

Nickel complexes with sulphur-containing ligands as initiators of the polymerization of phenylacetylene

A. M. Ciancusi, A. Furlani*, A. La Ginestra and M. V. Russo

Dipartimento di Chimica, Università 'La Sapienza', 00185 Roma, Italy

G. Pályi

Dipartimento di Chimica, Università di Modena, Modena, Italy

and A. Vizi-Orosz

MTA Petrolkémiai Kutató Csoport, 8200 Veszprém, Hungary

(Received 27 July 1989; revised 23 October 1989; accepted 20 November 1989)

The polymerization reaction of phenylacetylene in the presence of Ni(II) and Ni(III) catalysts, i.e. $[\text{Ni}(\text{dtb})_2]$ (dtb = dithiobenzene), $[\text{Ni}(N,N\text{-ddtc})_2]$ ($N,N\text{-ddtc} = N,N\text{-diethyldithiocarbamate}$), $[\text{Ni}(\text{oatp})_2]$ (oatp = *o*-aminothiophenolate), $[\text{Ni}(\text{mtb})_2]$ (mtb = monothiobenzoate) and $(\text{Bu}_4\text{N})[\text{Ni}(\text{tdt})_2]$ (tdt = toluene-3,4-dithiolate), gave polyphenylacetylene (PPA) in high yields and under mild reaction conditions. The complex $[\text{Ni}(\text{mtb})_2]$ reacts at -40°C , leading to highly stereoregular PPA. Infra-red and nuclear magnetic resonance spectra of PPA and conductivities (upon doping with I_2 and FeCl_3) are reported and discussed in comparison with literature data.

(Keywords: polyphenylacetylene; Ni(II), Ni(III) catalysts; conductivity)

INTRODUCTION

Active interest in $(\text{CH})_x$ and similar systems, such as polymers from monosubstituted acetylenes, continues: see refs. 1 for some state-of-the-art reviews and papers. Among the latter, polyphenylacetylene (PPA) has been much investigated. Recently, new catalyst-assisted polymerization procedures^{2,3}, electrochemical⁴, plasma⁵ and u.v.-induced polymerizations⁶ have been worked out. Both homogeneous⁷⁻¹⁰ and heterogeneous^{11,12} catalytic systems were proposed, and efforts to clear up the reaction mechanism¹³⁻²⁰ were reported.

E.s.r.²¹⁻²⁶, n.m.r.²⁷⁻³¹ and Raman³² studies led various authors to sometimes contradictory correlations between spectral properties and the structure of the PPA polymer chain. Theoretically, eight regular structures, due to *cis-cisoidal*, *cis-transoidal*, *trans-cisoidal* and *trans-transoidal* geometries of the hydrogens and the substituents with respect to the carbon-carbon single and double bonds and to head-to-tail or head-to-head enchainments, can be expected³³.

The structure of PPA obtained by different polymerization procedures was up till now correlated mainly to three of these structures, that is the head-to-tail *cis-cisoidal*, *cis-transoidal* and *trans-cisoidal* ones. However, the unresolved broad n.m.r. spectra usually observed²⁷⁻³⁰ do not suggest regular structures.

Recently we obtained, in the presence of Rh catalysts, PPA that exhibits well resolved ^1H and ^{13}C n.m.r. spectra³¹. A stereoregular structure of the polymer chain,

with a *cis-transoidal* configuration, was tentatively assigned to the product.

Some years ago we found³⁴ that the $[\text{NiBr}_2(\text{PBu}_3)_2]$ (A) and $[\text{NiI}_2(\text{PPh}_3)_2]$ (B) complexes are stereospecific catalysts in reactions with 2-methylbut-3-yn-2-ol: these Ni complexes induce regular head-to-tail (complex A) or head-to-tail-tail-to-head (complex B) enchainments of the monomer units with a *cis-cisoidal* chain configuration, leading selectively to 1,3,5- or 1,2,4-trisubstituted benzene derivatives, respectively. In the case of phenylacetylene (PA), however, the same Ni complexes give mixtures of polymers and cyclic trimers of PA³⁵.

In an attempt to find further molecules that initiate and/or catalyse the stereoregular polymerization of phenylacetylene, we set some conditions. Group VIII complexes were chosen because of the fact that the only known example (Rh³¹) is of this group. Higher-valent square planar complexes were taken to provide the possibility of S-type coordination for the acetylene (in the intermediate), which is favourable for the 'insertion' (C-C coupling) step³⁶. Strongly coordinating rigid, bidentate ligands, providing a medium-hard environment, were supposed to be favourable for the stereoregularity (regioselectivity of C-C coupling) and sufficient activation of the substrate. Precedent with Ni(0) and Ni(II) complexes in stoichiometric catalytic acetylene polymerization^{34,37}, together with these viewpoints, prompted us to choose Ni(II) and Ni(III) complexes of sulphur-containing ligands: bis(dithiobenzyl)nickel(II) (1), bis(*N,N*-diethyldithiocarbamate)nickel(II) (2), bis(*o*-aminothiophenolate)nickel(II) (3), bis(monothiobenzoate)nickel(II) (4) and tetra(*n*-butyl)ammonium-bis[*o*-toluene-3,4-dithiolato]nickel(III) (5) (see Table 1 for abbreviations).

* To whom correspondence should be addressed

EXPERIMENTAL

Methods and instruments

I.r. spectra were run on a Perkin-Elmer model 580B spectrometer as nujol mulls or films obtained by evaporating CH_2Cl_2 solutions of the polymer.

N.m.r. spectra were recorded on Varian EM 360A or Varian XL-300 spectrometers in CDCl_3 .

Gas chromatographic analyses were carried out on a Perkin-Elmer model 900 instrument, using stainless-steel columns (length 2 m, diameter 2.5 mm) filled with SE-30 10% on Chromosorb (60/80 mesh). The conditions used for the determination of unreacted PA and its cyclic trimers were described previously³⁵.

Molecular weights (*MW*) were measured by a Knauer Osmometer model 11 at 40°C using CCl_4 or CHCl_3 as solvent. For some samples *MW* were determined by g.p.c. using Shodex 80M + PL mixed-bed 10 μm columns, polystyrene standards and u.v. detection. Softening temperatures were measured with a Kofler apparatus.

Simultaneous t.g.-d.t.a. curves have been recorded with a Stanton 801 STA Thermoanalyzer, using Pt crucibles, Pt/(Pt, Rh 13%) thermocouples and heating rates of 5°C min^{-1} in air or N_2 atmosphere.

Elemental analyses were carried out by the Laboratorio di Microanalisi, Università di Pisa, Italy, and Institute of Organic Chemistry, University of Veszprém, Hungary.

Conductivity measurements were performed on pressed pellets (thickness ≈ 0.1 cm, diameter ≈ 1.3 cm) by using a Keithley 616 digital electrometer; measured resistance was converted into conductivity σ ($\Omega^{-1} \text{cm}^{-1}$). The pellets were prepared in a Specac hydraulic press P/N 150 at 8 tons.

Materials

Phenylacetylene (PA) (Fluka) was distilled prior to use; all the solvents were reagent-grade (Carlo Erba) and were used without further purification.

The nickel complexes were prepared by published methods³⁸ and characterized by spectra and analyses: 1—i.r., m.p. 292°C, lit. 292°C, dec.; 2—i.r., C, H, N analysis; 3—i.r., C, H, N analysis; 4—i.r., m.p. 178°C, lit. 177°C, C, H, N analysis; 5—i.r., C, H, N analysis.

Polymerization reactions

Reactions at reflux. In a typical synthesis procedure, 100 mg (≈ 0.2 mmol) of Ni catalysts were refluxed with 3 ml (27 mmol) of PA (freshly distilled) (catalyst/monomer ratio $\sim 7.4 \times 10^{-3}$) in bulk under stirring for

3–12 h. At the end of reaction a viscous brown mass was obtained, which was worked up with a known volume of benzene for the gas chromatographic determination of the unreacted PA and of the cyclic trimers, i.e. 1,3,5- and 1,2,4-triphenylbenzene (TPB). The solvent was then removed under vacuum and the polymer (PPA) was precipitated as a brown powder by addition of CH_3OH . The PPA was filtered off and washed with CH_3OH . From the filtrates, further solid fractions were recovered. PPA was recrystallized from benzene-petroleum ether or benzene-methanol. The elemental analyses of recrystallized PPA were in agreement with the theoretical values.

PPA was soluble in many organic solvents such as CHCl_3 , CH_2Cl_2 , C_6H_6 , THF (tetrahydrofuran) and CH_3COCH_3 .

Reaction at -40°C . Freshly distilled PA (3 ml) was degassed under reduced pressure, chilled to -40°C under N_2 and then 100 mg complex 4 (0.3 mmol) was added. The mixture was then stored at -40°C for six months. After this period the reaction mixture was worked up at room temperature as described above.

Doping procedure

A THF solution of weighed amounts of PPA was added to an appropriate amount of doubly sublimed I_2 or FeCl_3 dissolved in THF. The resulting solution was aged for 24 h, then THF was removed under reduced pressure and the residual black doped polymer was pressed into pellets for the d.c. conductivity measurements, which were performed under ambient conditions. In some experiments other solvents such as CH_3COCH_3 and C_6H_6 were used in the doping procedure.

RESULTS

Polymerization reactions

Polymerization reactions were carried out in bulk, since it was observed that in the presence of solvents the reaction rate is very low. PPA yields of about 60–90% with respect to the monomer were obtained (Table 1). Some 1,2,4- and 1,3,5-TPB (TPB = triphenylbenzene) were always found among the reaction products. The formation of both possible cyclic trimers suggests that either head-to-tail or head-to-tail-tail-to-head enchainments occur during the polymerization reaction. Both 1,2,4- and 1,3,5-TPB are more soluble than the linear polymers. The last fractions, which separate from the mother liquors, are richer in cyclic trimers and also

Table 1 Polymerization reactions of phenylacetylene (PA) in the presence of Ni(II) and Ni(III) complexes (full names given in the text)

Catalyst	Reaction time (h)	Unreacted PA (%)	Polymer yield (%)	TBP (%)		<i>MW</i> ^a (amu)	Softening temperature (°C)	Elemental analyses ^b (%)	
				1,2,4-	1,3,5-			C	H
[Ni(dtb) ₂]	(1) 5	5.5	72	8	7.2	600	158–165	93.4	5.8
[Ni(<i>N,N</i> -ddtc) ₂]	(2) 6	0	75	0.9	3.5	760 (2000) ^c	120–125	93.6	5.9
[Ni(oatp) ₂]	(3) 12	8.6	63	1.4	4.4	1000	140–145	93.7	5.8
[Ni(mtb) ₂]	(4) 12	5.5	81	2.6	3.2	1000	120–125	93.6	5.9
[Ni(mtb) ₂]	(4) 6 months ^d	—	32	4.4	0.9	1800	170–180	94.2	5.9
(Bu ₄ N)[Ni(tdt) ₂]	(5) 7	0	89	1.7	4.7	1300	195–200	91.6	5.3

^a Determined by vapour osmometric method

^b Calc. for (C_8H_6): C 94.08, H 5.92

^c No presence of trimers; polymer crystallized from benzene-methanol

^d Reaction carried out at -40°C

Table 2 Polymerization of PA in the presence of $[\text{Ni}(\text{mtb})_2]$ (4). Distribution of cyclic trimers (TPB) obtained in subsequent precipitates (ppt) from the reaction mother liquors

	ppt I (crude PPA)	ppt II	ppt III	ppt IV	ppt V
1,2,4-TPB (%)	5.9	2.9	13.4	14.5	16.5
1,3,5-TPB (%)	7.3	4.7	26.1	13.7	14.5
MW of ppt ^a	1100	900	407	465	389

^a Determined by vapour osmometric method

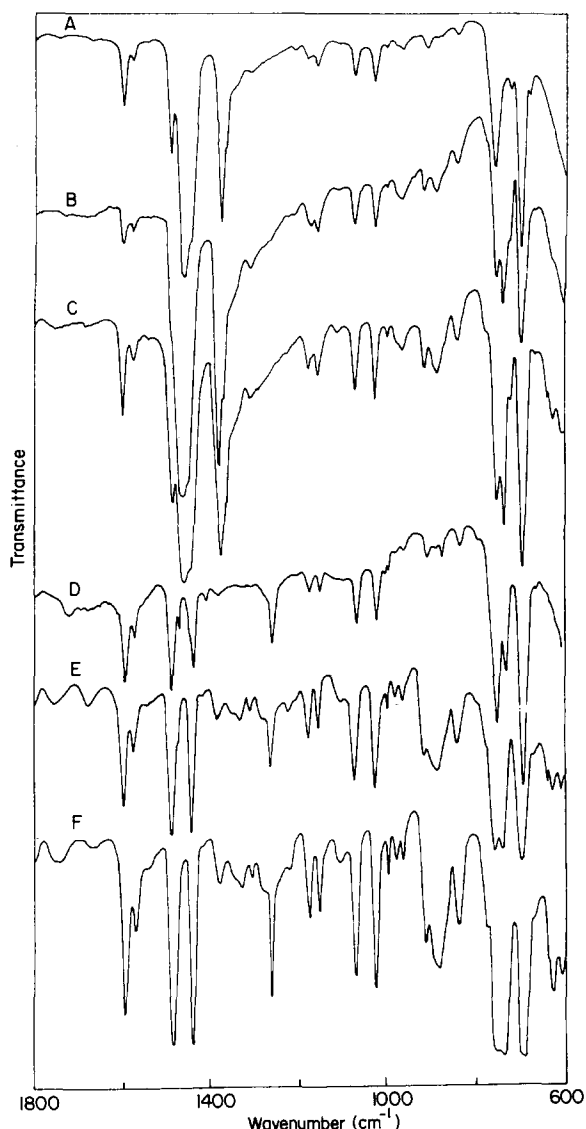


Figure 1 I.r. spectra of PPA samples: (A) catalyst $[\text{Ni}(\text{mtb})_2]$, reaction at reflux, nujol mull; (B) catalyst $[\text{Ni}(\text{mtb})_2]$, reaction at -40°C , nujol mull; (C) catalyst $[\text{Rh}(\text{cod})\text{Cl}]_2$, reaction at reflux, nujol mull; (D) catalyst $[\text{Ni}(\text{mtb})_2]$, reaction at reflux, film cast from CH_2Cl_2 solution on NaCl disc; (E) catalyst $[\text{Ni}(\text{mtb})_2]$, reaction at -40°C , film cast from CH_2Cl_2 solution on NaCl disc; (F) catalyst $[\text{Rh}(\text{cod})\text{Cl}]_2$, reaction at reflux, film cast from CH_2Cl_2 solution on NaCl disc

contain low-MW products, probably linear dimers or trimers, which can be detected by thin-layer chromatography but cannot be revealed by gas chromatographic analysis, probably because they are thermally polymerized in the column. As an example, we report the results for a reaction carried out in the presence of the complex (Table 2). Clearly the cyclic trimers and oligomers are

responsible for the low MW measured on crude PPA by the vapour-pressure osmometer (Table 1).

When PPA samples are recrystallized from benzene-methanol or benzene-petroleum ether the osmometric MW increases to values in the range 1700–2000 amu; the gas chromatographic analysis reveals that 1,2,4- and 1,3,5-TPB are completely removed. A MW determination of a $[\text{Ni}(\text{mtb})_2]$ -PPA sample performed by g.p.c. (calibration carried out by using a low-MW polystyrene standard) gave the following results. Crude sample: $M_n = 446$, $M_w = 770$, $M_w/M_n = 1.72$, $M_z = 1647$. Recrystallized sample: $M_n = 1510$, $M_w = 2346$, $M_w/M_n = 1.55$, $M_z = 4005$.

I.r. spectra

A typical i.r. spectrum (nujol mull) of PPA obtained in the presence of the Ni/S complexes at reflux is given in Figure 1A. The spectrum of the polymer obtained at -40°C with complex 4 is shown in Figure 1B. This i.r. spectrum is similar to the one of the stereoregular Rh-PPA³¹ (Figure 1C), characterized by a strong band at 740 cm^{-1} , which is absent, however, in the spectra of PPA obtained with the Ni/S complexes at reflux. (In the Rh catalyst, cod = cyclooctadiene.)

A new band at 1265 cm^{-1} was found in the i.r. spectra of the same PPA samples registered with films obtained by evaporation on NaCl discs of a CH_2Cl_2 solution, while the small band at 725 cm^{-1} disappeared under these conditions (Figures 1D–F). An additional band at 740 cm^{-1} is present in the spectrum of PPA obtained with complex 4 at reflux temperature (compare Figures 1A and 1D).

Influence of heating. The influence of heating was also investigated by warming PPA samples at constant temperature (160°C) for various periods, in air or under nitrogen atmosphere.

A sample of PPA prepared with complex 1 (MW 600 amu) containing 8.2% of 1,2,4- and 8.7% of 1,3,5-TPB was warmed at 160°C for 3 h in air. The mean MW and the cyclic trimer content were found to be the same before and after heating. No significant modifications in the i.r. spectra were observed (Figure 2A).

When PPA obtained with complex 4 at -40°C or with the $[\text{Rh}(\text{cod})\text{Cl}]_2$ complex were warmed at 160°C for 4 h, in their i.r. spectra the band at 740 cm^{-1} disappeared (Figures 2B and 2C). The MW of the latter PPA sample was reduced from 3000 amu (before heating) to 1500 amu (after heating). The cyclic trimers were absent before and after heating. The colour changed from orange-yellow to brown.

The PPA samples showed an analogous behaviour when warmed under nitrogen or in air, thus confirming their stability towards oxidation: only in a few cases were low-intensity carbonyl stretching bands at 1680 cm^{-1} (which can be attributed to oxidation) observed in the i.r. spectra of PPA samples warmed in air.

N.m.r. spectra

The ^{13}C n.m.r. spectrum of PPA obtained with complex 4 at -40°C (Figure 3a) is also similar to the one of the stereoregular PPA³¹.

The spectrum of the PPA obtained in the presence of the same catalyst at reflux is given in Figure 3b; the two signals at 142.86 and 139.29 ppm, due to quaternary

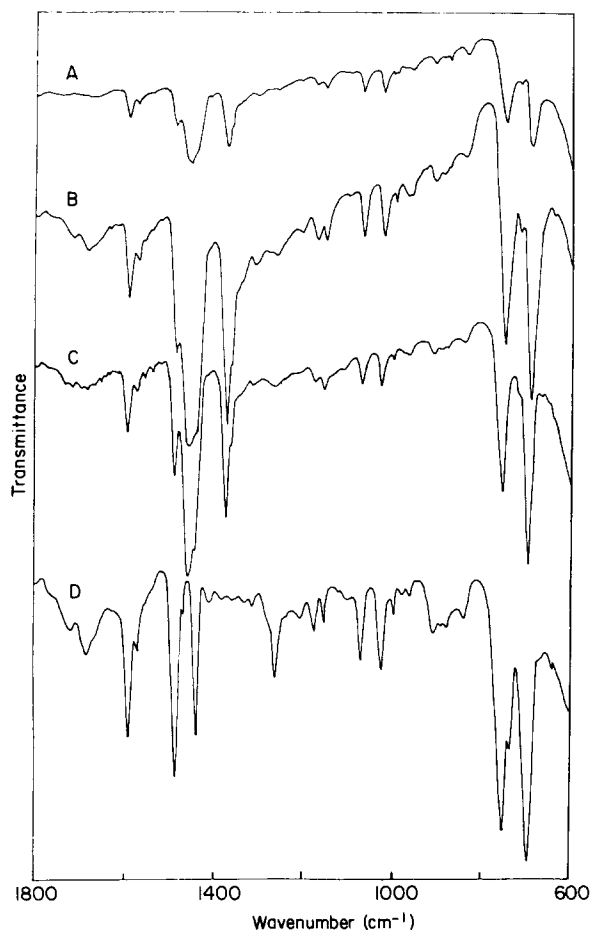


Figure 2 I.r. spectra of heated PPA samples: (A) catalyst $[\text{Ni}(\text{dtb})_2]$, heating at 160°C for 3 h in air; (B) catalyst $[\text{Ni}(\text{mtb})_2]$, reaction at -40°C , heating at 160°C for 4 h in air; (C) catalyst $[\text{Rh}(\text{cod})\text{Cl}]_2$, heating at 160°C for 4 h in air; (D) same sample as (B), film cast from CH_2Cl_2 solution

carbon atoms, cannot be clearly observed; other unresolved signals are in the range 125–130 ppm.

A similar spectrum was obtained with the PPA prepared with **4** at -40°C which was later warmed to 160°C for 4 h (Figure 3c); therefore a modification of the stereoregular structure takes place by warming. An expanded version of this spectrum is shown in Figure 4a. For comparison, similar spectra of a stereoregular PPA warmed for 4 h at 160°C (Figure 4b) and of a PPA obtained at reflux in the presence of complex **1** (Figure 4c) are reported too. The analogies of the three spectra (see tabulated peak values) indicate that similar configurations of PPA result after warming. The ^1H n.m.r. spectrum of PPA prepared with complex **4** at -40°C is given in Figure 5a. The signals at 5.85, 6.60 and 6.95 ppm, characteristic of stereoregular PPA, are present, but some additional bands and broad signals in the range 6–8 ppm indicate a lower degree of stereoregularity. As already reported³¹ the ^1H n.m.r. spectra are more sensitive to variations of the chain conformation.

The PPA prepared in the presence of Ni/S complexes at reflux exhibit ^1H n.m.r. spectra in which the signal at 5.8 ppm is absent and a broad feature is observed in the range 6.5–8 ppm. On the broad band envelope some signals become more or less separated and resolved. Two typical spectra are given in Figures 5b and 5c.

When PPA prepared with complex **4** at -40°C is

warmed to 160°C for 4 h the ^1H n.m.r. spectrum loses the typical band structure of stereoregular PPA (5.85, 6.6 and 6.95 ppm): the spectrum then consists of very broad signals between 7.2 and 8.1 ppm (Figure 5d). The same behaviour is observed by warming a stereoregular PPA (Figure 5e—see also modifications of the ^{13}C n.m.r. spectrum in Figure 4b).

In Figures 6a and 6b the ^1H n.m.r. spectra of a sample of PPA (obtained at reflux in the presence of the complex **1**) treated subsequently for 4 h at 160°C are given. The expanded spectrum indicates that the peaks between 7.2 and 8.1 ppm are not due (at least not exclusively) to 1,2,4- and 1,3,5-TPB (Figures 7a and 7b). The very intense peaks of 1,2,4-TPB at 7.13 ppm and the one at 7.61 ppm of 1,3,5-TPB are not evident among the typical signals of the various PPA samples, taken before and after heating.

We have observed also that the ^1H n.m.r. spectra of the more soluble fractions, which can be separated from the mother liquors of the polymerization reactions (Table

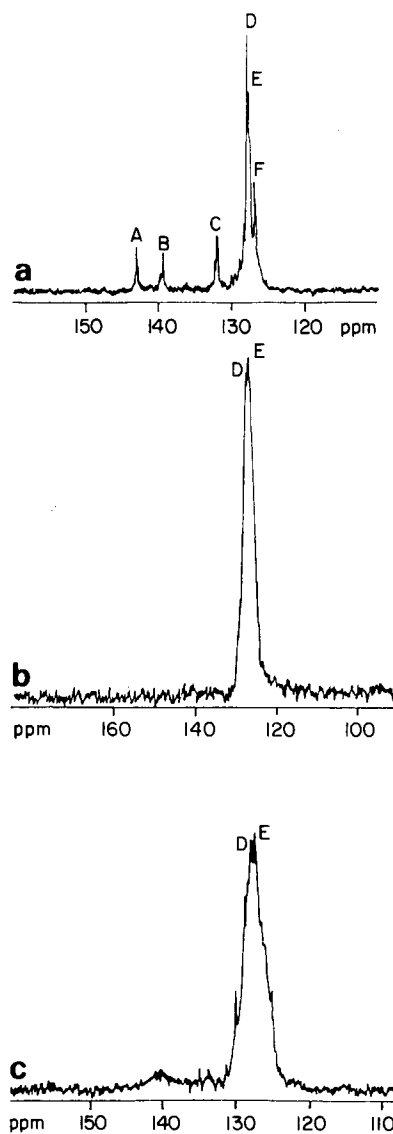


Figure 3 ^{13}C n.m.r. spectra (solvent CDCl_3) of PPA samples: (a) catalyst $[\text{Ni}(\text{mtb})_2]$, reaction at -40°C (A=142.860; B=139.289; C=131.812; D=127.785; E=127.535; F=126.706); (b) catalyst $[\text{Ni}(\text{mtb})_2]$, reaction at reflux (D=127.599; E=127.070); (c) catalyst $[\text{Ni}(\text{mtb})_2]$, reaction at -40°C , sample heated at 160°C for 4 h (D=127.901; E=127.348)

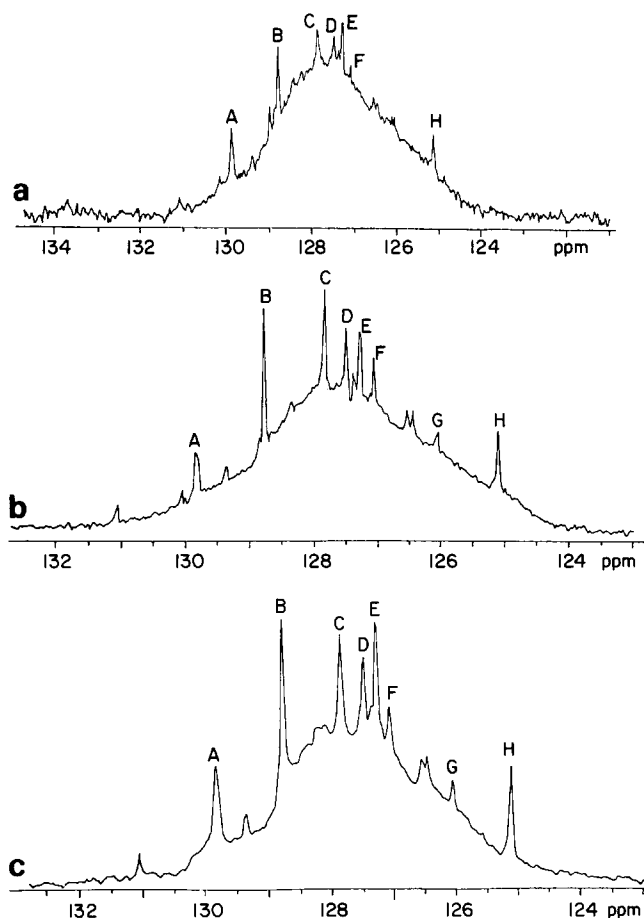


Figure 4 ^{13}C n.m.r. spectra (solvent CDCl_3) of heated (at 160°C for 4 h) PPA samples: (a) catalyst $[\text{Ni}(\text{mtb})_2]$, reaction at -40°C (A = 129.889; B = 128.834; C = 127.901; D = 127.535; E = 127.341; F = 127.127; H = 125.168); (b) catalyst $[\text{Rh}(\text{cod})\text{Cl}]_2$, reaction at reflux (A = 129.837; B = 128.805; C = 127.882; D = 127.529; E = 127.312; F = 127.092; G = 126.085; H = 125.136); (c) catalyst $[\text{Ni}(\text{dtb})_2]$, reaction at reflux (A = 129.837; B = 128.801; C = 127.878; D = 127.509; E = 127.312; F = 127.092; G = 126.078; H = 125.139)

2), are characterized by signals in the range 7.2–8.1 ppm, analogous to those reported in *Figure 6b*. Therefore, the separation of the various low-*MW* products and their characterization is now under investigation, in order to explore and then correlate their configuration and conformation to those of the higher-*MW* fractions.

Thermal analysis

The d.t.a.–t.g. curves observed depend on the synthesis procedure and pretreatments of the PPA samples. The results of thermal analysis can be summarized as follows:

(i) The d.t.a. curves of PPA samples obtained with $[\text{Rh}(\text{cod})\text{Cl}]_2$ or complex **4** at -40°C exhibit an exothermic peak in the range $165\text{--}185^\circ\text{C}$ without any weight loss. These samples show i.r. spectra with a band at 740 cm^{-1} and ^1H n.m.r. spectra with signals at 5.85, 6.60 and 6.95 ppm. The exothermic reaction has been attributed to a *cis-trans* isomerization³⁹. For all of these samples the d.t.a. curves exhibit an endothermic reaction at temperatures higher than $230\text{--}250^\circ\text{C}$, when the t.g. curves indicate a drastic weight loss due to the degradation of the polymer.

(ii) The same samples after heating in air for 1–4 h at constant temperature at around 160°C give d.t.a. curves with a broad endothermic peak in the range $130\text{--}200^\circ\text{C}$, accompanied by a slight weight loss (2–4%), which takes

place above 150°C . Also for these samples a drastic endothermic decomposition reaction occurs above $230\text{--}250^\circ\text{C}$.

(iii) The samples of PPA (obtained with Ni/S complexes at reflux) do not reveal any reaction in the range $160\text{--}180^\circ\text{C}$. Marked decomposition of the polymers takes place, also in this case, at about 230°C .

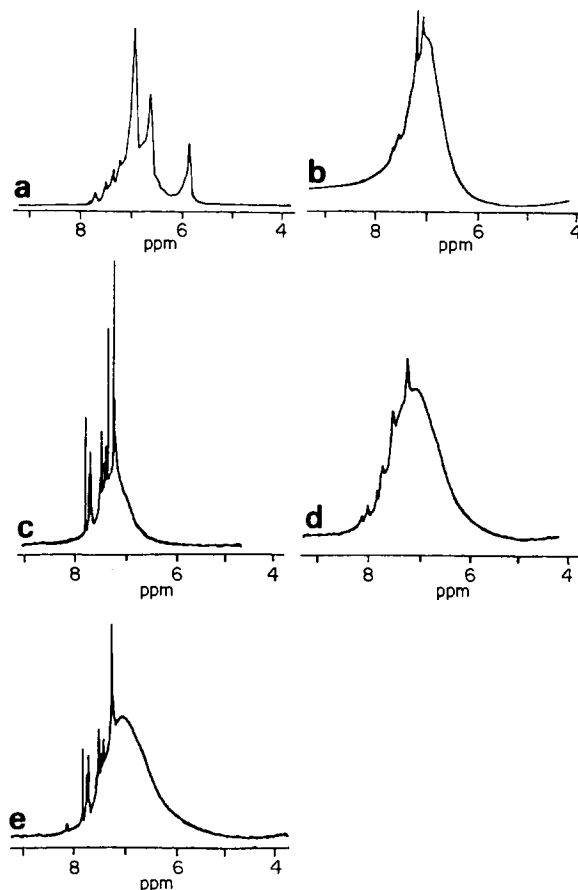


Figure 5 ^1H n.m.r. spectra (solvent CDCl_3) of PPA samples: (a) catalyst $[\text{Ni}(\text{mtb})_2]$, at -40°C ; (b) catalyst $[\text{Ni}(\text{mtb})_2]$, at reflux; (c) catalyst $[\text{Ni}(\text{dtb})_2]$, at reflux; (d) same sample as (a), heated at 160°C for 4 h; (e) catalyst $[\text{Rh}(\text{cod})\text{Cl}]_2$, heating at 160°C for 4 h

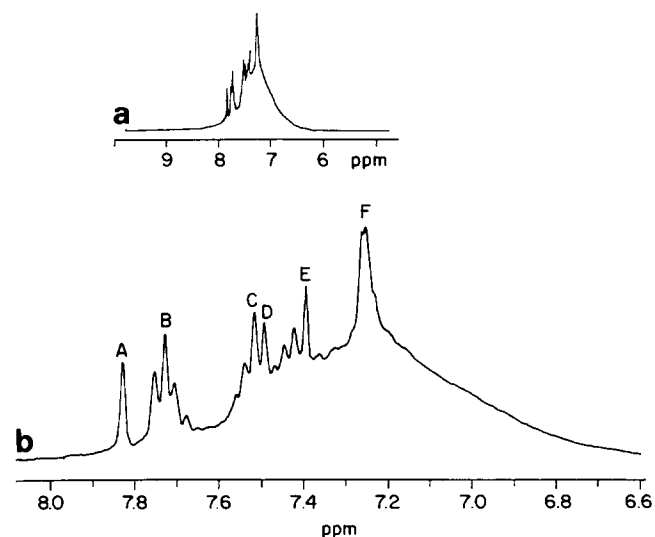


Figure 6 ^1H n.m.r. spectra (solvent CDCl_3) of PPA sample: (a) catalyst $[\text{Ni}(\text{dtb})_2]$, reaction at reflux, heated at 160°C for 4 h; (b) expanded spectrum of (a) (A = 7.826; B = 7.725; C = 7.515; D = 7.490; E = 7.391; F = 7.252)

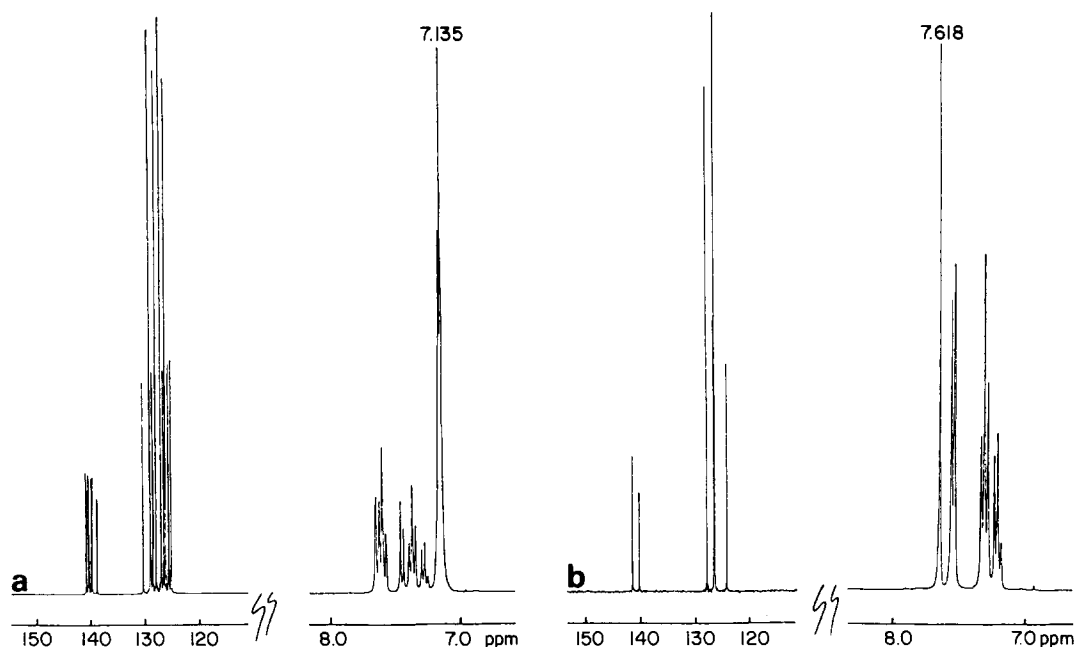

 Figure 7 ^{13}C and ^1H n.m.r. spectra (solvent CDCl_3) of (A) 1,2,4-TPB and (B) 1,3,5-TPB

 Table 3 Doping and conductivity σ of polyphenylacetylene^a

Catalyst	Dopant (%) (w/w)	Doping solvent	σ ($\Omega^{-1} \text{cm}^{-1}$)						Elemental analysis (%)			
			Fresh	After 3 days	After 1 month	After 2 months	After 3 months	After 4 months	C	H	I	Fe
[Ni(dtb) ₂] (1)	I ₂ (50)	THF	6.6×10^{-6}	6.6×10^{-6}					48.35	3.31	33.23	
	I ₂ (75)	THF	4×10^{-6}	4×10^{-6}	4×10^{-8}							
	FeCl ₃ (50)	THF	1×10^{-9}						41.69	3.96		10.64
[Ni(N,N-ddtc) ₂] (2)	I ₂ (50)	THF	3.3×10^{-6}				1.9×10^{-7}	4.3×10^{-7}	49.89	3.44	41.16	
	I ₂ (75)	THF	8.3×10^{-6}			1×10^{-7}	2.3×10^{-7}	45.86	2.99	42.44		
[Ni(oatp) ₂] (3)	I ₂ (50)	THF	1.4×10^{-5}		4.2×10^{-5}	6.6×10^{-6}	3.2×10^{-7}	3.2×10^{-7}	53.47	3.44	35.60	
	I ₂ (75)	THF	9×10^{-4}	2.1×10^{-5}			2×10^{-7}					
[Ni(mtb) ₂] (4)	I ₂ (50)	THF	4.3×10^{-5}		3.7×10^{-5}	4.1×10^{-5}		5.3×10^{-7}				
	I ₂ (75)	THF	6.6×10^{-5}	1.8×10^{-5}								
	I ₂ (50)	CH ₃ COCH ₃	6.6×10^{-8}		2.1×10^{-8}	2.1×10^{-8}		4×10^{-8}	49.95	3.60	39.57	
	I ₂ (75)	CH ₃ COCH ₃	1.7×10^{-8}	7.7×10^{-8}					46.88	4.22	48.25	
	I ₂ (50)	C ₆ H ₆	1.2×10^{-7}			4×10^{-7}			60.8	4.32	21.60	
Bu ₄ N[Ni(tdt) ₂] (5)	I ₂ (50)	THF	1.5×10^{-6}			1.5×10^{-8}			49.66	3.10	40.85	
	I ₂ (75)	THF	2.7×10^{-6}	5×10^{-8}			1.6×10^{-8}		45.73	3.04	45.38	
	I ₂ (50)	C ₆ H ₆	1.5×10^{-9}			1.8×10^{-9}			75.37	4.31	16.25	

^a Undoped PPA, $\sigma = 10^{-14}$ – $10^{-13} \Omega^{-1} \text{cm}^{-1}$

(iv) A sample of (iii) dissolved in CH_2Cl_2 and left to dry in air for two days exhibits a slow weight loss between 70 and 200°C, which may be due to adsorbed solvent, rather tightly bound to the polymer. Above 230°C polymer decomposition occurs in the same way as observed for the other samples.

Conductivity measurements

The conductivity of various PPA samples was measured on pressed pellets. Values in the range 10^{-13} – $10^{-14} \Omega^{-1} \text{cm}^{-1}$ were found. These values are close to the conductivity of undoped PPA, prepared with $[\text{Rh}(\text{cod})\text{Cl}]_2$. PPA samples were doped with I₂ and FeCl₃ in THF. In some cases the influence of other solvents on the doping procedure and on the resulting conductivity was also examined. Results are given in Table 3.

The conductivity of PPA doped with I₂ (nominal 50% and 75% w/w) in THF varies in the range 10^{-4} – $10^{-6} \Omega^{-1} \text{cm}^{-1}$. The highest values were measured on freshly prepared samples in which THF was not completely removed under vacuum, because it was found that by increasing the I₂ content the elimination of the solvent under vacuum was more and more difficult. To explain this fact we have studied the influence of I₂ on THF and we have observed that THF, in the presence of I₂, undergoes a partial polymerization⁴⁰. Therefore the systems obtained are a mixture of PPA–THF polymer and iodine (which is present as I₃⁻ as was demonstrated by Raman spectroscopy⁴⁰). The elemental analyses indicate that the iodine contents vary in the range 30–40% for various samples doped in THF at 50% w/w and 40–45% for samples doped with I₂ at 75% w/w.

An increase in conductivity does not seem to

correspond to an increase in the iodine content, but it appears instead correlated to the amount of unremoved THF and to the relative humidity of the measurement chamber. In the presence of high humidity (over 90%) the PPA pellets undergo rapid deterioration. A similar dependence of conductivity on humidity was also observed for pellets of iodine-doped PPA observed with Rh complexes. Detailed results will be reported in a subsequent paper. At room conditions (60–70% relative humidity) the doped PPA samples are rather stable. The conductivity variations of 1–2 orders of magnitude, observed on samples stored in air for 2 months, can be correlated to the elimination of residual unpolymerized THF, and (mostly) to fluctuations of room humidity.

Also other solvents have been used in the doping procedure, in order to investigate their effect on conductivity. When doping of PPA with iodine (nominal 50% w/w) is carried out in C₆H₆, lower uptake of iodine takes place (see Table 3: percentage of I₂ determined 16.25%) and the conductivity is $\approx 10^{-9} \Omega^{-1} \text{cm}^{-1}$.

When CH₃COCH₃ was used as solvent, the uptake of I₂ (nominal 50% w/w) in the doped polymer was about 40% (determined by elemental analysis) and the conductivity was $10^{-6} \Omega^{-1} \text{cm}^{-1}$.

PPA was doped also with FeCl₃ in THF. The conductivity of FeCl₃-doped samples is lower than that of I₂-doped PPA, but the systems are more stable. Their conductivity varies linearly with relative humidity, as reported in a separate paper⁴¹.

The FeCl₃-PPA samples might find a practical application in the preparation of humidity sensors.

DISCUSSION

The new investigations on PPA obtained with Ni/S complex catalysts require the correlations between i.r. and n.m.r. spectra and structures of PPA polymers to be reconsidered.

For the same PPA, variations of the intensities of the i.r. bands in the range 700–760 cm⁻¹ depending on the preparation of samples (nujol mulls or films; see Figures 1 and 2) were observed.

In the literature, however, the phenylacetylene polymers are commonly classified as *cis* or *trans* on the basis of the ratio between the two bands at 740–760 cm⁻¹ as proposed by Simionescu⁴². The PPA samples prepared in the course of this work gave i.r. spectra (as nujol mulls) in which the band at 740 cm⁻¹ was absent. These spectra suggest a *trans* structure, but when the spectra are recorded for films cast from CH₂Cl₂, bands at 740 cm⁻¹, which are regarded to be characteristic of *cis* sequences, appear. It should be pointed out that these modifications of the spectra of films of PPA in the range 740–760 cm⁻¹ are not followed by a corresponding change in the range 800–910 cm⁻¹, where bands of lower intensity are observed. These bands were correlated by Masuda to the *cis-trans* content of PPA⁴³.

Also we have observed that other i.r. bands can be clearly observed or masked depending on the preparation method of the i.r. sample, such as a band at 725 cm⁻¹, which was never previously discussed, and a band at 1265 cm⁻¹, which was considered characteristic of a *trans* structure⁴¹ and we found to be present in both Ni/S-PPA or Rh-PPA films when prepared from CH₂Cl₂. The bands at 740 and 1265 cm⁻¹ present in the i.r. spectra of PPA films, cast from CH₂Cl₂, are probably due to the

solvent, which is rather strongly bound to PPA, as was proved by the thermogravimetric analysis, and which exhibits i.r. bands at these frequencies.

These results indicate that the proposed methods for the determination of the *cis-trans* contents of PPA should be treated with considerable caution.

The [Ni(mtb)₂] complex (4) gives at -40°C in 6 months a PPA analogous to the one obtained at higher temperatures with the more active Rh catalysts, which give a stereoregular polymer characterized by well resolved ¹H and ¹³C n.m.r. spectra³¹. In order to increase the reaction rate in the presence of the catalytically less active Ni/S complexes, reactions must be carried out at reflux; therefore the growing PPA chains lose their stereoregularity and the n.m.r. spectra become broad and unresolved.

Low-intensity signals can be observed in the ¹H and ¹³C n.m.r. spectra of the Rh-PPA or Ni/S-PPA before and after heating. These signals can be correlated to low-MW products, which are formed in a larger amount in the presence of the Ni/S complexes, and seem to be the same in both the Rh-PPA and Ni/S-PPA. These products are now under investigation.

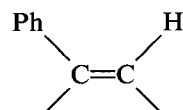
The modifications induced by treatment at 160°C of Ni/S-PPA (at -40°C) or Rh-PPA seem to be the same as shown by the similarity of changes in i.r. and n.m.r. spectra and d.t.a. curves. The i.r. and n.m.r. spectra of the heated PPA are similar to the ones of the Ni/S-PPA prepared at reflux. Their d.t.a. curves and also some other properties are different, however. For instance, pellets for conductivity measurements cannot be prepared with the heated polymers since they are very brittle. The MW of the heated Rh-PPA was reduced to about 1200 amu, but cyclic trimers before and even after heating have not been found by gas chromatographic analysis. In the Ni/S-PPA obtained at reflux 1,2,4- and 1,3,5-TPB are instead present in various amounts, as reported in Table 1.

Thermal degradation of the PPA chains leading to cyclic trimers was proposed by Berlin⁴⁴ and by Simionescu⁴⁵ on the basis of a moderate increase in the intensity of signals at about 7.6 ppm in the ¹H n.m.r. spectra of heated PPA samples; however, these authors did not confirm their hypothesis by a gas chromatographic analysis.

The conductivities of undoped Rh-PPA and Ni/S-PPA (at reflux) are comparable, even if the g.p.c. MW of Rh-PPA (50 000–100 000 amu³¹) are much higher than the MW of Ni/S-PPA. The FeCl₃-doped samples of Rh-PPA or Ni/S-PPA exhibit similar stability and conductivity behaviour towards humidity and temperature⁴¹. In the i.r. spectra of the doped PPA (nujol mulls) the band at 740 cm⁻¹ is absent.

By comparing the experimental observations reported above with those in the literature on PPA prepared with different catalysts or polymerization procedures, we can draw some conclusions.

It was suggested that the activation of the triple bond by coordination to a transition-metal atom results in a *cis* opening of the triple bond^{18,28,46}. Therefore *cis* units of PA



must be present in the PPA growing chains. We have been able to prepare by Rh catalysts^{31,47}, as well as by Ni/S catalysts at -40°C , a stereoregular PPA, with probably a *cis-transoidal* structure.

The presence of bulky phenyl groups, however, can hinder the planarity of the growing chain, by inducing coiled structures derived from rotations around single bonds as proposed by Berlin⁴⁴ and by Kern⁴⁸. The rotation around single bonds can take place to various extents, during the polymerization reaction or by different treatments (heating, doping, effect of solvents).

An all *trans-transoidal* polymer, with a planar structure of the main chain, seems to be unlikely, because it would only be possible, due to high steric interactions, if all the phenyl groups were perpendicular to the chain.

Berlin⁴⁴ reported that different coiled structures of PPA should have different signals in the ^1H n.m.r. spectra. Martin *et al.*⁴⁹ observed that in hydrocarbons formed by condensed benzene rings, progressive deviations from coplanarity induce shifts and broadening of the ^1H n.m.r. signals. Therefore, in our opinion, the broad n.m.r. spectra so far reported in the literature for various PPA should be correlated to coiled structures of the PPA chain.

In relation to the effect of heating on PPA structural modifications, Katz¹⁸, by ^{13}C nutation spectra, demonstrated that in some samples of PPA the double bonds, which are fixed at low temperature, move on warming. Simionescu⁵⁰ found an isomerization energy for PPA of about 10 kcal mol^{-1} , very close in value to the energy necessary to give a delocalized π -electron system of the main chain. E.s.r. measurements^{51,52} carried out on different PPA samples showed that PPA free radicals exist and are very stable; their stability is due to a π delocalization, which can be limited to a few monomer units. The presence of defects on the PPA chains is the origin of different segment structures such as *cis-transoidal* and *trans-cisoidal* ones, each of which can give different coiled structures.

All these phenomena can explain why regular structures of PPA are unstable and cannot be easily obtained, and also why it may be misleading to limit the discussion of the PPA structural modifications only to a *cis-trans* isomerization.

These considerations provide further indirect support to our supposition that sharp n.m.r. signals of PPA samples should correspond to a high degree of regioselectivity achieved in the C-C coupling step.

From the coordination chemistry side, the results obtained with the Ni/S complexes proved our starting hypothesis to be more or less correct. As a further goal it could be defined that similar ligands with somewhat more activating electron balance should be found. Work to achieve this aim is in progress.

ACKNOWLEDGEMENT

The authors wish to thank MPI (Ministero della Pubblica Istruzione, Italy) for financial support of this work.

REFERENCES

- Saxman, A. M., Liepins, R. and Aldissi, M. *Prog. Polym. Sci.* 1985, **11**, 57; Kröhnke, C. and Wegner, G. in 'Houben-Weil, Methoden der Organischen Chemie' (Eds H. Bart. and J. Falbe), Vol. E20, 'Makromolekulare Stoffe', Part 2, Thieme, Stuttgart, 1987, p. 1312; Naarman, H. *Synth. Metals* 1987, **17**, 223; Stelzec, F. and Leising, G. *Osterr. Chem. Z.* 1988, **89**, 136; Madruga, E. L. and San Roman, J. *Rev. Plast. Mod.* 1988, **55** (380), 213; and see also references cited within these works
- Schopov, I. and Iossifov, C. *Makromol. Chem., Rapid Commun.* 1983, **4**, 659
- Bainon, B., Belfira, A., Camps, M. and Montheard, J. P. *Makromol. Chem., Rapid Commun.* 1984, **5**, 477
- Iakubrowski, J. J. and Subramanian, R. V. *Polym. Bull.* 1979, **1**, 785
- Takai, Y., Inoue, M., Mizutani, T. and Ieda, M. *J. Phys. (D), Appl. Phys.* 1985, **18**, 1637
- Masuda, T., Kuwana, Y., Yamamoto, K. and Higashimura, T. *Polym. Bull.* 1980, **2**, 823
- Chiang, A. C., Waters, P. F. and Aldridge, M. H. *J. Polym. Sci., Polym. Chem. Edn* 1982, **20**, 1807
- Shen, Z. and Faron, M. F. *Polym. Bull.* 1983, **10**, 8
- Shen, Z. and Faron, M. F. *J. Polym. Sci., Polym. Chem. Edn* 1984, **22**, 1009
- Masuda, T., Yoshizawa, T., Okano, Y. and Higashimura, T. *Polymer* 1984, **25**, 503
- Kumor, V. G., Shoba, T. S. and Rao, K. V. C. *Tetrahedron Lett.* 1985, **26**, 6245
- Voicechovsky, Y. P., Slivinsky, E. V., Fichte, B. B. and Sokitey, S. M. *J. Polym. Sci., Polym. Chem. Edn* 1985, **23**, 1641
- Katz, T. J. and Lee, S. J. *J. Am. Chem. Soc.* 1980, **102**, 422
- Katz, T. J., Lee, S. J., Nair, M. and Savage, E. B. *J. Am. Chem. Soc.* 1980, **102**, 7940
- Katz, T. J., Savage, E. B., Lee, S. J. and Nair, M. *J. Am. Chem. Soc.* 1980, **102**, 7942
- Katz, T. J., Ho, T. H., Shih, N. Y., Ying, Y. C. and Stuart, V. I. W. *J. Am. Chem. Soc.* 1984, **106**, 2659
- Han, C. C. and Katz, T. J. *Organometallics* 1985, **4**, 2186
- Katz, T. J. and Hacker, S. M. *J. Am. Chem. Soc.* 1985, **107**, 2182
- Landon, S. J., Shulman, P. M. and Geoffrey, G. L. *J. Am. Chem. Soc.* 1985, **107**, 6739
- Mayer, A., Lee, K., Kjelsberg, M. A. and Van Engen, D. *J. Am. Chem. Soc.* 1986, **108**, 6079
- Whitte, W. M., Kang, E. T., Ehrlich, P., Carrol, J. B. Jr and Allendoerfer, R. D. *J. Polym. Sci., Polym. Chem. Edn* 1981, **19**, 1011
- Bartl, A., Frendenberg, G., Frohner, J., Pietrass, B. and Wuckel, L. *Makromol. Chem.* 1983, **184**, 2187
- Hwang, J. S. and Tsonis, C. P. *Macromolecules* 1983, **16**, 736
- Hwang, J. S., Saleem, M. M. and Tsonis, C. P. *Macromolecules* 1985, **18**, 2051
- Tabata, M., Matsuura, T., Okawa, S., Sohma, T. and Yokota, K. I.C.S.M. 86, 1-6 June 1986, Kyoto, p. 67
- Langner, A. and Ehrlich, P. *Synth. Metals* 1987, **17**, 419
- Sanford, T. I., Allendoerfer, R. D., Kang, E. T. and Ehrlich, P. *J. Polym. Sci., Polym. Phys. Edn* 1980, **18**, 2277
- Percec, V. *Polym. Bull.* 1983, **10**, 1
- Percec, V. and Rinaldi, P. L. *Polym. Bull.* 1983, **9**, 548
- Percec, V. and Rinaldi, P. L. *Polym. Bull.* 1983, **9**, 582
- Furlani, A., Napoletano, C., Russo, M. V. and Feast, W. J. *Polym. Bull.* 1986, **16**, 311; Furlani, A., Licocchia, S., Russo, M. V., Camus, A. and Marsich, N. *J. Polym. Sci. (A)*, *Polym. Chem.* 1986, **24**, 991
- Bloor, D. and Rhode, O. *Chem. Phys. Lett.* 1978, **56**, 244
- Furlani, A., Bicev, P., Carusi, P. and Russo, M. V. *J. Polym. Sci., Polym. Lett.* 1971, **9**, 19
- Bicev, P., Furlani, A. and Sartori, G. *Gazz. Chim. Ital.* 1973, **103**, 849; Russo, M. V. and Furlani, A. *Tetrahedron Lett.* 1976, **30**, 2656
- Furlani, A., Bicev, P., Russo, M. V. and Fiorentino, M. *Gazz. Chim. Ital.* 1977, **107**, 373
- Clark, H. C. and Manzer, L. E. *Inorg. Chem.* 1974, **13**, 1291; Sen, A. and Lai, T. W. 'Transition Met. Catal. Polym.', Symp. Ser. Vol. 4, MMI Press, 1983, p. 341
- Luttinger, L. B. *Chem. Ind. (Lond.)* 1960, 1135; *J. Org. Chem.* 1962, **27**, 1591; Luttinger, L. B. and Colthup, E. C. *J. Org. Chem.* 1962, **27**, 3752; Green, M. L. H., Neheme, M. and Wilkinson, G. *Chem. Ind. (Lond.)* 1960, 1136; Champetier, G. and Martynoff, M. *Bull. Soc. Chim. Fr.* 1961, 2083; Martella, J. P. and Kaska, W. C. *Tetrahedron Lett.* 1968, **47**, 4889; Ostoja-Starzewski, A. K. and Witte, J. *Angew. Chem., Int. Edn Engl.* 1988, **27**, 839
- Hieber, W. and Brücke, R. *Z. Anorg. Allg. Chem.* 1952, **269**, 13; Schrauzer, G. N. and Mayweg, V. T. *J. Am. Chem. Soc.* 1965, **87**, 1483; Stiefel, E. I., Waters, J. H., Billig, E. and Gray, H. B. *J. Am. Chem. Soc.* 1965, **87**, 3016; Williams, R., Billig,

- E., Waters, J. H. and Gray, H. B. *J. Am. Chem. Soc.* 1966, **88**, 43; Baker-Hawkes, M. J., Billig, E. and Gray, H. B. *J. Am. Chem. Soc.* 1966, **88**, 4870
- 39 Cukor, P. and Rubner, M. *J. Polym. Sci., Polym. Phys. Edn* 1980, **18**, 909
- 40 Polzonetti, G., Faruffini, V., Furlani, A. and Russo, M. V. *Synth. Metals* 1989, **29**, E495; Ferraro, J. R., Martin, K., Furlani, A. and Russo, M. V. *J. Appl. Spectrosc.* 1984, **38**, 267
- 41 Furlani, A., Russo, M. V., Ciancusi, A. M., Bruno, F., Mercuri, R., Paoletti, A. and D'Amico, A. *Chemtronics* 1988, **12**, 388
- 42 Simionescu, C. I., Percec, V. and Dumitrescu, S. *J. Polym. Sci., Polym. Chem. Edn* 1977, **15**, 2497
- 43 Masuda, T., Sasaki, N. and Higashimura, T. *Macromolecules* 1975, **8**, 717
- 44 Berlin, A. A. and Cherkashin, M. I. *Vysokomol. Soedin. (A)* 1971, **13**, 2289
- 45 Simionescu, C. I. and Percec, V. *J. Polym. Sci., Polym. Chem. Edn* 1980, **18**, 147
- 46 Bán, M. I., Révész, M., Bálint, I., Váradi, G. and Pályi, G. *J. Mol. Struct. (Theochem)* 1982, **88**, 357; Pályi, G., Váradi, G. and Markò, L. in 'Stereochemistry of Organometallic and Inorganic Compounds' (Ed. I. Bernal), Elsevier, Amsterdam, 1986, Vol. 1, p. 358; and references cited in these works
- 47 Furlani, A., Napoletano, C., Russo, M. V., Camus, A. and Marsich, N. *J. Polym. Sci. (A), Polym. Chem.* 1989, **27** (1), 75
- 48 Kern, R. J. *J. Polym. Sci. (A-1)* 1969, **7**, 621
- 49 Martin, R. H., Defay, N., Figeys, H. P., Flammang-Barbieux, M., Cosyn, J. P., Gelbcke, M. and Schurter, J. J. *Tetrahedron* 1969, **25**, 4985
- 50 Simionescu, C. and Negulescu, I. I. *J. Macromol. Sci., Chem. (A)* 1985, **22** (5-7), 1001
- 51 Cordischi, D., Furlani, A., Bicev, P., Russo, M. V. and Carusi, P. *Gazz. Chim. Ital.* 1971, **101**, 526
- 52 Holob, G. M., Ehrlich, P. and Allendoerfer, R. D. *Macromolecules* 1972, **5**, 569