to account for that characteristic.

Degradation

In order to investigate the possibility of polymer degradation during dissolution of the native polymer at the elevated temperature, samples were kept for periods greater than the time required for dissolution at temperatures up to 160°C in the absence of inhibitor, and also in the presence of 2-6 DTB-4 methylphenyl or Antioxidant 330. GPC chromatograms showed no detectable change from that of the reference sample which had been given minimum exposure to high temperature, provided the tests were performed under nitrogen. In the presence of oxygen or air, however, progressive degradation took place both in the presence and in the absence of these inhibitors. All molecular weight averages were reduced and, most significantly, the MWD became more symmetrical and the drop in w(M) at the high end became much less abrupt. Therefore, there is no evidence of polymer degradation during the preparation of room temperature soluble polymer. Although the possibility of some degradation cannot be eliminated, the narrow and asymmetric MWD cannot result from such a degradation step; on the contrary, these features might be even more pronounced in a truly "native" sample.

Intrinsic Viscosities

Having established means of determining the MWD, it became possible to determine the molecular weight dependence of the intrinsic viscosity, $[\eta]$. This relation was to be determined in the form of the Mark-Houwink equation

$$[\eta] = K\overline{M}_v{}^a \tag{2}$$

where K and a are constants and the viscosity-average molecular weight is defined by

$$\overline{M}_v = [\sum_i w_i M_i{}^a]^{1/a} \tag{3}$$

where w_i is the weight fraction of species i. Since the correct value of a found from Eq. (2) requires use of the correct values of $\overline{M}_v$,

TABLE 1. Samples Used for Intrinsic Viscosity Measurements

	$\overline{M}_w$	$\overline{M}_v$	$[\eta]$ (dl/g)
Fraction 1	4670	4800	0.078
Fraction 2	5220	5490	0.126
Fraction 3	6320	6410	0.177
Fraction 4	6570	6610	0.177
Whole polymer (THF extracted)	6160	6820	0.140

which are themselves functions of a, that constant and K had to be calculated by an iteration procedure.

Four fractions and a sample of whole polymer, extracted with THF, were used to determine the constants in Eq. (2). These samples are described in Table 1, and the corresponding Mark-Houwink plot is shown in Fig. 5. The constants satisfying Eq. (2) are K = 1.03 × 10^{-10} and a = 2.42.

The value of a seems high in terms of some simple hydrodynamic models which might be expected to have some applicability. We do not expect the molecule to show random coil behavior, both because of its relatively low molecular weight and because the GPC data indicate an asymmetric, relatively rigid structure.
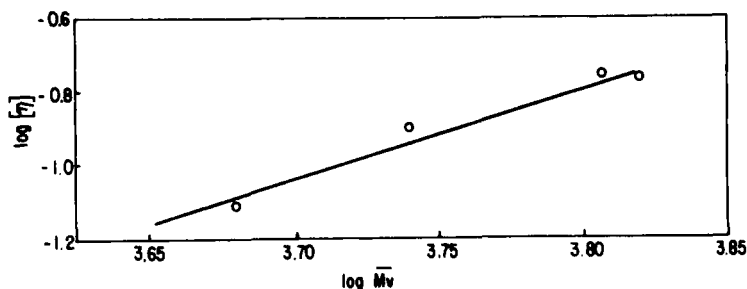

FIG. 5. Mark-Houwink plot of intrinsic viscosity vs viscosity average molecular weight of fractions.
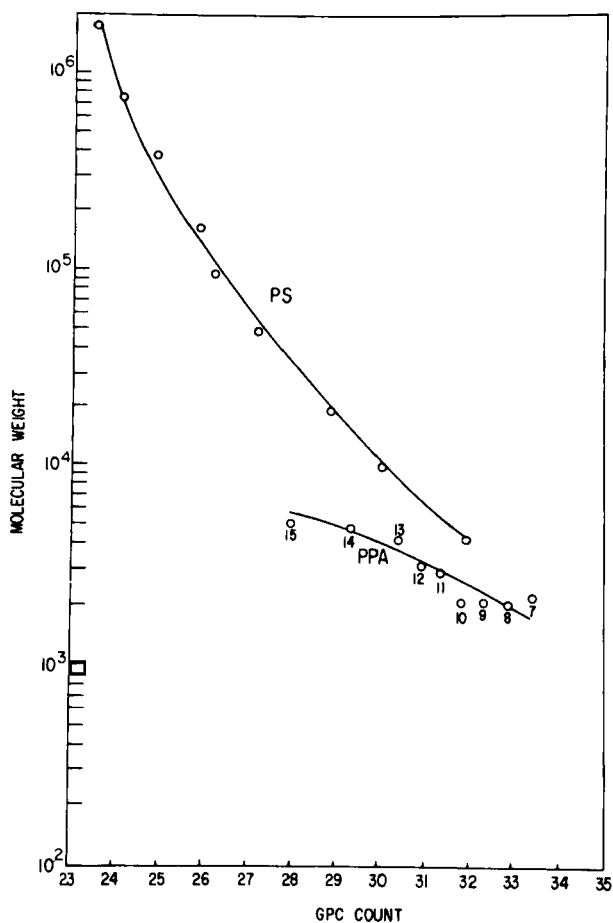
FIG. 6. Comparison of GPC behavior (log M vs elution count) of PPA fractions and polystyrene fractions.

Figure 6 contrasts the GPC behavior of PPA with that of polystyrene fractions. The behavior of the two polymers is grossly different and testifies to the high molecular asymmetry of the PPA molecule. But even Simha's model for rigid prolate ellipsoids leads, in the limit of large size, to a value of a of only 2.0 [8]. The molecule must, however, possess some flexibility which could express itself readily in values of a greater than 2.0. The molecular weight range of these measurements is, on the other hand, quite limited, and a cannot be evaluated with high precision.

DISCUSSION

It has been shown that the MWD of PPA-C is narrow and lacks a high molecular weight tail. To a lesser extent this is also true for the thermally polymerized PPA-T [9, 10]. It seems, therefore, that the polymerization kinetics of PPA-C, at any rate, are affected by some nonstochastic factor, probably thermodynamic origin, and possibly associated with the molecule's tendency to form paramagnetic "defect" states, both in the solid and in solution [3, 4]. It is unlikely that molecular orbital theories which attribute the limited size of linear conjugated polymers to increasing delocalization of the propagating center with increasing molecular size [11] can do adequate justice to the reaction mechanism, since this effect would only be operative with oligomers. In any case, such theories leave unanswered the question as to the nature of the termination step. In the lower molecular weight free radical polymer, initiated with azobisisobutyronitrile, the polymerization rate is close to first order in initiator [12], and mass spectrometry of the oligomers obtained in PPA-T indicates molecular weights of 204, 306, 408, 510, and 612; that is, hydrogen contents corresponding to a dicarbene structure [10]. All these data are consistent with the hypothesis that chain termination involves an intramolecular electronic rearrangement, in some cases unaccompanied by hydrogen transfer. Such an intramolecular electronic rearrangement might be common to all growing PPA chains, regardless of whether the propagating species is an ion, a radical, or a radical ion.

ACKNOWLEDGMENT

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Note Added in Proof. Woon and Farona have shown recently [J. Polym. Sci., Polym. Chem. Ed., 12, 1749 (1974)] that the polymerization of phenylacetylene catalyzed by arene-Group VIB tricarbonyls proceeds through ladder intermediates consisting of fused cyclobutane rings. The presence of such structures as intermediates in our PPA-C or as significant components of PPA-T cannot be ruled out; in the latter case, in fact, it receives some support from the mass spectrometry data referred to.