Macromol. Symp. ***127****, 77–87 (1998)*

INVESTIGATIONS ON HOMOPOLYMERIZATION AND COPOLYMERIZATION OF PHENYLACETYLENE AND 1-HEXYNE BY IRON-BASED ZIEGLER-NATTA CATALYST SYSTEMS

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Abstract : Homopolymerization and copolymerization of phenylacetylene (PA) and hex-1-yne (HX) were performed in the presence of two iron-based catalysts having various ligands : an organic salt, iron tripropionate [Fe(prop)$_3$] and a complex, iron triacetylacetonate [Fe(acac)$_3$], both in combination with the triethylaluminum (AlEt$_3$). The geometric structures of the resulting monosubstituted polyacetylene samples were investigated by ^{1}H-NMR, ^{13}C-NMR and IR spectroscopic techniques. The number-average molecular weights were also determined. The compositions of the PA-HX copolymers were obtained by ^{1}H-NMR analysis and the monomer reactivity ratios were calculated from these values using the Kelen-Tüdös method and a non-linear least squares curve-fitting procedure. The proportions of *cis* and *trans* structural units in polyalkynes and the relative reactivities of two monomers PA and HX during the copolymerization were found to be strongly associated with the nature of the initiating system.

INTRODUCTION

The polymerization of acetylenic monomers (alkynes) has been widely investigated since Natta *et al.* (Ref.1) have synthesized stereoregular polyacetylenes with the soluble catalyst formed from titanium (IV) *n*-butoxide and triethylaluminum. In the three last decades, many studies were achieved about various kinds of monosubstituted (terminal) or disubstituted (inner) acetylenes by using a great variety of promotor systems in search of new polymeric materials showing noteworthy properties as electrical conductors or permeable membranes (Refs.2-4). Alkyne derivatives can be polymerized by radical and ionic initiators, but in most cases low molecular weight products accompanied with cyclotrimers were obtained. Ziegler-Natta complexes are known to afford high polymers only from uncrowned monomers such as linear 1-alkynes. On the contrary, the polymerization of bulky group-containing acetylenes or inner alkynes, performed in the presence of W- or Mo-based metathesis initiators, produces high

CCC 1022-1360/98/$ 10.00

molecular weight polyenes. On the other hand, study of literature reveals that a few papers relate the copolymerization of alkynes : most of investigations were concerned with the polymerization of phenylacetylene with alkynes using metathesis catalysts (Refs.5,6).

The purpose of this article is to report on results pertaining to the synthesis and characterization of homo- and copolymers obtained from monosubstituted acetylenic monomers, *i.e.*, phenylacetylene (PA) and 1-hexyne (HX), with two Fe-based Ziegler-Natta catalyst systems : a novel initiator, *i.e.*, iron tripropionate [$Fe(prop)_3$] and the conventional compound, *i.e.*, iron triacetylacetonate [$Fe(acac)_3$], both in combination with triethylaluminum ($AlEt_3$). First, the influence of the initiator nature on the geometric structure of the homopolyalkynes was investigated by means of ^{1}H-NMR, ^{13}C-NMR and IR spectroscopies. The effects on the average molecular weights were also compared. After which, the reactivity ratios for the copolymerization of PA and HX have been computed using the Kelen-Tüdös (KT) approach and, for comparison, a non-linear least squares curve-fitting (NLLS) method.

EXPERIMENTAL PART

Materials : Toluene and cyclohexane (spectroscopic grade), used as the (co)polymerization solvents, were refluxed over and distilled from CaH_2. Phenylacetylene (purity : 98 %) and 1-hexyne (purity : 99 %) were dried by distillation in argon atmosphere over CaH_2 and then subjected to vacuum distillation on cold condensing surface. $AlEt_3$ (purity : 96%) was used without further purification after dilution in anhydrous toluene or cyclohexane. $Fe(acac)_3$ (purity : 98%) were recrystallized from toluene. $Fe(prop)_3$ was synthesized from $FeCl_3$ and propionic acid according to the method reported previously about scandium trinaphtenate (Ref.7).

Procedures : Polymerization reactions were performed on the basis of procedures earlier described in the literature, *i.e.*, $Fe(acac)_3$-$AlEt_3$ (Refs.8-11) and $Fe(prop)_3$-$AlEt_3$ (Refs.7,12). The runs were carried out under inert atmosphere in jacketed Pyrex reactors equipped with a magnetic stirring bar. The Fe-compounds were introduced first and the required amounts of liquid reagents were added by syringe. The catalyst solution was aged at the desired temperature before the monomer or comonomer addition. Detailed experimental conditions including concentration data are summarized in Tabs. 1 and 2. The (co)polymerizations were stopped by adding a few cm^3 of CH_3OH containing HCl (*ca.* 5% wt/v). The reaction mixtures were washed several times with water, treated with saturated $NaHCO_3$ solution and finally poured in a large excess of CH_3OH. The crude products were purified by dissolving in $CHCl_3$ followed by filtration through a Sartorius 0.2 μm filter in order to eliminate any insoluble materials, *e.g.*, catalyst residues, microgel. After that they were reprecipitated in CH_3OH, and dried under vacuum at 50°C until constant weight. Copolymers were prepared to conversion lower than 10 wt-%.

Analysis : IR spectra were recorded with a FTIR Bruker model IFS 25 spectrophotometer on thin films obtained from solutions in $CHCl_3$ by deposition on KBr plates. The overlapped bands were separated using the OPUS computer program. NMR measurements were made, at room temperature, at 200 MHz for ^1H in CCl_4 (CF_3COOH-*d* served to provide the deuterium lock frequency) and at 50 MHz for ^{13}C in $CDCl_3$ on a Bruker AC 200 apparatus. ^1H-NMR spectra were recorded on 2.5% (wt/v) sample solutions using a 45° flip angle (pulse width 2 μs), a pulse delay of 2 s and a spectral width of 3000 Hz. ^{13}C-NMR spectra were proton decoupled and obtained on about 20 % (wt/v) solutions using a flip angle of 30° (pulse width of 4 μs) and a pulse repetition time of 12 s ; spectral width of 12500 Hz and 16 K data points. These conditions ensure the complete relaxation of all the ^{13}C nuclei analyzed. Chemical shifts (δ in ppm) are reported down field with respect to tetramethylsilane (TMS) and the resonance signal areas were evaluated by the integrated curve technique. The calculations regarding the area measurements under overlapped peaks were achieved by using a Lorentzian-shaped curve-fitting computer program. Number-average molecular weights ($\overline{M}_n$) were determined by size exclusion chromatography (SEC) in THF (flow rate : 1 mL.min^{-1}) at 25°C on a Waters high pressure instrument (Model 510 pump, linear ultra-styragel columns, Waters 410 RI detector) using polyisoprene and polystyrene calibrations.

RESULTS AND DISCUSSION

It should be pointed out that for each catalyst system, the experimental conditions were chosen after preliminary experiments which have shown that they give the best compromise in terms of yields and average molecular weights.

Homopolymer characterization

Representative ^1H- and ^{13}C-NMR spectra of poly(1-hexyne) (PHX) and polyphenylacetylene (PPA) prepared in the presence of $Fe(acac)_3$-$AlEt_3$ catalyst are shown in Fig.1. Spectra of homologous materials obtained with the $Fe(prop)_3$-$AlEt_3$ initiator are similar. On the one hand, we recognized the typical spectrum shapes of PPA previously described in great details by several authors (Refs.4,13), on the other hand, we observed the different resonance peaks, earlier reported in the case of PHX synthesized with various Ziegler-Natta initiating systems (Refs.7,9).

The analysis of these spectra well agrees with the chemical structure of polyalkynes, indicating that there is no loss of unsaturation due to side reactions such as cyclization and/or cross-linking during the polymerizations.

In order to evaluate the amounts of *trans*- and *cis*-structures in PHX and PPA, we have examined the ethylenic and aromatic resonance signals observed in the ^1H- and ^{13}C-NMR spectra. However, as shown in Figs.2 and 3, these spectra exhibit quite a complicated splitting, resulting from overlapping of the signals due to a variety of proton or carbon atoms in various types of sequences. Therefore, to investigate the geometric structure, the fractional peak areas were measured assuming a Lorentzian shape for each component.

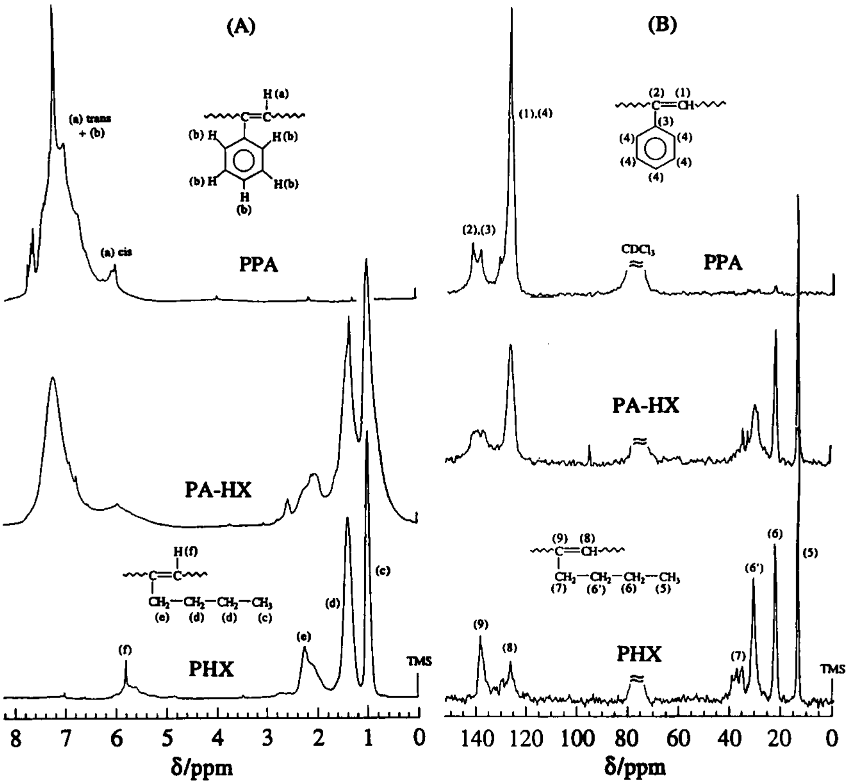

Fig. 1: 200 MHz ^{1}H-NMR spectra, in CCl_4, (A), and 50 MHz ^{13}C-NMR spectra, in $CDCl_3$, (B), of poly(1-hexyne) (PHX), polyphenylacetylene (PPA) and PA-HX copolymer (sample ZNA 2, see Tab.2) synthesized by the $Fe(acac)_3$-$AlEt_3$ catalyst system.

In the case of PHX, the proton resonance peaks (Fig.2, upper) located up to approximately 6 ppm are assigned, according to Leclerc *et al.* (Ref.14), to the HX-units in *trans*-configuration. On the other hand, the same authors have shown that the two signals observed at about 121 and 127 ppm (Fig.2, bottom) are imputable to the carbon atoms included in *cis*- and *trans*-structures, respectively. The data, thus obtained (Tab.1) from both NMR methods, are in very good agreement and reveal that the iron-based Ziegler-Natta catalysts give *trans*-rich poly(1-hexyne). For PPA (Fig. 3), we have decomposed the multiplets appearing between 5.5 and 8 ppm for ^{1}H-NMR and 120 and 150 ppm for ^{13}C-NMR. In the former case [Fig.3 (A), (B)], the *cis*-structure contents in the two PPA samples examined were evaluated by using the area of the *cis*-signal at about 5.8 ppm ($A_{5.8}$) and the total area of the spectum (A_t), according to the following Eq. (Ref.4) :

$$\%\ cis = 10^4 A_{5.8} / (16.66\, A_t) \qquad (1)$$

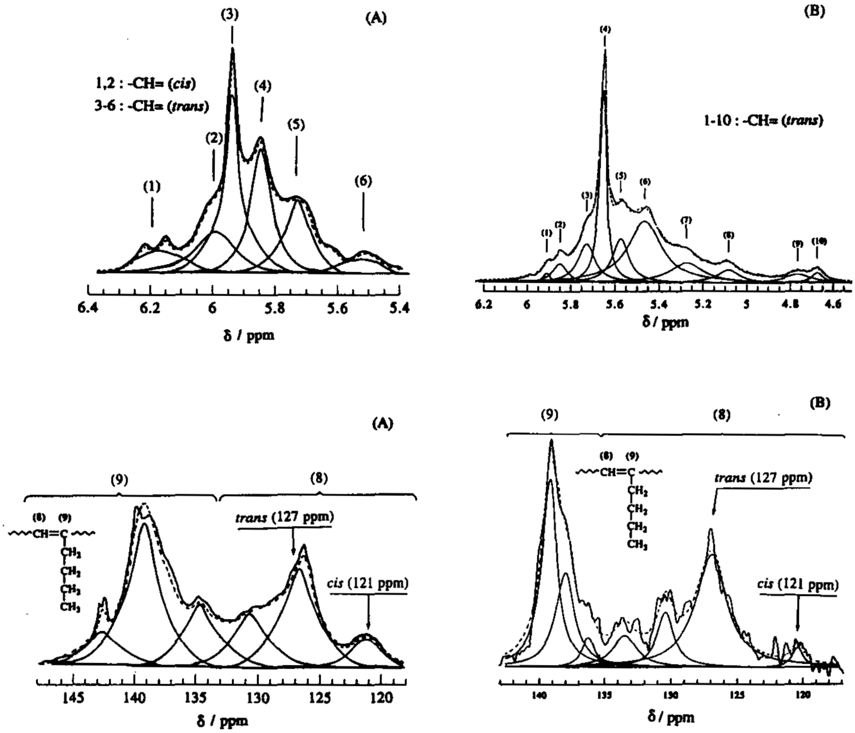

Fig. 2 : Decomposition in Lorentzian singlets of olefinic proton (upper) and carbon (bottom) resonances in poly(1-hexyne) (PHX) synthesized by the catalyst systems Fe(prop)$_3$-AlEt$_3$ (A) and Fe(acac)$_3$-AlEt$_3$ (B). Broken lines represent the spectra from curve fitting.

The results obtained from Eq.1 (Tab.1) indicate that, contrarily to PHX, the structure of PPA is strongly dependent upon the nature of iron compound. These values have been confirmed (Tab.1) by ^{13}C-NMR (Fig.3C) by comparing the *cis*-peak area (132 ppm) with that of *trans*-configuration (127 ppm). An additional study has been carried out by IR spectroscopy. A typical spectrum of PPA is shown in Fig.4 with an example of deconvolution of the absorption bands ranging from 730 to 780 cm^{-1}. Taking into account the value of 760/740 ratio between the respective absorbances of the band at 760 cm^{-1} assigned to the =C-H out-of-plane deformation from monosubstituted benzene ring and at 740 cm^{-1} corresponding to the out-of-plane vibration of the hydrogen atoms linked to the *cis* double bonds, the *cis*-content of PPA can be determined by the following Eq. (Ref.15) :

$$\%\ cis = 5.5\, A_{740} \,/\, 10^{-2}\, (5.5\, A_{740} + A_{760}) \tag{2}$$

The lowest limit of *cis*-content which can be determined from this Eq. is dependent on the presence of the 740 cm^{-1} band in the IR spectrum. It seems that *cis*-contents lower than 40% could not be evaluated in this way (Ref.4). This could explain the found difference between the values determined by IR and NMR analysis in the case of PPA-sample prepared by the Fe(acac)$_3$-AlEt$_3$ catalyst (Tab.1).

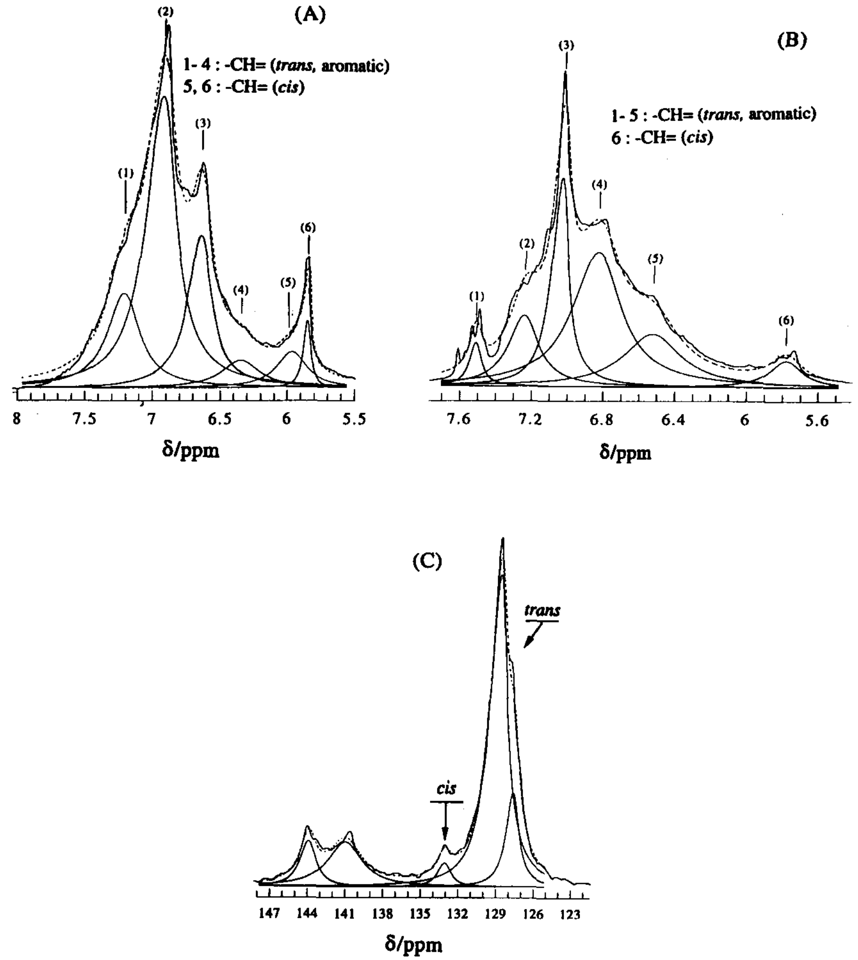

Fig. 3 : Decomposition in Lorentzian singlets of olefinic and aromatic proton [(A), (B)] and carbon (C) resonances in polyphenylacetylene (PPA) synthesized by the catalyst systems Fe(prop)$_3$-AlEt$_3$ (A) and Fe(acac)$_3$-AlEt$_3$ [(B), (C)]. Broken lines represent the spectra from curve fitting.

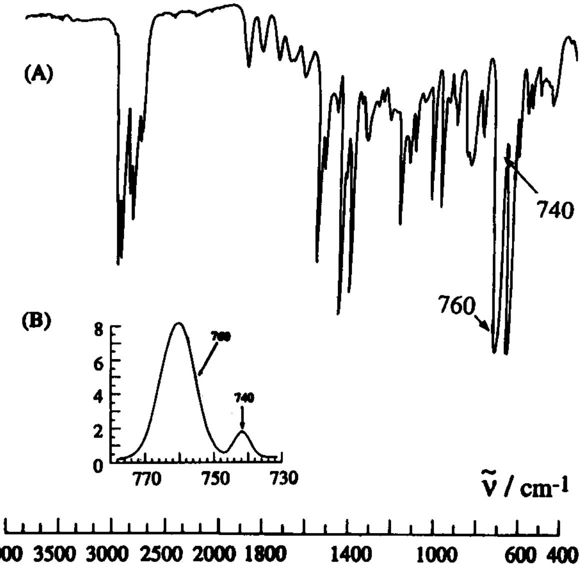

Fig. 4 : (A) : IR spectrum of polyphenylacetylene prepared by the Fe(acac)$_3$-AlEt$_3$ catalyst system. (B) : decomposition of the overlapping bands located at 740 cm^{-1} (=C-H *cis*) and 760 cm^{-1} (=C-H aromatic).

According to the literature data (Ref.4), the results pertaining to PPA-microstructure could be explained by a temperature effect. Indeed, it has been shown that an increasing of the temperature of the mixture provided a *cis* —> *trans* isomerization. In this work, the reaction temperature in the case of Fe(acac)$_3$ catalyst is higher than in the presence of Fe(prop)$_3$, *i.e.*, 50°C and 25°C, respectively. Nevertheless, the used solvents being also different, could play a role on the configuration of the resulting polymers.

Tab.1 : Geometric structures and number-average molecular weights of poly(1-hexyne) (PHX) and polyphenylacetylene (PPA) prepared by Fe-based Ziegler-Natta catalysts

	PHX			PPA			
	trans (%)		$\overline{M}_n$	*cis* (%)			$\overline{M}_n$
Catalyst system	^{1}H-NMR	^{13}C-NMR	g.mol^{-1}	IR	^{1}H-NMR	^{13}C-NMR	g.mol^{-1}
Fe(prop)$_3$-AlEt$_3$^{a}	85	83	61000	86	87	100	44000
Fe(acac)$_3$-AlEt$_3$^{b}	100	95	3400	39	31	27	1250

[a] Solvent = cyclohexane ; [HX] = 1 mol.L^{-1} ; [PA] = 2 mol.L^{-1} ; [Fe] = 1.15 mmol.L^{-1} ; [Al] / [Fe] = 2 ; Ageing time and temperature = 1 h at 50°C ; Polymerization temperature = 25°C.

[b] Solvent = toluene ; [HX] or [PA] = 2 mol.L^{-1} ; [Fe] = 35 mmol.L^{-1} ; [Al] / [Fe] = 3 ; Ageing time and temperature = 30 min at 50°C ; Polymerization temperature = 50°C.

In Tab.1 are also given the values of $\overline{M}_n$ for the various polyalkyne samples synthesized. The data obtained with $Fe(acac)_3$ are comparable to those previously reported (Refs.9,11). It is interesting to note that the iron salt appears to be much more effective than the iron complex. Until now, these experimental findings have not been explained and further studies are in progress.

Copolymer compositions

A typical ^1H-NMR spectrum of PA-HX copolymer (sample ZNA 2 in Tab.2) synthesized by $Fe(acac)_3$-$AlEt_3$ is presented in Fig.1. The comparison between homopolymers (PHX and PPA) and copolymer spectra reveals no new resonance peak. On the basis of assignments quoted in Fig.1, the composition of all copolymer samples has been calculated by comparing the total area (H_p) of the aliphatic proton resonances (0.5 - 2.5 ppm) with those (H_a + H_e) of the signal area due to olefinic and aromatic hydrogen atoms, appearing in the range 4.5 - 8 ppm. By assuming, like in the homopolymers, that there is no loss of unsaturation in the studied copolyalkynes, their compositions in terms of molar fractions of PA- and HX-units, denoted $P_1(PA)$ and $P_1(HX)$ according to the notations of Ito and Yamashita (Ref.16), may be evaluated by using the following expressions :

$$P_1(PA) = (9 - \rho) / (9 + 5\rho) \tag{3}$$

$$P_1(HX) = 1 - P_1(PA) \tag{4}$$

where $\rho = H_p / (H_a + H_e)$ (5)

In Tab.2 are summarized the data thus obtained for the two sets of PA-HX copolymers synthesized in this work.

Tab.2 : Copolymerization of phenylacetylene (PA) with 1-hexyne (HX) by Fe-based Ziegler-Natta catalysts

$Fe(prop)_3$ - $AlEt_3$[a]			$Fe(acac)_3$ - $AlEt_3$[b]		
Sample	f_{PA}[c]	$P_1(PA)$[d]	Sample	f_{PA}[c]	$P_1(PA)$[d]
ZNP 1	0.10	0.022	ZNA 1	0.05	0.225
ZNP 2	0.15	0.040	ZNA 2	0.1	0.302
ZNP 3	0.30	0.100	ZNA 3	0.2	0.430
ZNP 4	0.36	0.120	ZNA 4	0.3	0.501
ZNP 5	0.60	0.226	ZNA 5	0.4	0.540
ZNP 6	0.80	0.378	ZNA 6	0.5	0.640
ZNP 7	0.92	0.650	ZNA 7	0.6	0.690
			ZNA 8	0.7	0.730
			ZNA 9	0.8	0.800
			ZNA 10	0.9	0.875
			ZNA 11	0.95	0.940

[a] [HX] + [PA] = 1 mol.L^{-1} ; [b] [HX] + [PA] = 2 mol.L^{-1} ; the other conditions are the same as those reported in Tab.1. [c] Molar fraction of PA in monomer feed. [d] Molar fraction of PA in copolymer determined by ^1H-NMR according to Eq. (3).

Determination of reactivity ratios

It is usual to characterize the monomer behaviour in copolymerization in terms of reactivity ratios. These parameters can be obtained from the Mayo-Lewis equation or terminal-unit model (Ref.17) which postulates that only the active chain end of a growing polymer enchainment affects the addition probability of one or the other comonomer. Most of the copolymerization systems described in the literature are in a good agreement with this model (Ref.18). The accurate knowledge of reactivity ratios is of great signifance since it allows to predict copolymer composition and monomer sequence distributions for any starting mixture.

The reactivity ratio values, here denoted r_{PA} and r_{HX} for PA and HX, are determined from the compositions of the monomer feeds and those of the corresponding copolymers formed at low conversions according to several procedures based on the linearization of the instantaneous copolymerization equation. Among them, we have used the method proposed by Kelen-Tüdös (KT) (Refs.19, 20) which affords the best estimate of copolymerization parameters obtainable by linear least-squares calculations. The KT equation is :

$$\eta = \left(r_{PA} + \frac{r_{HX}}{\alpha} \right) \xi - \frac{r_{HX}}{\alpha} \qquad (6)$$

with

$$\eta = \frac{x(y-1)}{\alpha y + x^2}, \quad \xi = \frac{x^2}{\alpha y + x^2}, \quad x = \frac{f_{PA}}{1 - f_{PA}}, \quad y = \frac{F_1\,(PA)}{1 - F_1\,(PA)} \qquad (7)$$

and where f_{PA} is the mole fraction of PA in the initial feed.

The parameter α is a positive arbitrary constant defined by the following relation :

$$\alpha = [(x^2/y)_{max} \cdot (x^2/y)_{min}]^{0.5} \qquad (8)$$

whose both factors represent respectively the highest and the lowest values of the (x^2/y) experimental ratio.

This method allows to plot a straight line where the experimental data are uniformly and symmetrically displayed on the variation interval of ξ (0,1). Therefore, it is possible better to appreciate the linearity of the spread and thus to be sure that the incorporation of both comonomers is only resulting of terminal effect. For comparison, the reactivity ratios have been also computed by using a non-linear least squares curve-fitting procedure.

By processing composition data (Tab.2) according to the KT equation (6) and NLLS-procedure, the r_{PA}- and r_{HX}-values were calculated. The results obtained are compiled in Tab.3. As shown in Fig.5, the KT method gives rise to straight lines, on the whole composition range, clearly indicating that the terminal-unit model adequately describes the copolymerization for both examined systems. The values found using the NLLS-curve fitting approach are the same. It follows that the experimetal data well-coincide with the theoretical composition curves (Fig.6). It was not possible to compare the reactivity ratio values with literature since these new results are reported for the first time.

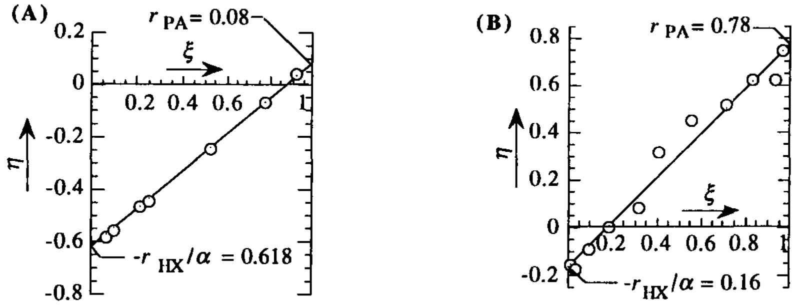

Fig.5 : Kelen-Tüdös plots for PA/HX copolymerization by the Fe(prop)$_3$-AlEt$_3$ (A) and Fe(acac)$_3$-AlEt$_3$ (B) catalyst systems. Constants of KT equation : $\alpha = 6.515$ and $\alpha = 0.811$, respectively.

Tab.3 : Reactivity ratios for the copolymerization of phenylacetylene (PA) and 1-hexyne (HX) by Fe-based Ziegler-Natta catalysts

Method	Fe(prop)$_3$-AlEt$_3$		Fe(acac)$_3$-AlEt$_3$	
	r_{PA}	r_{HX}	r_{PA}	r_{HX}
Kelen-Tüdös	0.08 ± 0.03^a	4.03 ± 0.16^a	0.78 ± 0.06^a	0.13 ± 0.04^a
Curve-fitting	0.09 ± 0.006^a	4.16 ± 0.18^a	0.79 ± 0.02^a	0.15 ± 0.015^a

^{a} 95% confidence interval

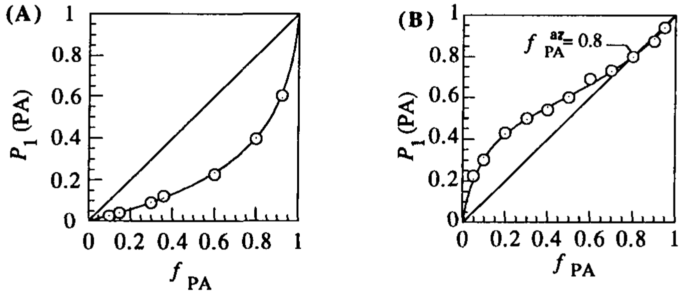

Fig. 6 : Composition curves for PA/HX copolymerization by the catalyst systems Fe(prop)$_3$-AlEt$_3$ (A) and Fe(acac)$_3$-AlEt$_3$ (B). O : experimental data ; — : curves calculated from terminal-unit model with $r_{PA} = 0.08$; $r_{HX} = 4.03$ (A) and $r_{PA} = 0.78$; $r_{HX} = 0.13$ (B).

The shape of the composition curve for the reactions initiated by the $Fe(prop)_3$-$AlEt_3$ catalyst (Fig.6A) suggests that HX is randomly copolymerized with PA and more reactive than it. The product $r_{PA} \cdot r_{HX} < 1$ (0.32) with $r_{PA}<1$ and $r_{HX}>1$ reveals a slight alternating tendency with propensity to formation of HX-homosequences. On the other hand, the curve describing the copolymerization behaviour in the presence of $Fe(acac)_3$-$AlEt_3$ system is very different (Fig.6B) and indicates in contrast that the relative reactivity of PA is higher than that of HX. The copolymerization appears to be somewhat alternating, according to the value of $r_{PA} \cdot r_{HX} < 1$ (0.10) with both reactivity ratios below unity. Consequently, the system presents an azeotropic composition ($f_{PA}^{az} = 0.8$). These very unlike findings suggest that the chemical nature of ferric compounds takes a very prominent part in the copolymerization mechanisms in terms of competitive coordination of the acetylenic monomers to iron of the active species.

REFERENCES

(1) G. Natta, G. Mazzanti, G. Corradini, *Atti. Acad. Naz. Lincei. Rend. Class. Sci. Fis. Mat. Nat.* **25**, 3 (1958)

(2) T. Masuda, T. Higashimura, *Adv. Polym. Sci.* **81**, 121 (1987)

(3) G. Costa, "*Comprehensive Polymer Science*", edited by G. C. Eastmond, A. Ledwith, S. Russo, P. Sigwalt, Pergamon Publ., vol. 4, New York 1989, p.155

(4) C. I. Simionescu, V. Percec, *Prog. Polym. Sci.* **8**, 133 (1982)

(5) T. Masuda, T. Yoshizawa, Y. Okano, T. Higashimura, *Polymer* **25**, 503 (1984)

(6) Y. Abe, T.Masuda, T.Higashimura, *J. Polym. Sci. : Part A : Polym. Chem.* **27**, 4267 (1989)

(7) Z. Shen, M. F. Farona, *J. Polym. Sci. Polym. Chem. Ed.* **22**, 1009 (1984)

(8) T. Masuda, Y. -X. Deng., T. Higashimura, *Bull. Chem. Soc. Jpn.* **56**, 2798 (1983)

(9) K. Yokota, M. Ohtubo, T. Hirabayashi, Y. Inai, *Polym. J.* **25**, 1079 (1993)

(10) S. Kambara, N. Yamazaki, M. Hatano, *Am. Chem. Soc.* **9**, A-23 (1964)

(11) C. I. Simionescu, V. Percec, S. Dumitrescu, *J. Polym. Sci. Polym. Chem. Ed.* **15**, 2497 (1977)

(12) Z. Shen, M. F. Farona, *Polym. Bull.* **10**, 8 (1983)

(13) V. Percec, P. L. Rinaldi, *Polym. Bull.* **9**, 548 (1983)

(14) M. Leclerc, R. E. Prud'homme, A. Soum, M. Fontanille, *J. Polym. Sci. Polym. Phys. Ed.* **23**, 2031 (1985)

(15) C.I. Simionescu, I. Negulescu, C. Mihailescu, I. Diaconu, Gh. Drägan, IUPAC, Florence, Italy, September 1980, Preprints, vol.2, p. 433

(16) K. Ito, Y. Yamashita, *J. Polym. Sci. Part A-1* **3**, 2165 (1965)

(17) F.R. Mayo, F.M. Lewis, *J. Am. Chem. Soc.* **66**, 1594 (1944)

(18) R.Z. Greenley, "*Polymer Handbook*", 3rd Edn, edited by J. Brandrup and E. H. Immergut, Wiley, New York, 1989, p.II / 153

(19) T. Kelen, F. Tüdös, *J. Macromol. Sci.- Chem.* **A9**, 1 (1975)

(20) F. Tüdös, T. Kelen, *J. Macromol. Sci.-Chem.* **A16**, 1283 (1981)