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Synthesis and Study of the Thermal and Chiro-Optical Properties of Polyacetylenes with Bulky Side Groups: Poly(1-ethynyl-4-biphenyl), Poly(1-ethynyl-4- phenoxybenzene) and Poly(1-ethynyl-4-pentylbenzene)

Franco Cataldo[a][b]; Ornella Ursini[c]; Giancarlo Angelini[c]
[a] Lupi Chemical Research, Rome, Italy [b] INAF- Osservatorio Astrofisico di Catania, Catania, Italy [c] Institute of Chemical Methodologies CNR, Rome, Italy

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Synthesis and Study of the Thermal and Chiro-Optical Properties of Polyacetylenes with Bulky Side Groups: Poly(1-ethynyl-4-biphenyl), Poly(1-ethynyl-4-phenoxybenzene) and Poly(1-ethynyl-4-pentylbenzene)

FRANCO CATALDO[1,*], ORNELLA URSINI[2] and GIANCARLO ANGELINI[2]

[1] *Lupi Chemical Research, Via Casilina 1626/A, 00133 Rome, Italy and INAF- Osservatorio Astrofisico di Catania, Via S. Sofia 78, 95123 Catania, Italy.*
[2] *Institute of Chemical Methodologies CNR Via Salaria Km. 29,300 00016 Monterotondo Stazione (Rome) Italy*

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The monosubstituted acetylenes 1-ethynyl-4-biphenyl, 1-ethynyl-4-phenoxybenzene and 1-ethynyl-4-pentylbenzene were polymerized to the corresponding polyacetylenes with bulky side substituents: PEBIP, PEPHENO and PEPB, respectively, using a Rh(I) complex as polymerization catalyst. The FT-IR and UV-VIS spectra of PEBIP, PEPHENO and PEPB were studied using the corresponding spectra of polyphenylacetylene (PPA), polytolylacetylene (PETOL) and poly(1-ethynyl-naphthalene) PEN as reference. Based on the spectral analysis, high cis-trasoid structures were assigned to PEBIP, PEPHENO and PEPB. The specific optical rotation of PEBIP, PEPHENO and PEPB was measured in the chiral solvent α(-)pinene and, only for PEPB, also in α(+)pinene. It was found that even at low concentration PEBIP, PEPHENO and PEPB cause changes in the specific optical rotation of the chiral medium where they have been dissolved. This phenomenon has not been observed when toluene or atactic polystyrene are dissolved in the same chiral solvent in similar concentration. This suggests that the polyacetylenes with bulky side groups are able to rearrange in a helical configuration (prevalently right-handed or vice-versa, depending on the type of chiral medium used) once hosted in a chiral medium giving a contribution to the chirality of the solvent where they have been dissolved. The thermal stability of PEBIP, PEPHENO and PEPB was studied under N_2 flow by thermal analysis (TGA, DTG and DTA) in comparison to reference monosubstituted polyacetylenes PPA, PETOL and PEN. The results show that the thermal stability of monosubstituted polyacetylenes is greatly improved by the presence of bulky substitutents as theoretically expected, and similarly, also the char-forming tendency increases with the bulkiness of the side groups.

Keywords: Polyacetylenes, bulky side groups, FT-IR spectroscopy, UV-VIS spectroscopy, helical conformation, chirality, interaction with chiral media, polarimetry, thermal stability, char formation tendency.

1 Introduction

Rh(I) complexes are effective polymerization catalysts both for acetylene (1, 2) and for monosubstituted acetylenes (3). Particularly effective polymerization catalysts of acetylenes are the complexes with cyclooctadiene (Cod) and with norbornadiene (NBD): $[Rh(Cod)Cl]_2$ and $[Rh(NBD)Cl]_2$ respectively (2–4). An amine or an alkoxyde co-catalyst is always needed to initiate the polymerization reaction to cleave the Rh(I) complex producing the active specie which initiates the polymerization. The polymerization of acetylene and monosubstituted acetylenes with Rh(I) complexes is stereospecific (2, 4) and, in appropriate conditions, can be also living (5).

Monosubstituted polyacetylenes are stable semiconductive polymers with interesting physical properties such as magnetic susceptibility and polyradical structure (6, 7), non-linear optical properties (8) and photoconductivity (9). Additionally, monosubstituted polyacetylenes have potential applications in the synthesis of perm-selective membranes for instance in gas separation (10) and in gas sensors devices (11). At present, great interest on polyacetylenes is focused on their ability to interact with chiral media so that a right- or left-handed helical conformation is induced in these macromolecules with the interaction with chiral additives (12, 13). This has raised the concept of "memory

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*Address correspondence to: Franco Cataldo, Lupi Chemical Research, Via Casilina 1626/A, 00133 Rome, Italy and INAF-Osservatorio Astrofisico di Catania, Via S. Sofia 78, 95123 Catania, Italy. E-mail: franco.cataldo@fastwebnet.it of macromolecular helicity" (13) and polyacetylenes are used in complex macromolecular self assembly, in building chiral supramolecular structures (14, 15) and in the detection and amplification of chirality (16). In the field of chiral detection, chiral amplification and chiral self-assembly, the application of polyacetylenes is currently flourishing (17–22). Polyacetylenes show potential also as materials for organic solar cells thanks to their semiconductive and photoconductive properties (23, 24). Thanks to the most recent synthetic and technological achievements (25–29), the attention to polyacetylenes application to solar cells is going to flourish as well.

Additionally, polyacetylenes can be used as model molecules for conjugated addition reactions (30), and are also of interest in astrochemistry (31, 32). In particular, poly(phenylacetylene) has been synthesized and cyclized to macromolecular polycyclic aromatic hydrocarbon (32) which are thought to be present in certain interstellar and circumstellar media (33, 34). In this context, the polymerization of monosubstituted acetylenes with bulky side groups could be an interesting starting point to produce new and very large polycyclic aromatic hydrocarbons (32). Such polymerization although thermodynamically allowed $\Delta G^{\circ}_{polym} = -108$ kJ/mol, may be kinetically constrained by the steric hindrance of the side group. However, the combination of $[Rh(NBD)Cl]_2$ with t-BuOK co-catalyst has been proved to be effective in the polymerization of 1-ethynylnaphthalene (35), having the bulky naphthalene side group. The present work is an extension of such promising results to the polymerization of monsubstituted acetylene monomers with new bulky side substituents like biphenyl, phenoxybenzene and 4-pentylbenzene (Scheme 1).

2 Experimental

2.1 Materials and Equipment

The monosubstituted acetylene monomers, namely phenylacetylene, 1-ethynyl-naphthalene, 4-tolylacetylene, 1-ethynyl-4-biphenyl, 1-ethynyl-4-phenoxybenzene and 1-ethynyl-4-pentylbenzene were obtained from Aldrich and used as received.

The complex $[Rh(NBD)Cl]_2$ with NBD = norbornadiene, and the co-catalyst potassium tert-butoxide (t-BuOK) were obtained from Fluka.

Solvents: $\alpha(-)$pinene, $\alpha(+)$pinene, tetrahydrofuran (THF) and methanol were obtained from Aldrich or Fluka. The FT-IR spectra were obtained on a Nicolet IR-300 from Thermo-Electron. The FT-IR spectra of the liquid monomers were recorded in transmittance as thin film between two KBr disks; the spectra of solid monomers were obtained in KBr pellets. Similarly, the FT-IR spectra of all polymers were obtained in transmittance mode with the polymer embedded in KBr pellet.

Polarimetric measurements were made on a Jasco polarimeter model P2000 equipped with a monochromator to select the wavelengths visible in the corresponding D line of Na (589 nm) and those of mercury at 578, 546 and 436 nm. The sensitivity of the polarimeter is 1/1000 of deg.

The thermal analysis of all samples were made on a Linseis thermobalance model L81+DTA under N_2 flow (20 L/h).

2.2 Typical Polymerization Procedure

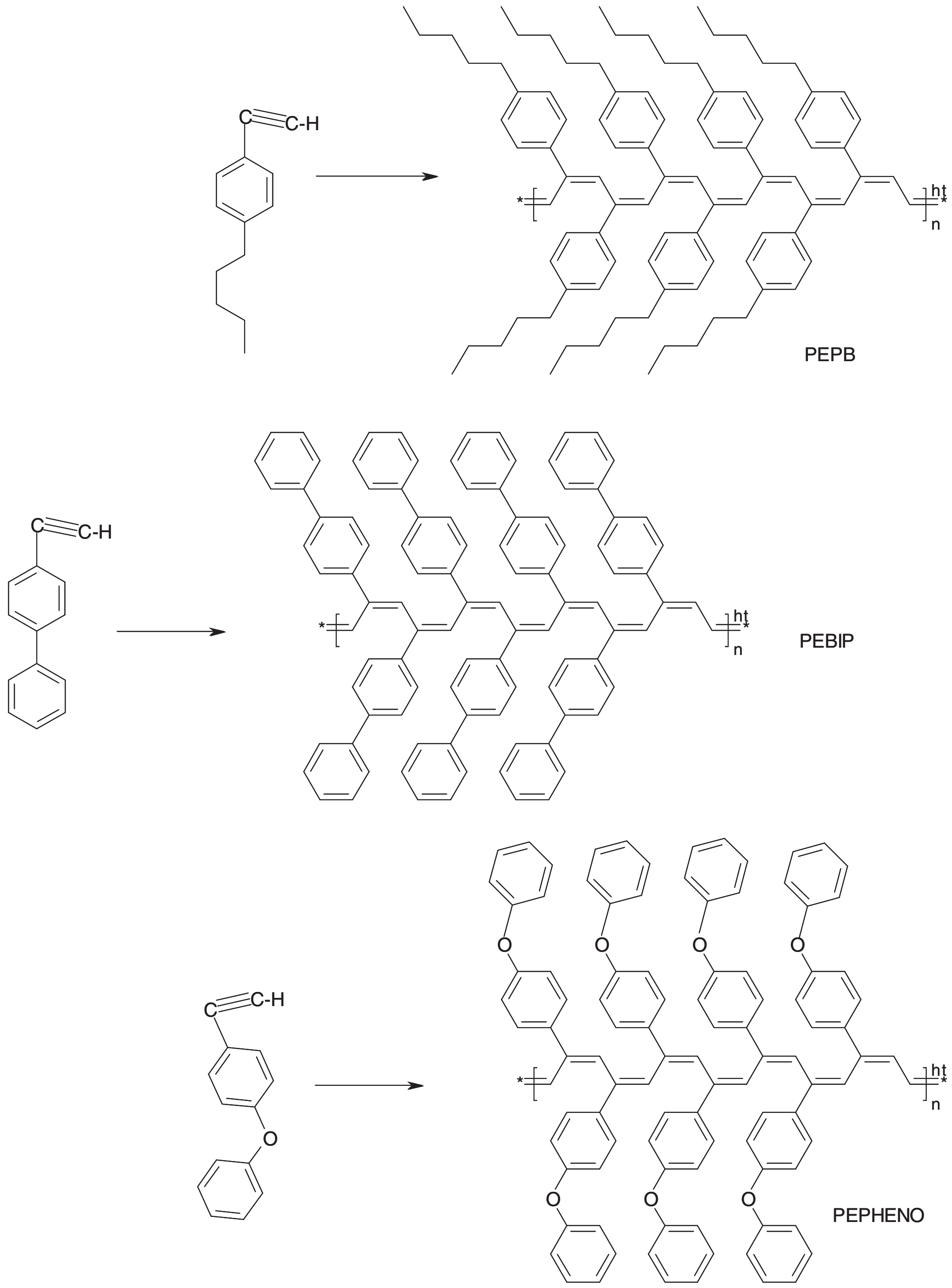
The monosubstituted acetylene monomer (1,0 g or 1,0 ml) was placed in a flask and diluted with 12 ml of THF. The solution was magnetically stirred at room temperature and the $[Rh(NBD)Cl]_2$ (35 mg) was added. The addition of the Rh(I) catalyst was followed by the addition of the co-catalyst t-BuOK (6.0 mg). The polymerization reaction starts immediately and a darkening of the mixture, an increase in its viscosity and evolution of heat can be observed. In a few minutes, all the monomer is consumed and the mixture is no longer magnetically stirrable and the polymer separated as an insoluble yellow or orange mass from THF solvent.

The polymer is treated with an excess of methanol to remove solvent and catalyst. If necessary, it is broken into small pieces to facilitate washing and it was left to dry in air.

The above procedure was applied for all monomers (Table 1). Only for 1-ethynyl-naphthalene, it was necessary to heat to refluxing temperature the reaction mixture for some hours (see ref. 35).

Table 1. Summary of the polymerization of monosubstituted acetylenes

Monomer	*Polymer Abbreviation*	*Polymer Yield (% by weight on monomer)*	*Notes*
Phenylacetylene	PPA	99.0	Orange powder
Tolylacetylene	PETOL	99.0	Orange-reddish powder
1-Ethynyl-4-biphenyl	PEBIP	99.0	Orange powder
1-Ethynyl-4-phenoxybenzene	PEPHENO	99.0	Yellow-orange, highly fibrous
1-Ethynyl-4-penylbenzene	PEPB	97.3	Yellow-orange, hard mass
1-Ethynyl-naphthalene	PEN	31.0	Brown-violet powder



Sch. 1. Schematic structures of PEPB, PEBIP and PEPHENO obtained by Rh(I) catalyst.

3 Results and Discussion

3.1 FT-IR and Electronic Absorption Spectroscopy of the Monosubstituted Polyacetylenes

The characteristic infrared absorption bands of monosubstituted acetylenes are the C≡C-H stretching and the related bending, respectively located at about 3280–3350 cm^{-1} and at 680–610 cm^{-1} (35). Additionally, the C≡C stretching occurs at 2130–2160 cm^{-1} as weak absorption band (35). As shown in Scheme 1, the polymerization of monosubstituted acetylenes involves the opening of the triple bond with the formation of a polyene chain backbone with pendant side groups. Thus, the polymerization of the selected monomers used in the present study is testified by the disappearance of the typical acetylenic stretching and bending bands. In Figure 1 are reported the FT-IR spectra

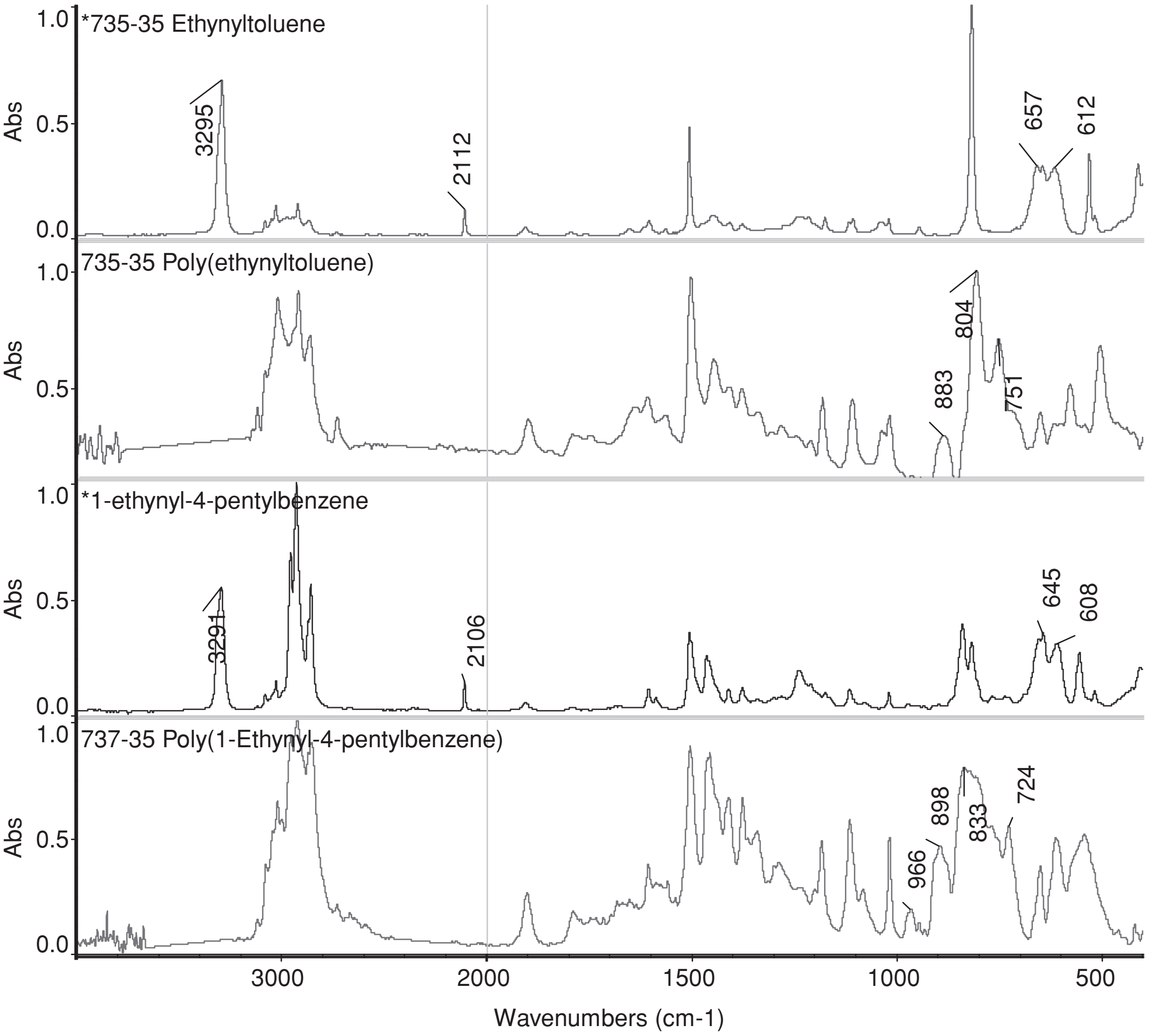


Fig. 1. FT-IR spectra in KBr (from top to bottom): 1-ethynyl-4-toluene, poly(1-ethynyl-4-toluene) = PETOL, 1-ethynyl-4-pentylbenzene and poly(1-ethynyl-4-pentylbenzene) = PEPB.

of a couple of alkylarylacetylenes and their polymerization products. Ethynyl-4-toluene (or 4-tolylacetylene) and 1-ethynyl-4-pentylbenzene show the C≡C-H stretching band at 3295 and 3291 cm^{-1} and bending occurs at about 610 and 650 cm^{-1} in both cases. The resulting polymers PETOL and PEPB do not show the C≡C-H stretching and the associated bending any longer. The C≡C stretching in the two monomers in Figure 1 can be observed at about 2110 cm^{-1} and is completely absent in the corresponding polymers PETOL and PEPB, respectively.

A similar reasoning applies to the case of polymerization diarylacetylenes where the bulky side groups are represented by biphenyl or by phenoxybenzene, respectively. Figure 2 shows the C≡C-H stretching band at 3274 and 3287 cm^{-1}, respectively for the two monomers. As expected, after polymerization, the C≡C-H stretching band is completely absent in the resulting polymers PEBIP and PEPHENO (Fig. 2).

From the FT-IR spectra of the resulting polymers PETOL, PEPB, PEBIP and PEPHENO it is not possible to derive their steroisomerism. However, it is well known that Rh(I) complexes and, in particular $[\text{Rh(NBD)Cl}]_2$, produces stereoregular cis-transoid rich polymers even when monosubstituted acetylenes with bulky side groups are polymerized (3, 4, 37–39). Therefore, it is also expected that the new polymers reported in the present work and, in particular PEPB, PEBIP and PEPHENO, were obtained in preferred cis-transoid configuration.

Indications about the stereoisomerism of monosubstituted polyacetylenes can be derived from their electronic absorption spectra (32, 35, 40). In fact, cis-rich polyacetylenes are characterized by a long wavelength absorption band at about 400 nm with sub-bands (32, 40). Even polyacetylenes with bulky side groups like poly(ethynylnaphthalate), PEN, show such absorption bands with features up to 500 nm (35). Conversely,

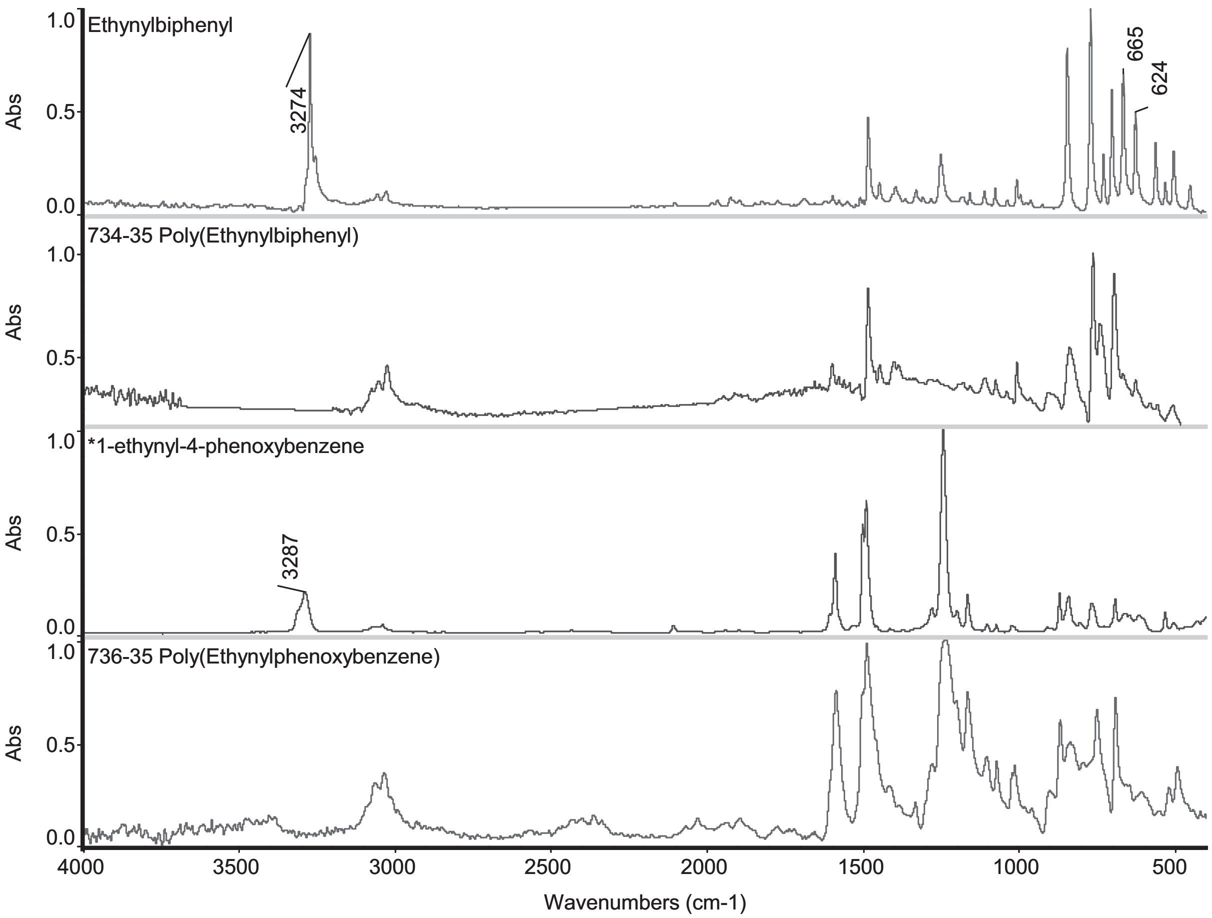


Fig. 2. FT-IR spectra in KBr (from top to bottom): 1-ethynyl-4-biphenyl, poly(1-ethynyl-4-biphenyl) =PEBIP, 1-ethynyl-4-phenoxybenzene and poly(1-ethynyl-4-phenoxybenzene) = PEPHENO.

trans-rich polyacetylenes are characterized by a much weaker and shorter wavelength transition (40). The cis-transoid structure of PEPB, PEBIP and PEPHENO are shown in Scheme 1.

Using α(-)-pinene as solvent, we have examined the spectra of PETOL, PEPB, PEBIP and PEPHENO. Among these, only PEBP is fully soluble in α(-)-pinene, all the other polymers show only a limited solubility which was, in any case, sufficient for analyzing the electronic absorption spectra of their solutions. Figure 3 shows the electronic absorption spectra of PEPB and PEPHENO. Both polymers show an absorption maximum at 291 nm, but the position of this maximum is affected by the cut off of the solvent used which occurs at about 275 nm. PEPB shows an marked long wavelength tail with a shoulder at 405 nm. The tail is more intense than that of PEPHENO, which in any case, shows a shoulder at 340 nm and another weaker transition at 420 nm. From these spectra, it can be inferred the cis-transoidal rich configuration of PEPB, since its spectrum resembles that of a cis-rich polyphenylacetylene (PPA) (32, 40). PEPHENO shows its long wavelength transition at only 340 nm, a value already observed in the case of cis-rich PEN prepared with the same synthetic procedure and co-catalyst adopted in the present work (33). The spectrum of PEBIP is very similar to that of PEPHENO and is not shown in Figure 3 and confirms its cis-rich nature. PETOL was practically insoluble in α(-)-pinene and its spectrum was recorded in $CHCl_3$ and found similar to that of cis-rich PPA (32, 40).

3.2 Effect of Monosubstituted Polyacetylenes on the Optical Activity of Chiral Media

As reported in the introduction, the application of monosubstituted polyacetylenes in the detection, in the alteration and in the amplification of chirality is currently a hot topic (12–22, 41–43). In the present study, we have tried to dissolve the monosubstituted polyacetylenes we have synthesized in a chiral solvent like $\alpha(-)$pinene or $\alpha(+)$pinene. The chiral environment should induce a helical structure in the monosubstituted polyacetylene solute with alteration of the specific optical rotation of the solvent. Previous studies have shown that the introduction of bulkier substituents to the polymers enhanced the persistence length of the

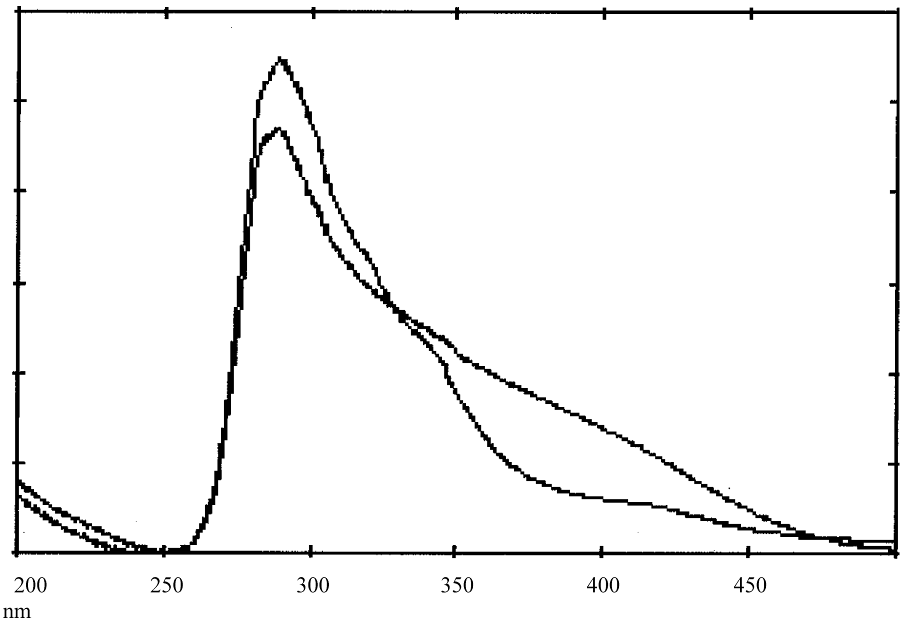


Fig. 3. Electronic absorption spectra in α(-)-pinene of poly(1-ethynyl-4-pentylbenzene) = PEPB showing a pronounced shoulder at about 400 nm and of poly(1-ethynyl-4-phenoxybenzene) = PEPHENO.

one-handed helix, resulting in an increase in the magnitude of Cotton effects and optical rotations (44). Additionally, stereoregularity of the polymers influences the polymer conformation so that the helical polymer-chiral media interaction occurs only for stereoregular polymers (41–44). This concept is illustrated in Tables 2A and 2B where the specific optical rotations $[\alpha]$ of pure α(-)pinene measured at four different wavelengths are compared with solutions of α(-)pinene containing small amounts of toluene or atactic polystyrene; the latter is a polymer which does not undergo helical induction in chiral media. In fact, Tables 2A and 2B show that the specific optical rotations remain

Table 2. Specific optical rotation of polyacetylenes in pinene solvent

POLYMER and/or SOLVENT	*Concentration mg/ml*	$[\alpha]_{589}$	$[\alpha]_{578}$	$[\alpha]_{546}$	$[\alpha]_{436}$
A. ACTUAL VALUES in Deg ml g^{-1} dm^{-1}					
pure a(-)-pinene	neat	−47.81	−49.76	−56.31	−93.66
toluene in a(-)pinene	5.0	−47.61	−49.96	−56.28	−93.69
polystyrene in a(-)pinene	5.0	−48.15	−50.14	−56.47	−93.72
PETOL in a(-)pinene	saturated ≈ 1.0	−46.12	−47.81	−53.43	n.d.
PEBIP in a(-)pinene	saturated ≈ 1.0	−45.33	−47.12	−53.21	−88.23
PEPHENO in a(-)pinene	saturated ≈ 1.0	−47.31	−49.12	−55.66	−91.08
PEPB in a(-)pinene	18.3	−47.06	−48.79	−55.23	−86.21
PEPB in a(+)pinene	18.3	48.61	50.39	56.18	n.d.
pure a(+)-pinene	neat	50.44	52.42	59.33	n.d.
B. INDEX VALUES [(Polymer solution/reference solvent)x100]					
pure a(-)-pinene	neat	100	100	100	100
toluene in a(-)pinene	5.0	99.6	100.4	99.9	100.0
polystyrene in a(-)pinene	5.0	100.7	100.8	100.3	100.1
PETOL in a(-)pinene	saturated ≈ 1.0	96.5	96.1	94.9	n.d.
PEBIP in a(-)pinene	saturated ≈ 1.0	94.8	94.7	94.5	94.2
PEPHENO in a(-)pinene	saturated ≈ 1.0	99.0	98.7	98.8	97.2
PEPB in a(-)pinene	18.3	98.4	98.1	98.1	92.0
PEPB in a(+)pinene	18.3	96.4	96.1	94.7	n.d.
pure a(+)-pinene	neat	100	100	100	n.d.

identical to that of pure α(-)pinene even in the presence of toluene or polystyrene. The situation changes completely when monosubsituted polyacetylenes synthesized in the present work are dissolved in α(-)pinene. Unfortunaltely, only PEPB is completely soluble in α(-)pinene, all the other polyacetylenes PETOL, PEBIP and PEPHENO are sparingly soluble. Tables 2A and 2B show that the specific optical rotation at four different wavelengths were measured for all the monosubstituted polyacetylenes and all the samples, irrespective for their concentration in α(-)pinene, were able to alter the specific optical rotation of the chiral solvent by changing it by some percent. Table 2B is reporting the actual [α] data of Table 2A as index values making 100 the specific optical rotation of the reference solvent. Thus, in Table 2B it is possible to appreciate the level of alteration of the [α] values by dissolving the monosubstituted polyacetylenes in α-pinene.

The alteration of the specific optical rotation of the chiral α(-)pinene is certainly attributable to the formation of a helical structure by the monosubstituted polyacetylenes once dissolved in the chiral medium. Such an effect appears slightly more pronounced with PEBIP than for PETOL and is instead somewhat less impressive in the case of PEPHENO. However, it is quite astonishing that even at so high dilution these three polymers are sparingly soluble in α(-)pinene, it is possible to appreciate an impact in the specific optical rotation of the solvent. PEPB is instead very soluble in α(-)pinene, probably thanks to the alkyl chain attached to the benzene pendant group. For this reason, we have studied its effect on the specific optical rotation of both α(-)pinene and α(+)pinene (see Table 2A and 2B). Curiously, the effect of alteration of the optical activity of the chiral medium appears more pronounced in the latter solvent. To explain this fact, it can hypothesized that PEPB has a preference to assume, for instance, a left-handed helix rather than the right-handed and hence, its interaction with one of the two α-pinene enantiomers is more pronounced.

A limitation of the present study is certainly the fact that we have made only polarimetric measurements at wavelengths $\lambda > 436$ nm. It is well known that the chromophores of the monosubstituted polyacetylenes have their most important transitions in the ultraviolet spectra region and below 400 nm (12, 16, 44). Therefore, the ideal spectral range to be explored for studying the interaction of helical polymers with chiral media is at $\lambda < 400$ nm possibly with circular dichroism spectroscopy rather than spectropolarimetry. Notwithstanding these limitations, we were able to detect the interaction between the monosubstituted polyacetylenes and the chiral solvents.

3.3 Thermal Stability of Monosubstituted Polyacetylenes

The Rh(I) catalyst is an extremely effective catalyst in the polymerization of monosubstituted acetylenes and has permitted to synthesize polyacetylenes with bulky side groups. An example is represented by the successful synthesis of poly(1-ethynyl-naphthalene) or PEN and the study of its thermal behavior (35). From one side, unsubstituted polyacetylene is very sensitive to oxidation and degradation even at room temperature (45) and the presence of side groups improves considerably the stability of polyacetylenes, but reduces the conjugation along the polymer backbone (46). Bulky substituents raise the temperature of cis-trans isomerization of polyacetyelenes and improve further their thermal stability and their char-forming tendency.

The thermal stability of a polymer can be measured by thermogravimetry (TGA) under inert atmosphere. The first derivative of the thermogravimetric curve is called differential thermogravimetry (DTG) and the resulting peak corresponds to the maximum decomposition rate T_d. Normally, such event can be also detected by differential thermal analysis (DTA) which, in our case, is run simultaneously with the TGA.

Van Krevelen (47) has shown that the thermal stability of polymers can be calculated *a priori* by a group incremental approach using a simple equation (Equation 1) and tabulated values:

$$\left(\sum_i Yi\right) M^{-1} = T_d \tag{1}$$

With Y the tabulated group increment for the thermal decomposition associated to the chemical structure of a given polymer and M the molecular weight of the polymer repeating unit.

Similarly, even the char-forming tendency of a given polymer can be predicted using another equation (Equation 2) and tabulated data (47):

$$\left(\sum_i Xi\right) M^{-1} = \text{Char}\,\% \tag{2}$$

With X the tabulated group increment for the char-forming tendency associated to the chemical structure of a given polymer and M the molecular weight of the polymer repeating unit.

The results of our TGA measurements are shown in Figure 4 where it can be observed that polyacetylenes with bulkier side groups give the highest char residue. The results are also summarized in Table 3 and compared with the calculated amount of char expected according to Equation 2. The agreement between the calculated and observed values is very good and confirms once again the validity of the Van Krevelen's approach in the prediction of this polymer property. Thus, the bulky groups biphenyl (PEBIP), phenoxybenzene (PEPHENO) and naphthyl (PEN) leave about 50% of the initial weight into the char. The data about char-forming tendency and thermal stability of PEN are taken from a previous work (35).

The first derivatives of the TGA curves (DTG) are shown in Fiure 5 and represent the maximum decomposition rate

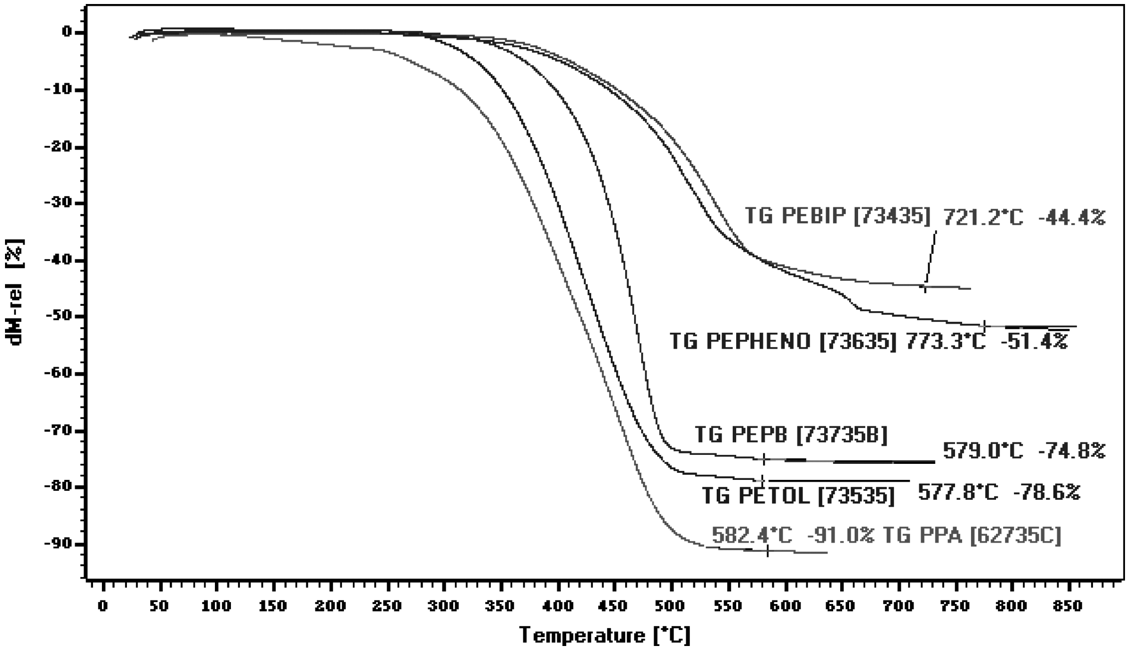


Fig. 4. Thermogravimetric analysis under N_2 flow of polyacetylenes with bulky substituents PEBIP, PEPHENO, PEPB, PETOL in comparison to reference polyphenylacetylene (PPA). Note that the char-forming tendency increases by increasing the bulkiness of the side groups.

T_d at the main peak. The results are summarized in Table 3. Also in this case, the agreement between the calculated (according to Equation 1) and observed values is good with the exception of PEPB where the calculated is significantly underestimated. The data confirm that the bulky side groups greatly improve the thermal stability of the polyacetylenes. For example PEBIP reaches the T_d at 535°C while reference PPA decomposes at only 401°C.

In Figure 6, the DTA confirms the data of DTG in terms of thermal decomposition temperature of the polymer

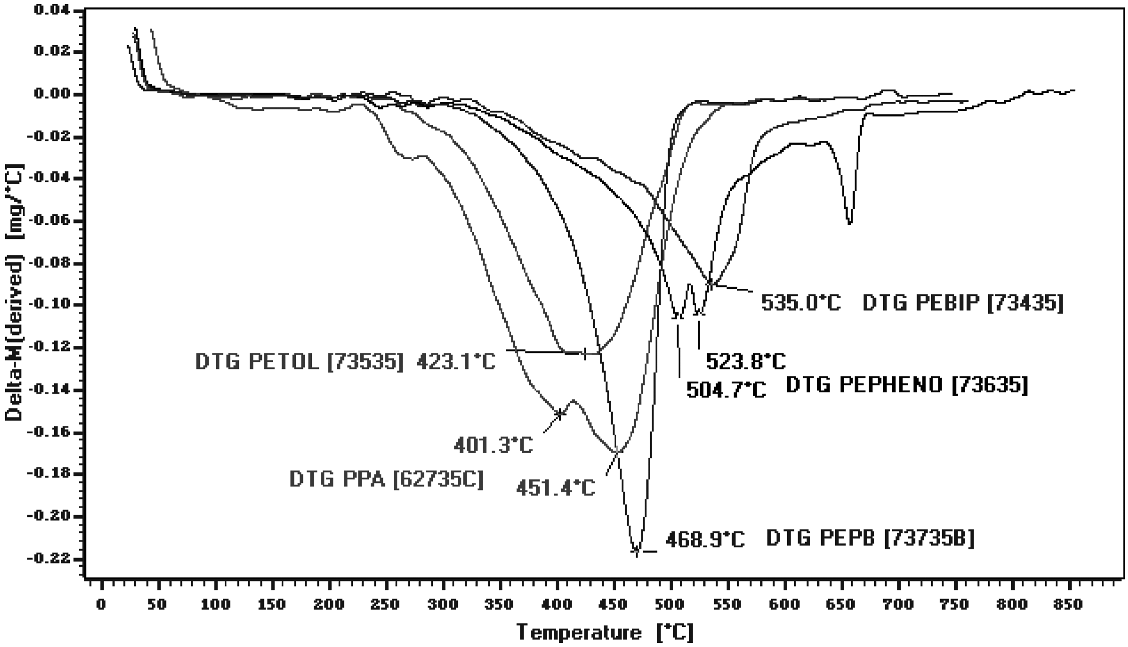


Fig. 5. DTG, the first derivative of the TGA traces of the previous figure showing the maximum decomposition rate events. It is evident that the most thermally stable polyacetylene examined is PEBIP followed by PEPHENO and PEPB. PPA and PETOL are the less thermally stable.

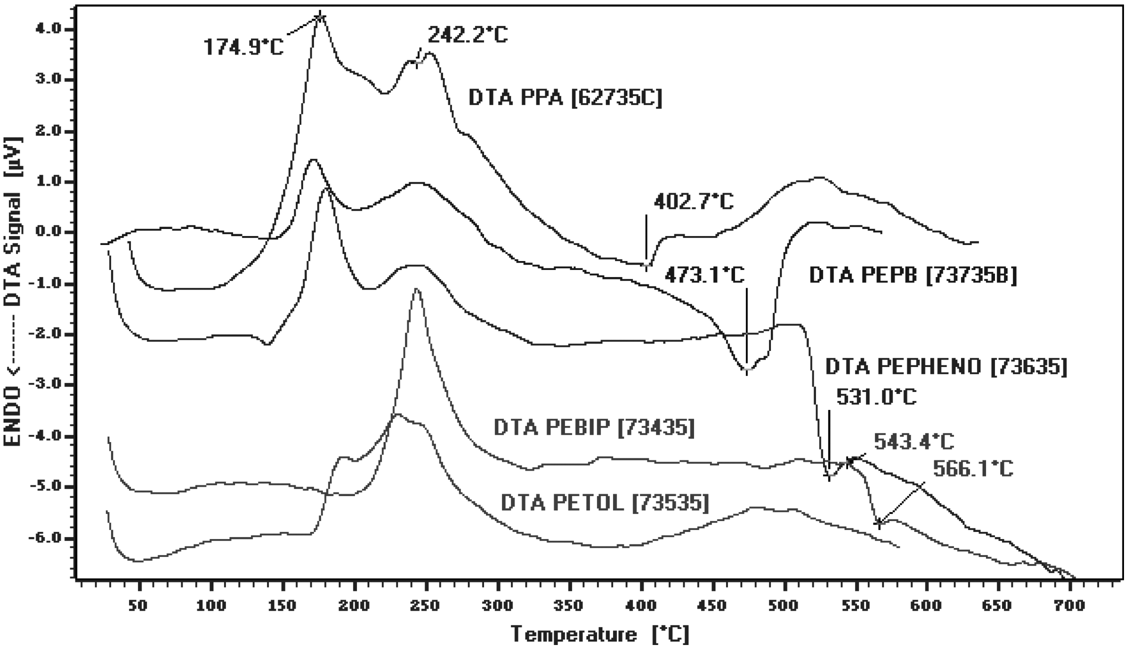


Fig. 6. Differential Thermal Analysis (DTA) under N_2 flow of the monosubstituted polyacetylenes. The exothermal peaks above 150°C are linked to melting and cis-trans isomerization transitions. At higher temperatures also the thermal decomposition events can be observed.

examined and in the case of PEBIP this temperature appears shifted to higher values (see also Table 3). The DTA suggests that the thermal decomposition mostly an endothermal event for the polymer examined probably for the associated formation of char. The DTA shows also exothermal transitions at lower temperature. At about 175–180°C PPA, PEPB, PEPHENO and also PETOL show a transition which is associated to the softening point of the polymer. Another transition occurs at 242–245°C and can be associated to the cis-trans isomerizaton of other kinds of rearrangements. Only for PEBIP the transition at 245°C is unique and probably associated to the melting point and cis-trans isomerization.

Table 3. Summary of thermal properties of polyacetylenes

	Char Residue %		*Maximum Decomposition (°C)*		
Polymer	*CALC (*)*	*OBS*	*CALC (*)*	*OBS DTG*	*OBS DTA*
PPA	11,8	9,0	403	401 and 451	403
PETOL	25,9	21,4	425	423	n.d.
PEN	47,4	49,0	391	400 and 460	400
PEPB	25,9	25,2	419	469	473
PEPHENO	49,5	48,6	510	504 and 524	531
PEBIP	53,9	55,6	536	535	543 and 566

(*)According to Van Krevelen (47)

4 Conclusions

A series of polyacetylenes with bulky side groups (PEBIP, PEPHENO and PEPB) were successfully synthesized with a Rh(I) complex using t-BuOK as co-catalyst in THF and their properties were compared with reference polyacetylene like PPA and PETOL and with PEN, another polyacetylene with bulky side group synthesized previously (35). PEBIP, PEPHENO and PEPB when dissolved in small amounts in a chiral solvent like α(-)pinene show an alteration of the specific optical rotation of the host solvent and this phenomenon has been observed also in the case of PETOL. Instead the dissolution of small amounts of toluene or polystyrene in α(-)pinene does not cause any alteration of the optical activity of the solvent. This fact has been interpreted in terms of chiral induction exerted by the chiral solvent to the monosubstituted acetylenes in assuming an helical configuration. Thus, achiral polymers like monosubstituted polyacetyelenes becomes optically active when interacting with a chiral medium because they assume a preferential right-handed (or left handed, depending from the chiral solvent) helical configuration.

The thermal stability and the char-forming tendency of PEBIP, PEPHENO and PEPB was studied in comparison to that of PPA, PETOL and PEN. It has been confirmed that bulky side groups improve considerably the thermal stability of polyacetylenes and increase their char-forming tendency.

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