ELSEVIER

Polymer 40 (1999) 589–597

polymer

Copolymerization of phenylacetylene and 1-hexyne using Ziegler–Natta and metathesis catalyst systems: copolymer compositions and reactivity ratios by ^1H n.m.r. spectroscopy

Sandrine Duc[1], Alain Petit*

Laboratoire de Chimie-Physique Macromoléculaire, CNRS-UMA 7568, ENSIC-INPL, 1 rue Grandville, BP 451, 54001 Nancy cedex, France

Received 10 November 1997; revised 7 April 1998

Abstract

Phenylacetylene (PA) and 1-hexyne (HX) were copolymerized in solution using two kinds of Ziegler–Natta catalysts, $Ti(On\text{-}Bu)_4$-$AlEt_3$ and $Fe(acac)_3$-$AlEt_3$, in toluene and by metathesis with the WCl_6-Ph_4Sn initiating system in toluene and 1, 4-dioxan. The compositions of copolymers, obtained under various monomer charge ratios in the range of 5–95 mol% of PA or HX, were determined from their 200 MHz ^1H n.m.r. spectra. The experimental data processed according to the Kelen–Tüdös approach and, for comparison, by using a non-linear least squares curve-fitting procedure indicated that, for the four investigated systems, the copolymerization process of the PA/HX-pair can be adequately described by the terminal-unit model. The reactivity ratio values calculated from both methods were the same. Based on these findings, the relative reactivity of two acetylenic monomers was discussed. Interestingly, the results obtained with the Ziegler–Natta catalysts showed that the propagation step mechanisms changed greatly not only with the type of transition metal compound [$Ti(On\text{-}Bu)_4$ and $Fe(acac)_3$], but also with the chemical nature of ligands bonded to transition metal [$Fe(acac)_3$ and $Fe(propionate)_3$]. On the other hand, the reaction promoted by W-containing metathesis initiator was found to be strongly dependent on the polymerization solvent. The number-average molecular weights of copolymer samples and the number-average sequence lengths of PA and HX-units were also reported.

Keywords: Poly(phenylacetylene-*co*-1-hexyne); ^1H n.m.r. spectroscopy; Reactivity ratio

1. Introduction

The polymerization of acetylenic monomers, alternatively called alkynes, has been widely investigated since Natta et al. [1] described for the first time in 1958, the synthesis of stereoregular polyacetylene with the soluble catalyst formed by mixing titanium (IV) *n*-butoxide [$Ti(On\text{-}Bu)_4$] and triethylaluminium ($AlEt_3$). In the three last decades, many researches [2–6] have been carried out with various kinds of monosubstituted (terminal) or disubstituted (inner) acetylenes, among which phenylacetylene was probably the most studied, by using a great variety of catalytic systems. This was in order to develop new polyconjugated polymeric systems especially in view of their potential applications as electrically conducting materials [4,7–9] and in the field of membrane separation processes, i.e. gas permeation [10–12] and pervaporation [13,14].

Monosubstituted alkynes are known to polymerize, yielding high polymers with number-average molecular weight ($\bar{M}_n$) ranging from 10 000 to 100 000 g mol^{-1} in the presence of Ziegler–Natta catalysts only in the case of uncrowded monomers bearing primary or secondary aliphatic groups [15–18]. The reactivity of acetylene derivatives decreases with the enhancement of the steric hindrance [19]. On the other hand, the polymerization of bulky group-containing acetylenes, like *tert*-butylacetylene or disubstituted alkynes, produces high molecular weight polymeric materials with $\bar{M}_n$ above 100 000 g mol^{-1} in the presence of W- and Mo-based metathesis initiators such as WCl_6 and $MoCl_5$ used alone or sometimes with a cocatalyst, for example tetraphenyltin (Ph_4Sn) [5,20,21].

However, perusal of the literature shows that few studies have been reported about the alkyne copolymerization. Some investigations were devoted to the radical copolymerization of acetylenic derivatives and methacrylic or conjugated diene monomers [22–26]. Several works were concerned with the metathesis copolymerization involving different

---

* Corresponding author.

[1] Present address: BP Chemicals, Centre de Recherche et de Technologie, BP no. 6, 13117 Lavéra, France.

PII S0032-3861(98)00284-5

kinds of terminal or inner alkynes[27–32]. Otherwise, it must be stressed that we found little information concerning the polymerization of alkyne pairs using Ziegler–Natta type systems [2,33–37].

Some reports have appeared on the quantitative estimation of the geometrical structure *cis/trans* of acetylenic polymers [38–43], but there is to our knowledge no publication dealing with the copolyalkyne microstructure, in terms of the chain regularity, i.e. head-to-tail, head-to-head and tail-to-tail monomer junctures and sequence distributions. In general, the stereochemical configuration of monomeric units as well as their arrangement along the macromolecular chains are factors of great significance to the physico-chemical properties and industrial applications [44–46].

The foregoing remarks encouraged us to pursue exhaustive research on this topic with the aim of obtaining quantitative data on the microstructure of copolyalkynes. In the present paper, we report and compare results pertaining to the copolymerization of phenylacetylene (PA) and 1-hexyne (HX) by using either Ziegler–Natta initiating systems such as $Ti(On\text{-}Bu)_4$-$AlEt_3$ and $Fe(acac)_3$-$AlEt_3$ (acac = acetylacetonate) or metathesis catalyst like WCl_6-Ph_4Sn. PA and HX have been chosen as the starting comonomers because they are convenient for estimating accurately, by n.m.r. spectroscopic method, the compositions of the resulting copolymer samples from which were calculated the monomer reactivity ratios, and subsequently the number-average sequence lengths, characterizing the kinetic scheme of the propagation step.

2. Experimental

2.1. Materials

Catalyst components: $AlEt_3$ (Merck, purity: 96%) was used without further purification and diluted in anhydrous toluene. WCl_6 (Aldrich, purity: 99.9%) was employed as received and handled in a glove-bag under an argon atmosphere. $Fe(acac)_3$ (Acros, purity: 98%) and Ph_4Sn (Fluka, purity: 99.8%) were recrystallized from toluene and chloroform, respectively. $Ti(On\text{-}Bu)_4$ supplied from Aldrich was refined by reduced-pressure distillation under a slow argon bleed and used as a toluene solution.

Monomers: 1-hexyne (Janssen Chimica, purity: 99%) and phenylacetylene (Aldrich, purity: 98%) were dried by refluxing in inert atmosphere over CaH_2 and then subjected to vacuum distillation on cold condensing surface. These monomers were kept under argon at −20°C and over 4 nm-type molecular sieves in the case of 1-hexyne.

Solvents: toluene (Aldrich, purity: 99.8%) was refluxed over and distilled from CaH_2. 1, 4-dioxan (Aldrich, purity: 99.9%) was first allowed to stand several days over potassium hydroxide pellets and distilled from $LiAlH_4$. Both solvents were stored under argon over molecular sieves (4 nm-type).

2.2. Procedure

Polymerization reactions were performed on the basis of several procedures previously described in the literature, i.e. $Ti(On\text{-}Bu)_4$-$AlEt_3$ [47,48], Fe(acac)-$AlEt_3$ [20,49,50,51,52], WCl_6-Ph_4Sn [21,29,52]. The runs were carried out under dry nitrogen in jacketed Pyrex reactor equipped with a magnetic stirring bar. When $Fe(acac)_3$, WCl_6 and Ph_4Sn were used as catalysts, they were introduced first. The required amounts of liquid reagents were added by syringe. After ageing at the desired temperature the two-component catalyst solution, was charged the monomer mixture. Detailed experimental conditions, including concentration data, are summarized in Tables 1 and 2 for Ziegler–Natta and metathesis processes, respectively. The copolymerizations were quenched by adding a few ml of methanol containing hydrochloric acid (*ca* 5% wt/v). In the case of the Ziegler–Natta catalysts only, the reaction mixtures were washed successively with saturated $NaHCO_3$ solution and several times with water. All the copolymer samples formed were isolated by precipitation into a large amount of methanol. The crude products were purified by dissolving in chloroform followed by filtration through a Sartorius 0.2 μm filter in order to remove any insoluble materials, e.g. catalyst residues or microgel, after which they were reprecipitated in methanol and vacuum dried at 50°C to constant weight. Most copolymers were prepared to lower than 10 wt% conversion, measured by gravimetry, except the set of samples synthesized in toluene using WCl_6-Ph_4Sn as catalyst because of the very high rate of the corresponding reactions.

2.3. Characterization

The copolymer compositions were determined by ^1H n.m.r. spectroscopy. The spectra were run using about 0.025 g ml^{-1} solutions of the samples in CCl_4 at ambient probe temperature and recorded on a Bruker AC 200 P spectrometer operating at 200.13 MHz. CF_3COOH-*d* served to provide the deuterium lock frequency. Proton chemical shifts were quoted relative to tetramethylsilane (TMS) and the resonance signal areas were evaluated by the integration curve technique.

The number-average molecular weights ($\bar{M}_n$) were obtained by size exclusion chromatography (s.e.c.) in tetrahydrofuran (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.

Table 1
Copolymerization of phenylacetylene (PA) with 1-hexyne (HX) by Ziegler–Natta catalysts in toluene solution

$Ti(On\text{-}Bu)_4\text{-}AlEt_3^a$						$Fe(acac)_3\text{-}AlEt_3^b$					
Sample	f^c_{PA}	$P_1(PA)^d$	Reaction time (h)	Conversion (wt%)	$\bar{M}^e_n$ (g mol^{-1})	Sample	f^c_{PA}	$P_1(PA)^d$	Reaction time (h)	Conversion (wt%)	$\bar{M}^e_n$ (g mol^{-1})
Ti 1	0.1	0.022	0.75	9.6	3317	Fe 1	0.05	0.225	6	7.7	3000
Ti 2	0.2	0.052	1	1.3	2200	Fe 2	0.1	0.302	6	10	2780
Ti 3	0.3	0.075	1	11.6	1650	Fe 3	0.2	0.430	7.5	10	2460
Ti 4	0.4	0.115	3	7.5	1540	Fe 4	0.3	0.501	7.5	10	3180
Ti 5	0.5	0.175	3	8.5	—	Fe 5	0.4	0.540	7.5	13	2020
Ti 6	0.6	0.226	3	10.5	1250	Fe 6	0.5	0.640	8	12	1831
Ti 7	0.7	0.330	1	9.2	—	Fe 7	0.6	0.690	8	8.5	1650
Ti 8	0.8	0.438	1	7	1010	Fe 8	0.7	0.730	7	11	1466
Ti 9	0.9	0.599	1	11	860	Fe 9	0.8	0.800	6	9	1055
Ti 10	0.95	0.738	0.75	8.7	500	Fe 10	0.9	0.875	5	9.5	980
						Fe 11	0.95	0.940	5	7	850

[a] $[PA] + [HX] = 2$ mol l^{-1} $[Ti(On\text{-}BU)_4] = 10$ mmol l^{-1}; $[Al]/[Ti] = 5$; ageing time and temperature of catalyst system: 15 min at 25°C; polymerization temperature: 25°C.
[b] $[PA] + [HX] = 2$ mol l^{-1}; $[Fe(acac)_3] = 35$ mmol l^{-1}; $[Al]/[Fe] = 3$; ageing time and temperature of catalyst system: 30 min at 50°C; polymerization temperature: 50°C.
[c] Mole fraction of PA in monomer feed.
[d] Mole fraction of PA in copolymer determined by ^1H n.m.r. spectroscopy.
[e] Number-average molecular weight measured by s.e.c.

3. Results and discussion

3.1. Copolymer compositions

In Fig. 1(A) and (B) are shown, as examples, representative ^1H n.m.r. spectra at 200 MHz of poly(1-hexyne) (PHX), polyphenylacetylene (PPA) and PA–HX copolymers containing 17.5 and 43 mol% of PA-units, obtained using the Ziegler–Natta catalyst $Ti(On\text{-}Bu)_4\text{-}AlEt_3$ and by the $WCl_6\text{-}Ph_4Sn$ metathesis initiator system in 1, 4-dioxan, respectively. Spectra of homologous materials achieved by the catalytic systems based on $Fe(acac)_3$ and WCl_6 in toluene solution are quite similar. First, one recognizes the typical shapes of PPA-spectra previously described in great detail by several workers [3,38,42,53]. Second, one discerns the four resonance signals, at 0.8, 1.3, 2.1 and 5.9 ppm, earlier assigned for PHX synthesized with various transition metal-based initiating systems [52,54]. The analysis of homopolymer spectra supports the expected polyene structure indicating that there is no loss of unsaturation due to side reactions such as cyclization and/or cross-linking in the course of the polymerizations. The comparison between the spectra of the copolymers and those of the corresponding homopolymers reveals no new peak. On the basis of the signal attributions quoted in Fig. 1, the copolymer compositions have been calculated by comparing the cumulated area (H_p) of the aliphatic proton resonances (0.5–2.5 ppm) with those ($H_a + H_p$) of the

Table 2
Copolymerization of phenylacetylene (PA) with 1-hexyne (HX) by metathesis catalyst in toluene and 1, 4-dioxan solution

$WCl_6\text{-}Ph_4Sn$/toluene^a						$WCl_6\text{-}Ph_4Sn$/1, 4-dioxan^a					
Sample	f^b_{PA}	$P_1(PA)^c$	Reaction time (min)	Conversion (wt%)	$\bar{M}^d_n$ (g mol^{-1})	Sample	f^b_{PA}	$P_1(PA)^c$	Reaction time (h)	Conversion (wt %)	$\bar{M}^d_n$ (g mol^{-1})
MT 1	0.114	0.040	10	19	19 750	MD 1	0.106	0.050	22	15	30 400
MT 2	0.222	0.097	35	16.6	20 100	MD 2	0.202	0.110	23	4	29 500
MT 3	0.336	0.167	25	17	21 210	MD 3	0.303	0.150	19	4	31 200
MT 4	0.434	0.216	25	19	21 900	MD 4	0.402	0.245	18	3	36 300
MT 5	0.537	0.320	5	16.2	25 150	MD 5	0.509	0.320	17	9	38 300
MT 6	0.630	0.445	5	19.7	25 500	MD 6	0.606	0.430	16	6.5	39 400
MT 7	0.728	0.530	7	20.7	28 300	MD 7	0.709	0.510	15	8	46 500
MT 8	0.820	0.707	3	29.6	30 350	MD 8	0.804	0.690	14	7	—
MT 9	0.913	0.866	2	44.5	35 620	MD 9	0.903	0.840	8.5	9	62 400
MT 10	0.956	0.938	1	47.7	36 600	MD 10	0.951	0.920	6	9	65 500

[a] $[PA] + [HX] = 2$ mol l^{-1}; $[WCl_6] = [Ph_4Sn] = 10$ mmol l^{-1}; ageing time and temperature of catalyst system: 15 min at 30°C; polymerization temperature: 30°C.
[b] Mole fraction of PA in monomer feed.
[c] Mole fraction of PA in copolymer determined by ^1H n.m.r. spectroscopy.
[d] Number-average molecular weight measured by s.e.c.

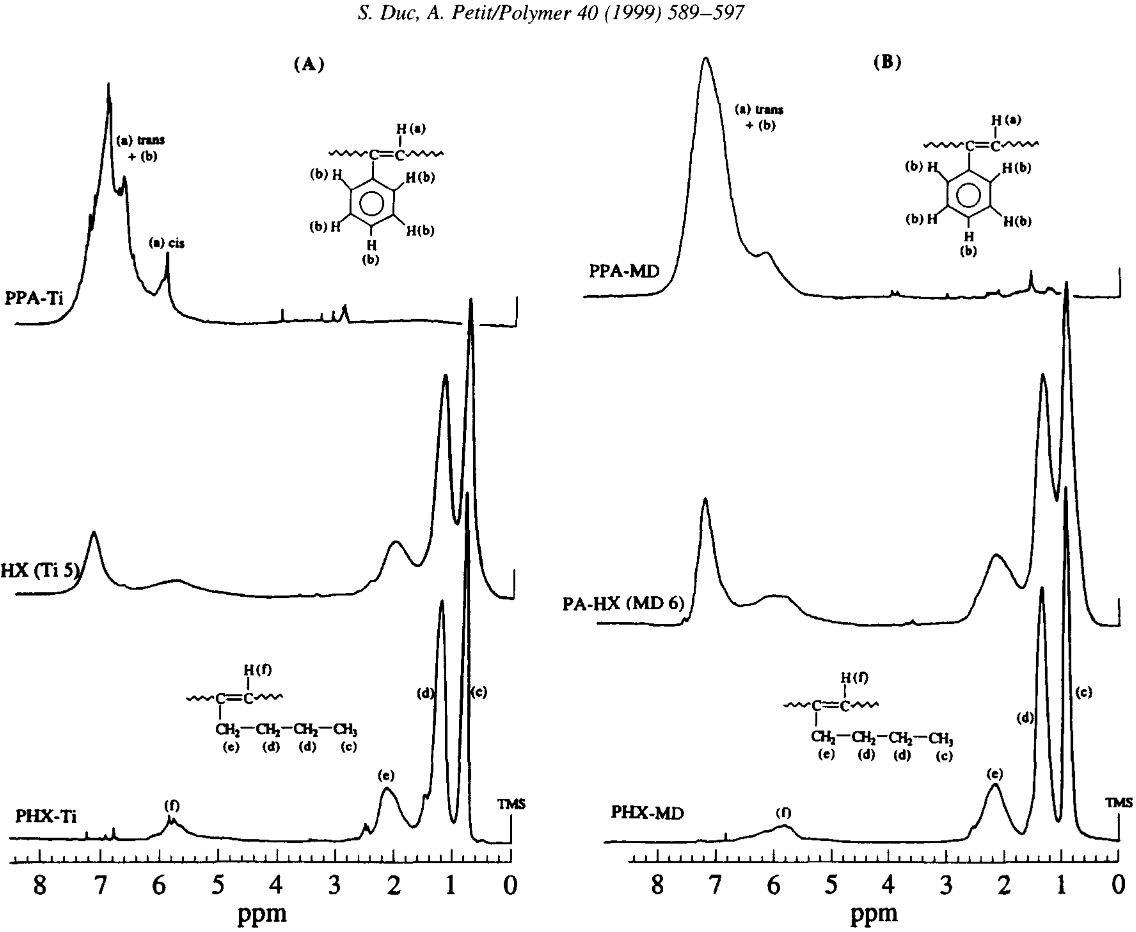

Fig. 1. 200 MHz ^{1}H n.m.r. spectra, in CCl_4, of polyphenylacetylene (PPA), poly(1-hexyne) PHX and PA-HX copolymer. (A) synthesized, in toluene, by the Ti(O*n*-Bu)$_4$-AlEt$_3$ Ziegler–Natta catalyst (Ti 5: 17.5 mol% of PA in copolymer). (B) Synthesized, in 1, 4-dioxan, by the WCl_6-Ph_4Sn metathesis catalyst (MD 6: 43 mol% of PA in copolymer).

signal area due to olefinic and aromatic hydrogens, appearing in the range 4.5–8 ppm.

By assuming, like in the case of homopolymers, that there is no loss of unsaturation in the studied copolyalkynes, their compositions in terms of molar fractions of PA- and HX-structural units, denoted P_1(PA) and P_1(HX) according to the notations of Ito and Yamashita [55], may be evaluated by using the following expressions:

$$P_1(\mathrm{PA}) = \frac{9-\rho}{9+5\rho} \qquad (1)$$

$$P_1(\mathrm{HX}) = 1 - P_1(\mathrm{PA}) \qquad (2)$$

where

$$\rho = H_p/(H_a + H_p) \qquad (3)$$

In Tables 1 and 2 are summarized the data thus obtained together with the $\bar{M}_n$ values for the four series of PA–HX copolymers samples synthesized in this work.

3.2. *Determination of reactivity ratios*

A thorough examination of the literature shows that most copolymerization systems have been successfully treated [56] by using the well-known differential equation of Mayo-Lewis [57], alternatively called the terminal-unit model, which postulates that only the active chain end of a growing polymer enchainment affects the addition probability of each comonomer. This classical kinetic scheme is described by two copolymerization parameters, i.e. the monomer reactivity ratios, denoted r_{PA} and r_{HX} for the PA/HX-pair investigated in the present work. There are various reasons for evaluating the *r*-parameters with the highest possible precision, among other things to predict accurately copolymer composition and monomer sequence distribution for any starting mixture. The determination of these structural data is of paramount importance for tailor-making materials with required physicochemical properties and in evaluating the end applications of copolymers.

To determine the reactivity ratio values from the composition of monomer feeds and those of the resulting copolymers formed at low conversions, several procedures based on the linearization of the instantaneous copolymerization equation have been developed. Among them, we have used the method proposed by Kelen–Tüdös (K-T) [58,59], which provides the best estimate of *r*-parameters obtainable by linear least-squares calculations. The K-T equation is:

$$\eta = \left(r_{PA} + \frac{r_{HX}}{\alpha}\right)\xi - \frac{r_{HX}}{\alpha} \qquad (4)$$

Table 3
Reactivity ratios for the copolymerization of phenylacetylene (PA) with 1-hexyne by Ziegler–Natta catalysts

Method	Ti(O*n*-Bu)$_4$-AlEt$_3$			Fe(acac)$_3$-AlEt$_3$		
	r_{PA}	r_{HX}	$r_{PA}r_{HX}$	r_{PA}	r_{HX}	$r_{PA}r_{HX}$
K-T	0.15 ± 0.025[a]	4.80 ± 0.23[a]	0.72	0.78 ± 0.06[a]	0.13 ± 0.04[a]	0.10
NLLS	0.14 ± 0.015[a]	4.47 ± 0.30[a]	0.63	0.79 ± 0.02[a]	0.15 ± 0.015[a]	0.12

[a] 95% confidence interval.

with

$$\eta=\frac{x(y-1)}{\alpha y+x^2},\quad \xi=\frac{x^2}{\alpha y+x^2},\quad x=\frac{f_{PA}}{1-f_{PA}},\quad y=\frac{P_1(PA)}{1-P_1(PA)} \tag{5}$$

where f_{PA} is the mole fraction of PA in the initial charge and α is a positive arbitrary constant defined by the following relation:

$$\alpha=[(x^2/y)_{max}\,(x^2/y)_{min}]^{1/2} \tag{6}$$

whose both factors stand, respectively, for the highest and the lowest values of the variable x^2/y. This method allows one to plot a straight line where the experimental data are uniformly and symmetrically displayed on the variation interval of $\xi(0, 1)$. Therefore, it is possible better to appreciate the linearity of the distribution and thus to be sure that the incorporation of comonomers only results from the terminal effect. The K-T equation is obviously suitable for low conversion data, but the upper limit is dependent upon the system being studied. In most cases up to levels of 5–10 wt%, the fluctuations of initial feed concentration can be neglected. However, it has been shown that this approach can be successfully applied to systems with rather high conversions of at least up to about 50 wt% without much loss of precision with respect to the values of copolymerization parameters [60]. In the 'extended' Kelen–Tüdös method, an average monomer composition is assigned to the corresponding copolymer composition for computation purposes.

For the sake of comparison, we have also applied another more elaborate treatment by using a non-linear least squares (NLLS) curve-fitting procedure involving iterations on r_{PA} and r_{HX}.

Thus, by processing experimental data listed in Tables 1 and 2 according to the K-T Eq. (4) (or the extended K-T method in the case of the PA/HX-pair polymerized by metathesis in toluene solution) and the NLLS procedure, the values of reactivity ratios r_{PA} and r_{HX} were calculated for the four sets of copolymerization systems examined. The results obtained are compiled in Tables 3 and 4 together with error estimations.

As shown in Fig. 2, the K-T method gives rise to straight lines on the whole composition range, clearly indicating that the terminal-unit model provides an appropriate description of the copolymerization for all investigated systems. The values computed using the NLLS approach agree within the limits of experimental precision (Tables 3 and 4). It follows that, as illustrated in Fig. 3, experimental data coincide well with the theoretical composition diagrams.

It is not possible to compare these reactivity ratio values with literature since these are reported for the first time, except the two parameters corresponding to the samples (denoted MT in Table 2) obtained by metathesis copolymerization in toluene solution. In a previous study on the same system, Masuda et al. [29] found the reactivity ratios $r_{PA} = 0.28\_ \pm 0.05$ and $r_{HX} = 4.27 \pm 0.27$, fairly near of our own results, i.e. $r_{PA} = 0.54 \pm 0.05$ and $r_{HX} = 3.26 \pm 0.23$. The variation is attributed to the dependence of reactivity ratios on copolymerization conditions and/or evaluation techniques.

3.3. Copolymerization by Ziegler–Natta catalysts

Fig. 3(A) and (B) shows composition curves for the copolymerization of PA and HX with Ti- and Fe-based initiating systems, respectively. The shape of the plot in the case of titanium-containing catalyst suggests that 1-hexyne is randomly copolymerized with phenylacetylene and much more reactive than it. The product $r_{PA}r_{HX} < 1$ (0.72) with $r_{HX} > 1$ (4.80) and $r_{PA} < 1$ (0.15) is consistent with a slight tendency towards alternating copolymerization and propensity to formation of long HX-homosequences. Table 5 shows the number-average sequence lengths $\bar{N}_{PA}$

Table 4
Reactivity ratios for the copolymerization of phenylacetylene (PA) with 1-hexyne by metathesis catalyst

Method	WCl$_6$-Ph$_4$Sn/toluene			WCl$_6$-Ph$_4$Sn/1, 4-dioxan		
	r_{PA}	r_{HX}	$r_{PA}r_{HX}$	r_{PA}	r_{HX}	$r_{PA}r_{HX}$
K-T[a]	0.54 ± 0.05[b]	3.26 ± 0.23[b]	1.76	0.58 ± 0.005[b]	2.36 ± 0.10[b]	1.37
NLLS	0.50 ± 0.08[b]	3.155 ± 0.44[b]	1.58	0.57 ± 0.01[b]	2.43 ± 0.30[b]	1.38

[a] Extended K-T procedure for runs in toluene solution.

[b] 95% confidence interval.

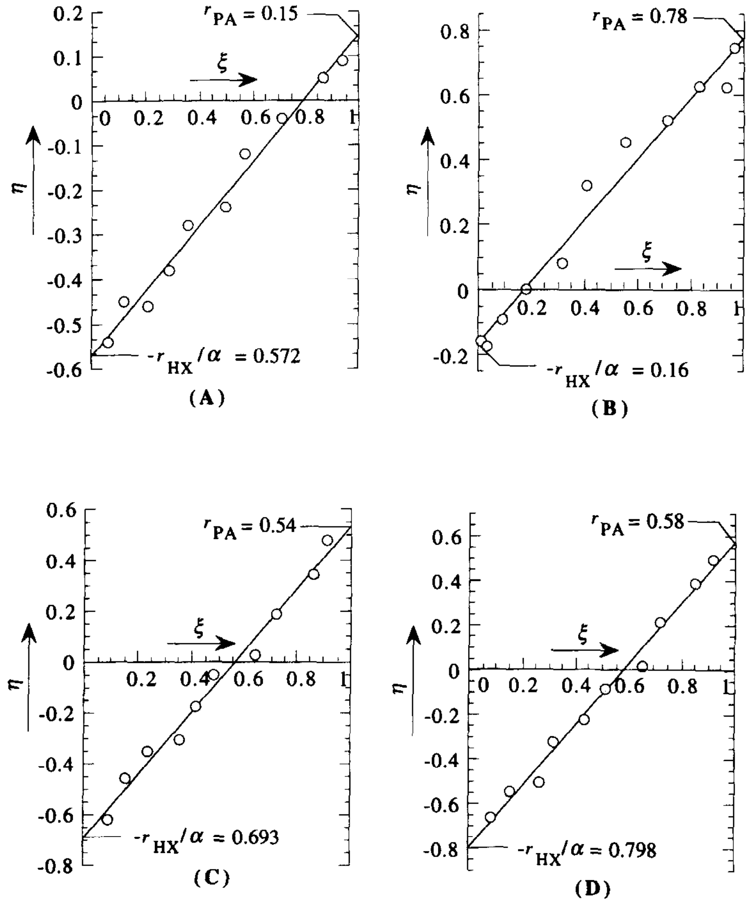

Fig. 2. Kelen–Tüdös plots for the Ziegler–Natta and metathesis copolymerizations of phenylacetylene (PA) with 1-hexyne (HX). (A) Ti(O*n*-Bu)$_4$-AlEt$_3$/toluene catalyst ($\alpha = 8.390$). (B) Fe(acac)$_3$-AlEt$_3$/toluene catalyst ($\alpha = 0.811$). (C) WCl$_6$-Ph$_4$Sn/toluene catalyst ($\alpha = 4.702$). (D) WCl$_6$-Ph$_4$Sn/1, 4-dioxan catalyst ($\alpha = 2.958$).

and $\bar{N}_{HX}$ representing the mean numbers of structural units PA and HX that form the PA- and HX-sequences in copolymer chains. These quantities, for the terminal model, are related simply to the reactivity ratios and feed compositions in the following manner:

$$\bar{N}_{PA} = 1 + r_{PA}(f_{PA}/f_{HX}) \quad (7)$$

$$\bar{N}_{HX} = 1 + r_{HX}(f_{HX}/f_{PA}) \quad (8)$$

From Table 5, it is obvious that the number of 1-hexyne units strongly decreases in copolymers obtained from the Ti-containing catalyst, as the mole fraction of 1-hexyne in monomer feed diminishes. Noteworthy in the results of Table 5 is the very rapid build-up of HX-units in copolymer beyond 60 mol% (sample Ti 4) of hexyne in the monomer charge.

It is reasonable to assume that the great discrepancy in relative reactivity of these alkynes should come from their structural difference. First, the phenyl group exerts a larger steric hindrance than the butyl-substituent, thus contributing to the decreased relative reactivity of PA compared to HX [29]. Second, the resonance effect of phenyl group brings about an electron deficiency in acetylene moiety resulting in a lower reactivity at the electron-deficient active species formed by reaction between Ti(O*n*-Bu)$_4$ and AlEt$_3$. On the contrary, in the case of 1-hexyne, the electron-releasing butyl group increases the electron-density of the acetylene moiety resulting in a much higher reactivity of HX than PA towards the active sites for the copolymerization.

On the other hand, the curve (Fig. 3(B)) and data (Table 5) describing the behaviour of the PA/HX-pair polymerized with the iron-containing catalyst are very different and disclose that in this case, the reactivity of PA is higher than that of HX. According to the value of $r_{PA}r_{HX} < 1(0.10)$ with both reactivity ratios below unity (Table 3), the propagation mechanism appears to be somewhat alternating as evidenced by the shape of the composition diagram (Fig. 3(B)) and also by the $\bar{N}$-values compared in Table 5 with the ones calculated for titanium-based catalyst. Fig. 3(B) shows that when the PA-content in the initial charge is high, about 80 mol%, the composition curve is very close to the diagonal of the square diagram. This fact indicates that the reactivity of HX towards PA propagating end is similar to that of PA ($1/r_{PA} = 1.28$). The system exhibits an azeotropic composition corresponding to $P_1(\mathrm{PA}) = f_{PA} = 0.80$.

Furthermore, it should be pointed out that previously we reported results involving another Fe-based

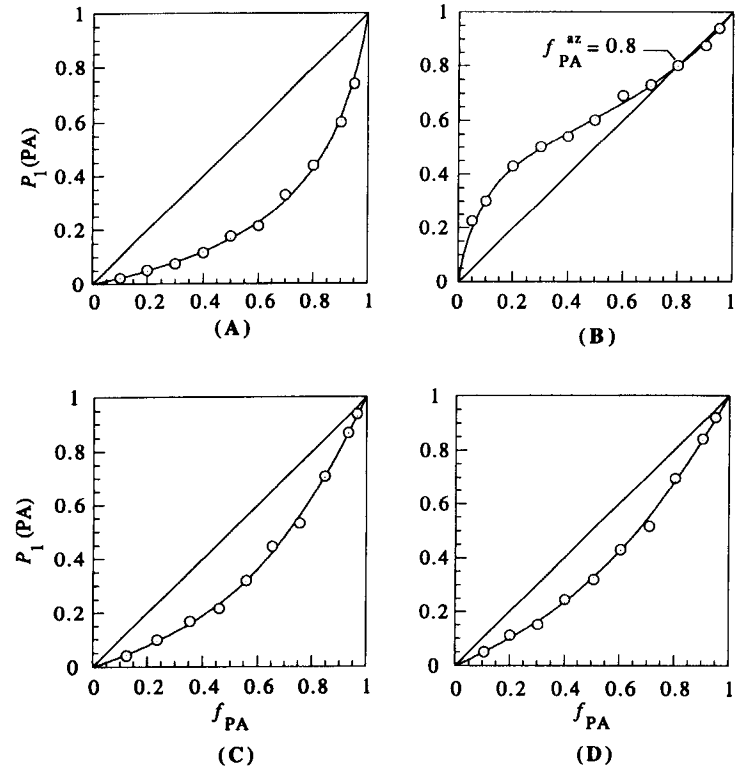

Fig. 3. Composition curves for the Ziegler–Natta and metathesis copolymerizations of phenylacetylene (PA) with 1-hexyne (HX). (A) Ti(O*n*-Bu)$_4$-AlEt$_3$/toluene catalyst. (B) Fe(acac)$_3$-AlEt$_3$/toluene catalyst ($f_{PA}^{az} = 0.8$: azeotropic composition). (C) WCl$_6$-Ph$_4$Sn/toluene catalyst. (D) WCl$_6$-Ph$_4$Sn/1, 4-dioxan catalyst. (○) Experimental data; (———) curves calculated from terminal-unit model with $r_{PA} = 0.15$, $r_{HX} = 4.80$ (A); $r_{PA} = 0.78$, $r_{HX} = 0.13$ (B); $r_{PA} = 0.54$, $r_{HX} = 3.26$ (C); $r_{PA} = 0.58$, $r_{HX} = 2.36$ (D).

Ziegler–Natta catalyst consisting of iron tripropionate and triethylaluminium [37]. This initiating system affords results, i.e. $r_{PA} = 0.11$ and $r_{HX} = 4.21$, nearly the same as those obtained with the titanium tetrabutoxyde-based catalyst. Therefore, it can be argued that the chemical nature of ligands of ferric derivatives plays a very prominent part in the copolymerization mechanisms in terms of competitive coordination of alkyne monomers to iron-atom of the propagating sites.

We have not as yet completely interpreted all experimental findings but we are further investigating these systems in order to try to explain the diverse copolymerization behaviour.

Table 5
Number-average sequence lengths ($\bar{N}$) of phenylacetylene (PA) and 1-hexyne (HX) units in PA–HX copolymers synthesized by Ziegler–Natta catalysts[a]

Ti(O*n*-Bu)$_4$-AlEt$_3^b$						Fe(acac)$_3$-AlEt$_3^c$					
Sample	f_{PA}^d	$\bar{N}_{PA}$	$\bar{N}_{HX}$	$\bar{N}_{PA}$:$\bar{N}_{HX}$	Distribution[e]	Sample	f_{PA}^d	$\bar{N}_{PA}$	$\bar{N}_{HX}$	$\bar{N}_{PA}$:$\bar{N}_{HX}$	Distribution[e]
Ti 1	0.1	1.02	44.2	1:44		Fe 1	0.05	1.04	3.47	1:3	-PHHHP-
Ti 2	0.2	1.04	20.2	1:20		Fe 2	0.1	1.09	2.17	1:2	
Ti 3	0.3	1.06	12.2	1:12		Fe 3	0.2	1.20	1.52	1:1	
Ti 4	0.4	1.10	8.2	1:8		Fe 4	0.3	1.33	1.30	1:1	-PHPH-
Ti 5	0.5	1.15	5.8	1:6		Fe 5	0.4	1.52	1.20	1:1	
Ti 6	0.6	1.22	4.2	1:4	-PHHHHP-	Fe 6	0.5	1.78	1.13	2:1	-PPHPP-
Ti 7	0.7	1.35	3.06	1:3		Fe 7	0.6	2.17	1.09	2:1	
Ti 8	0.8	1.60	2.20	2:2	-PPHHPP-	Fe 8	0.7	2.82	1.06	3:1	-PPPHPPP-
Ti 9	0.9	2.35	1.53	2:1		Fe 9	0.8	4.12	1.03	4:1	
Ti 10	0.95	3.85	1.25	4:1	-PPPPHPPPP-	Fe 10	0.9	8.02	1.01	8:1	
						Fe 11	0.95	15.82	1.00	16:1	

[a] For experimental conditions: see Table 1.

[b] $r_{PA} = 0.15$; $r_{HX} = 4.80$.

[c] $r_{PA} = 0.78$; $r_{HX} = 0.13$.

[d] Mole fraction of PA in monomer feed.

[e] Only some cases are illustrated; P and H denote PA and HX-units, respectively.

Table 6
Number-average sequence lengths ($\bar{N}$) of phenylacetylene (PA) and 1-hexyne (HX) units in PA–HX copolymers synthesized by metathesis catalyst[a]

WCl_6-Ph_4Sn/toluene[b]						WCl_6-Ph_4Sn/1, 4-dioxan[c]					
Sample	f^{d}_{PA}	$\bar{N}_{PA}$	$\bar{N}_{HX}$	$\bar{N}_{PA}$:$\bar{N}_{HX}$	Distribution[e]	Sample	f^{d}_{PA}	$\bar{N}_{PA}$	$\bar{N}_{HX}$	$\bar{N}_{PA}$:$\bar{N}_{HX}$	Distribution[e]
MT 1	0.114	1.07	24.46	1:24		MD 1	0.106	1.07	21.0	1:21	
MT 2	0.222	1.16	11.67	1:12		MD 2	0.202	1.15	10.3	1:10	
MT 3	0.336	1.29	6.97	1:7		MD 3	0.303	1.25	6.43	1:6	-PHHHHHHP-
MT 4	0.434	1.46	4.83	1:5	-PHHHHHP-	MD 4	0.402	1.39	4.51	1:5	
MT 5	0.537	1.68	3.57	2:4	-PPHHHHPP-	MD 5	0.509	1.60	3.28	2:3	
MT 6	0.630	2.02	2.73	2:3	-PPHHHPP-	MD 6	0.606	1.89	2.53	2:3	
MT 7	0.728	2.66	2.06	3:2	-PPPHHPPP-	MD 7	0.709	2.41	1.97	2:2	
MT 8	0.820	3.92	1.60	4:2		MD 8	0.804	3.38	1.57	3:2	
MT 9	0.913	8.40	1.24	8:1		MD 9	0.903	6.40	1.25	6:1	-HPPPPPPH-
MT 10	0.956	15.50	1.12	15:1		MD 10	0.951	12.26	1.12	12:1	

[a] For experimental conditions: see Table 2.
[b] $r_{PA} = 0.54$; $r_{HX} = 3.26$.
[c] $r_{PA} = 0.58$; $r_{HX} = 2.36$.
[d] Mole fraction of PA in monomer feed.
[e] Only some cases are illustrated; P and H denote PA and HX-units, respectively.

3.4. Copolymerization by metathesis catalyst

The composition plots for the copolymerization of PA with HX by WCl_6-Ph_4Sn in toluene or 1, 4-dioxan (Fig. 3(C) and (D)) are of same kind. Their shapes are very similar to that relative to the reaction promoted by Ti-based catalyst indicating that random propagations are taking place. However, in these cases the reactivity ratios, given in Table 4, show that 1-hexyne is less reactive and phenylacetylene more reactive when compared to their respective behaviour with the Ti(O*n*-Bu)$_4$-AlEt$_3$ system. This is in favorable agreement with the results of the homopolymerizations. Therefore, as evidenced by comparing data summarized in Tables 5 and 6, the PA–HX copolymers prepared using metathesis catalyst contain both longer PA-blocks and shorter HX-sequences than the homologous materials achieved with Ti-catalyst.

In addition, it is interesting to note the very great influence of polymerization solvent. Thus, when 1, 4-dioxan was employed as a solvent instead of toluene, the yield as well as the rate of reaction decreased considerably, whereas the number-average molecular weight ($\bar{M}_n$) of the copolymer increased by a factor of about 1.5–2 (Table 2). Similar tendencies, previously reported [17,53,61] in various oxygen-containing solvents, were ascribed to the molecular interactions between tungsten of the active species and lone pair electrons of oxygen atoms.

4. Conclusion

The copolymers of phenylacetylene with 1-hexyne were synthesized in solution by Ziegler–Natta and metathesis initiating systems. ^{1}H n.m.r. spectroscopy can be conveniently used for accurate determination of copolymer compositions. The reactivity ratios were computed by both the Kelen–Tüdös method and a non-linear least squares curve-fitting procedure. The values thus obtained were in good agreement and indicated clearly that the terminal-unit model was quite suitable to describe the copolymerization behaviour for the four systems investigated in this work.

In the case of runs performed using Ziegler–Natta catalysts, i.e. Ti(O*n*-Bu)$_4$-AlEt$_3$ and Fe(acac)$_3$-AlEt$_3$, low molecular weight materials, up to $\bar{M}_n$ values of the order of 3000 g mol^{-1}, were obtained. The relative reactivity of two acetylenic monomers during the copolymerization was found to be drastically dependent upon the chemical nature of transition metal compounds as well as that of ligands linked to metal atom, e.g. iron triacetylacetonate and iron tripropionate.

As expected, the W-based metathesis catalytic system produced copolymers whose $\bar{M}_n$ were remarkably higher compared to those observed for the homologous materials recovered by using the Ziegler–Natta catalysts. Moreover, it was evidenced that the polymerization solvent, e.g. toluene and 1, 4-dioxan, had a very prominent effect on the average molecular weights of synthesized copolymers, the yield and the rate of reaction.

Some results presented above are still too scanty for any sound conclusion concerning all observations reported in this paper. In view of this goal, further studies are now in progress.

References

[1] Natta G, Mazzanti G, Corradini P. Atti Acad Naz Lincei, Cl. Sci Fis Mat Nat Rend 1958;25:3.
[2] Chauser MG, Rodionov YuM, Misin VM, Cherkashin MI. Russ Chem Rev 1976;45:348.
[3] Simionescu CI, Percec V. Prog Polym Sci 1982;8:133.
[4] Gibson HW. In Skotheim TA, editor. Handbook of conducting polymers, vol. 1. New York: Dekker, 1986:405.
[5] Masuda T, Higashimura T. Adv Polym Sci 1987;81:121.

[6] Costa G. In Eastmond GC, Ledwith A, Russo S, Sigwalt P, editors. Comprehensive polymer science, vol. 4. New York: Pergamon, 1989:155.

[7] Kang ET, Bhatt AP, Villaroel E, Anderson WA, Ehrlich P. J Polym Sci, Polym Lett Edn 1982;20:143.

[8] Cukor P, Krugler JI, Rubner MF. Makromol Chem 1981;182:165.

[9] Ehrlich P, Anderson WA. In Skotheim TA, editor. Handbook of conducting polymers, vol. 1. New York: Dekker, 1986:441.

[10] Higashimura T, Masuda T, Okada M. Polym Bull 1983;10:114.

[11] Takada K, Matsuya H, Masuda T, Higashimura T. J Appl Polym Sci 1985;30:1605.

[12] Masuda T, Isobe E, Higashimura T. Macromolecules 1985;18:841.

[13] Masuda T, Tang B, Higashimura T. Polym J 1986;18:565.

[14] Nagase Y, Takamura Y, Matsui K. J Appl Polym Sci 1991;42:185.

[15] Trepka WJ, Sonnenfeld RJ. J Polym Sci, Part A1 1970;8:2721.

[16] Ciardelli F, Lanzillo S, Pieroni O. Macromolecules 1974;7:174.

[17] Oh S-E, Oguri F, Agaki K, Shirakawa H. J Polym Sci: Part A, Polym Chem 1993;31:781.

[18] Oh S-E, Ezaki R, Agaki K, Shirakawa H. J Polym Sci: Part A, Polym Chem 1993;31:2977.

[19] Masuda T, Kawasaki M, Okano Y, Higashimura T. Polym J 1982;14:371.

[20] Masuda T, Deng YX, Higashimura T. Bull Chem Soc Jpn 1983;56:2798.

[21] Masuda T, Higashimura T. Acc Chem Res 1984;17:51.

[22] Doak WK. J Am Chem Soc 1950;72:4681.

[23] Percec V, Natansohn A, Simionescu CI. Polym Bull 1980;2:63.

[24] Simionescu CI, Natansohn A, Percec V. J Macromol Sci-Chem 1981;A15:643.

[25] Simionescu CI, Natansohn A, Percec V. J Macromol Sci-Chem 1981;A15:659.

[26] Simionescu CI, Simionescu BC, Mihailescu C. Acta Polym 1983;34:62.

[27] Hasegawa KI, Masuda T, Higashimura T. Macromolecules 1975;8:255.

[28] Abe Y, Masuda T, Higashimura T. J Polym Sci: Part A, Polym Chem 1989;27:4267.

[29] Masuda T, Yoshizawa T, Okano Y, Higashimura T. Polymer 1984;25:503.

[30] Okano Y, Masuda T, Higashimura T. J Polym Sci, Polym Chem Edn 1985;23:2527.

[31] Tlenkopatchev MA, Korshak YV, Miranda E, Ogawa T. Polym Bull 1995;34:405.

[32] Liaw D-J, Chiang H-H, Jin B-H, Kang E-T. Eur Polym J 1996;32:215.

[33] Duncan PM, Forbes WG. In The chemistry of polymerization process. London: Soc Chem Ind, Monograph no. 20, 1966:23.

[34] Chien JCW, Wnek GE, Karasz FE, Hirsch JA. Macromolecules 1981;14:479.

[35] Chiang AC, Waters PF, Aldrige MH. J Polym Sci, Polym Chem Edn 1982;20:1807.

[36] Sebenik A, Osredkar U, Leben S. Vest Slov Kem Drus 1989;36:445.

[37] Aouak T, Petit A. Eur Polym J 1997;33:33.

[38] Simionescu CI, Dumitrescu SV, Percec V. J Polym Sci, Polym Symp 1978;64:209.

[39] Percec V, Rinaldi L. Polym Bull 1983;9:548.

[40] Leclerc M, Prud'homme RE, Soum A, Fontanille M. J Polym Sci, Polym Phys Edn 1985;23:2031.

[41] Masuda T, Okano Y, Tamura K, Higashimura T. Polymer 1985;26:793.

[42] Furlani A, Licoccia S, Russo MV. J Polym Sci: Part A, Polym Chem 1986;24:991.

[43] Matsunami S, Watanabe T, Kamimura H, Kakuchi T, Ishii F, Tsuda K. Polymer 1996;37:4853.

[44] Roussel R, Galin JC. J Macromol Sci Chem 1977;A11:347.

[45] Merle L, Merle Y. Macromolecules 1982;15:360.

[46] Brar AS, Saini AK. J Appl Polym Sci 1986;32:4607.

[47] Simionescu CI, Dumitrescu S. Eur Polym J 1970;6:635.

[48] Simionescu CI, Dumitrescu S. Makromol Chem 1970;136:47.

[49] Kambara S, Yamazaki N, Hatano M. American Chemistry Society Chicago Meeting, vol. 9, 1964:A-23.

[50] Kern RJ. J Polym Sci, Part A1 1969;7:621.

[51] Biyani B, Campagna AJ, Daruwalla D, Srivastava CM, Ehrlich P. J Macromol Sci Chem 1975;A9:327.

[52] Yokota K, Ohtubo M, Hirabayashi T, Inai I. Polym J 1993;25:1079.

[53] Percec V. Polym Bull 1983;10:1.

[54] Shen Z, Farona MF. J Polym Sci, Polym Chem Edn 1984;22:1009.

[55] Ito K, Yamashita Y. J Polym Sci, Part A 1965;3:2165.

[56] Greenley RZ. In Brandrup J, Immergut EH, editors. Polymer handbook, 3rd ed. New York: Wiley, 1989:II/153.

[57] Mayo FR, Lewis FM. J Am Chem Soc 1944;66:1594.

[58] Kelen T, Tüdös F. J Macromol Sci Chem 1975;A9:1.

[59] Tüdös F, Kelen T. J Macromol Sci Chem 1981;A16:1283.

[60] Kelen T, Tüdös F, Turcsanyi B, Kennedy JP. J Polym Sci, Polym Chem Edn 1977;15:3047.

[61] Masuda T, Takahashi T, Yamamoto K, Higashimura T. J Polym Sci, Polym Chem Edn 1982;20:2603.