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ESR and NMR Studies of a Novel Conjugated Donor−Acceptor Polymer Containing Magnetic Spins: Poly[bicarbazolylene-*alt*-phenylene-bis(cyanovinylene)]

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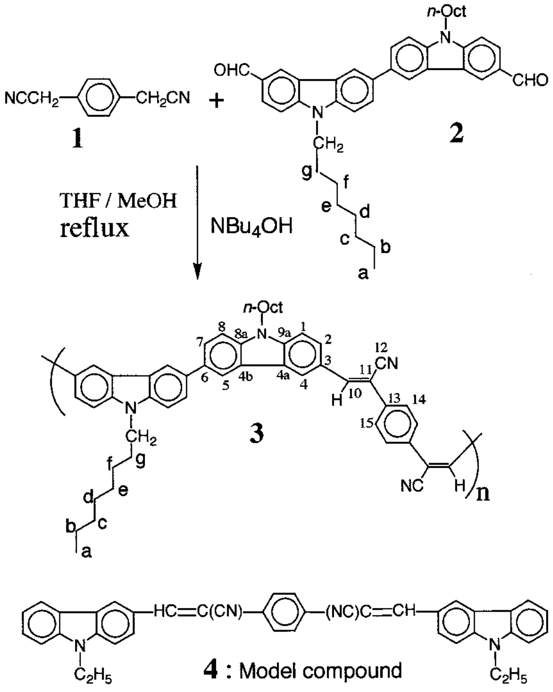
ABSTRACT: A conjugated alternating copolymer, poly[bicarbazolylene-*alt*-phenylenebis(cyanovinylene)] (named PCPV), was prepared via the Knoevenagel condensation in the presence of tetrabutylammonium hydroxide. Tetrahydrofuran-soluble low molecular weight materials and insoluble polymer were obtained. The two fractions were characterized in detail by ESR and solid and solution NMR spectroscopies. Strong ESR signals were observed from the pristine PCPV polymer in both fractions. This was explained by the rotational cleavage of the cis vinylic bond to produce two π radicals, called biradicals, which diffuse along the main chains to form radical cations stabilized by conjugation in the alternating repeating moieties. In particular, the insoluble fraction shows an extremely strong and sharp line width signal with a spin concentration equal to 5.8×10^{17} spins/g. The alternating copolymer synthesized can be considered as a novel conjugated material analogous to substituted polyacetylenes with respect to the mobile unpaired electrons. The solid NMR spectrum of the insoluble fraction of the PCPV copolymer is reported for the first time. By comparison with solution NMR studies of the soluble fraction and of a model compound of the repeating unit, the structure of the copolymer was established. The ^{1}H NMR spectrum of the soluble fraction allowed calculation of the DPn whose values roughly agree with that estimated by SEC measurements. However, the NMR signals of the soluble fraction were somewhat broadened because of the presence of unpaired electrons in the main chains.

Introduction

Since the discovery of the electroluminescence properties of poly(*p*-phenylenevinylene),[1] numerous conjugated polymers have been used as emissive layers in light-emitting diodes (LEDs). Over the past few years, important improvements have been obtained concerning the control of color, the luminescence efficiency, and the durability of polymer LEDs.[2,3] In particular, blends of conjugated polymers with poly(*N*-vinylcarbazole) as a hole-transporting matrix have been achieved and have shown significant increase of the luminescence efficiency.[4] We have previously reported on the synthesis of soluble multiblocks (N-alkyl-3,6-carbazolylene)$_2$-b-(3-octylthiophene)$_m$ copolymers which can display tunable electronic properties such as electrochromism, thermochromism, and a yellow to red electroluminescence as a function of copolymer composition.[5,6] The presence of carbazole units in the main chains was found to increase the electroluminescence efficiency with respect to that of the octylthiophene homopolymer. We also recently described the synthesis of a new alternating donor−acceptor copolymer (PCPV) which is composed of electron-donor bicarbazolylene and electron-acceptor 1,4-phenylenebis(cyanovinylene) moieties (see Scheme 1).[7]

Scheme 1



The solvent-processable polymer fraction has been found to exhibit a green electroluminescence[8] arising from the emission of the internal charge-transfer (CT) created between the carbazole subunits and the cyanovinylenephenylene entities. As a drawback, this CT was found to be partly responsible for the rigidity of the macromolecular chains, which explain their low solubility. Thus, we were interested by the study of their structural and electronic features in the solid state and, in particular, with the objective to evaluate their magnetic properties.

We previously performed such investigations on polyacetylene derivatives. Indeed, we reported that trans

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monosubstituted aromatic polyacetylenes generated by pressure-induced isomerization of the pristine cis isomers prepared with a Rh complex catalyst[9] possessed a large amount of π-radical spins which magnetically behave as typical mobile unpaired electrons called solitons, such as those found in nonsubstituted polyacetylenes synthesized by Ziegler−Natta catalysis.[10] In this paper we discuss the presence and the origin of the radicals observed in the PCPV copolymer by ESR measurements. The structure of PCPV is also investigated by solid and solution NMR spectroscopies.

Experimental Section

The synthesis and the workup of the PCPV copolymer have already been described previously.[7,8] SEC measurements of the soluble fraction were performed in tetrahydrofuran (THF) with Ultrastyragel columns (100, 500, and 10^3 Å) equipped with a differential refractometer (Waters). Polystyrene standards (Aldrich) were used for calibration of molecular weight and its dispersity. CP MAS ^{13}C NMR spectra were observed using Bruker MSL360, and solution ^{13}C (90.48 MHz) and ^{1}H NMR (360 MHz) spectra were observed using a JEOL GX400 at 30 °C in $CDCl_3$. Electron spin resonance (ESR) spectra were recorded on a JEOL FE1XG X band spectrometer with 100 kHz field modulation using a temperature control unit. The computer simulation of the observed spectrum was performed using a Macintosh Computer: iMac.

Results and Discussion

Synthesis. The copolymer, poly[bicarbazolylene-*alt*-phenylene-bis(cyanovinylene)] (PCPV), was prepared according to our previous method in a refluxing mixture of THF/MeOH with tetrabutylammonium hydroxide as catalyst (see Scheme 1).[7,8] The polymerization was stopped by adding a large amount of methanol in order to favor the precipitation of all products. The resulting solids were then filtered off and fractionated as two components, i.e., insoluble part, PCPVi, and soluble part in THF or chloroform, PCPVs, as low molecular weight products, i.e., oligomers. A qualitative study of the geometry of the vinylene bonds formed in a number of Knoevenagel condensations has suggested the mechanism for the elimination step, shown in eqs 4 and 5 in Scheme 2.[11] The mechanism described leads generally to a trans configuration of the double bond, but in the case of condensations of aromatic compounds, both the cis and trans isomers can be obtained. In our case, the carbanion formed in eq 4 isomerized in order to lead a mixture of cis/trans double bonds as shown in eq 5 in Scheme 2.

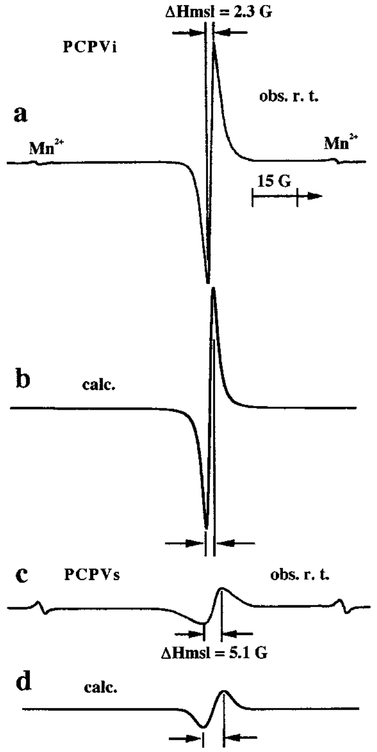
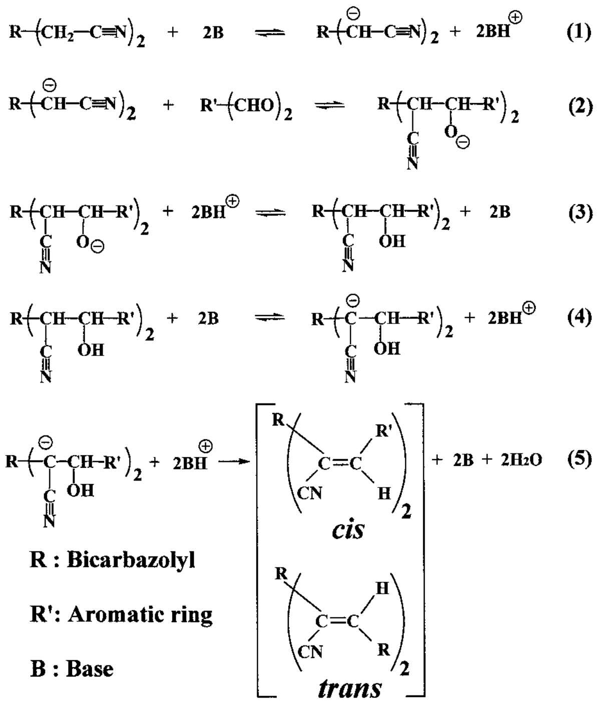


Figure 1. ESR spectra of the insoluble (PCPVi) and soluble (PCPVs) polymer fractions: (a) spectrum of PCPVi observed at room temperature, (b) simulated spectrum of PCPVi, (c) spectrum of PCPVs observed at room temperature, and (d) simulated spectrum of PCPVs.

Scheme 2



ESR Analyses. The insoluble and soluble fractions of PCPV were examined by electron spin resonance (ESR) spectroscopy to determine whether the main chains possess unpaired electrons, called π-radicals, which may be generated by rotational scission of the cis vinylene bonds. Effectively, this behavior has already been observed in the case of trans nonsubstituted polyacetylenes prepared with the Ziegler−Natta[10] and monosubstituted polyacetylenes obtained from a Rh complex catalyst[9] where the cis and trans isomers have been characterized in detail using the ESR method. We found that the PCPVi and PCPVs fractions (see Scheme 1) reveal a fairly clear ESR signal, even at room temperature as shown in Figure 1. To the best of our knowledge, no data relative to such ESR signals, in not only this copolymer but also other types of carbazolyl polymers, have been reported. Figure 1 shows the ESR spectra of the insoluble PCPVi and soluble PCPVs fractions of the copolymer, observed under vacuum, ca. 10^{-3} Torr at room temperature. It is clear that the insoluble PCPVi gives a much stronger ESR signal compared with that of the soluble PCPVs, although the line width in the case of PCPVs is much wider than that of PCPVi. The line shape observed in the PCPVi polymer was completely simulated with the so-called Lorentzian line shape (see Figure 1b). The observed line

Table 1. ESR Parameters Observed in the Soluble and Insoluble PCPV Polymers, and Its Model Compound[a]

		$\Delta Hmsl$(Gauss)		spin concn[b]		
polymer	g value	rt	77 K	(spins/g) × 10^{16}	spins/unit[c]	color
PCPVi	2.0029	2.3	5.6	114.0	1.44×10^{-3}	red
PCPVs	2.0032	5.1	6.8	44.9	5.67×10^{-4}	yellow
model compd	2.0031	2.8		16.1	1.51×10^{-4}	orange

[a] Samples were evacuated at ca. 10^{-3} Torr for 24 h at room temperature. [b] Measured at room temperature. [c] Spins/mol of repeated unit.

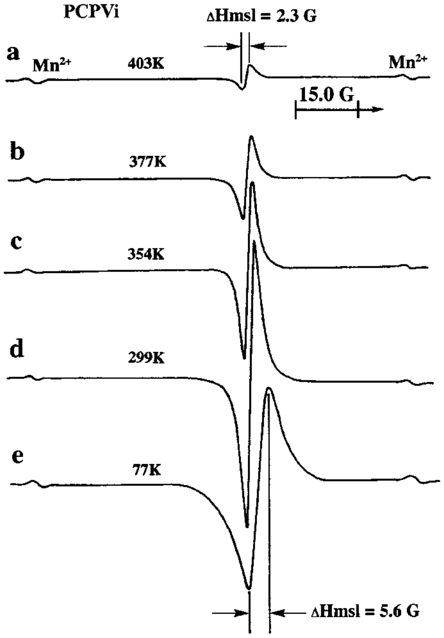


Figure 2. Temperature dependences of the observed ESR spectra of the insoluble PCPVi polymer: (a) 403, (b) 377, (c) 354, (d) 299, and (e) 77 K.

shape suggests formation of fairly longer trans conjugation lengths in the PCPVi fraction as reported in the cases of trans polyacetylene[10] and monosubstituted aromatic polyacetylene bearing planar trans conjugated sequences which were created by thermal isomerization or pressure-induced isomerization[9,12] of the original cis form polymer. On the other hand, in the case of the soluble PCPVs polymer, the so-called Gaussian line shape spectrum was observed (see Figure 1c,d). A similar shape has been obtained for the pristine cis monosubstituted polyacetylene which was prepared by the Rh catalyst.[9,12] The above differences in the line width between insoluble and soluble fractions undoubtedly reflect a longer conjugated sequence for PCPVi. This may be supported by the fact that the soluble fraction is composed of a mixture of low molecular weight oligomers with DPn = 5 (see hereafter NMR and SEC parts) which are not long enough to stabilize the resulting π radical as mobile unpaired electrons. The π radicals found in insoluble PCPV may be also called solitons[10] as in the case of polyacetylenes, unlike those of the soluble fraction, PCPVs. It is noteworthy that the ESR signals due to π-radicals were observed even in the model compound (see Scheme 1 and Table 1) as evidence of the vinylene double-bond cleavage.

Soluble and insoluble fractions clearly show a large temperature dependence in the line widths of the ESR spectra when cooled from room temperature down to 77 K (see Table 1 and Figure 2). It is concluded, therefore, that both polymer fractions have conjugation sequences having π-radical in the main chain and that the unpaired electrons show motional narrowing as observed in the line width. Thus, in the PCPV polymer fairly sharp ESR signals can be detected, especially in the insoluble fraction where an extremely strong and sharp line width signal with spin concentration, 1.14×10^{18} spins/g, $g = 2.0029$, and $\Delta H_{\mathrm{msl}} = 2.3$ G was observed at room temperature. It should be noted that the line width in the PCPVi polymer is sharper than not only those of the cis polyacetylene[10] but also monosubstituted polyacetylenes[9,12] bearing longer trans conjugation sequences.[9,10,12] Therefore, such much narrow line width observed in the PCPV polymer may be explained by the *so-called spin exchange of unpaired electrons* other than motional narrowing which is induced among the generated unpaired spins as has been already proposed in the case of trans polyacetylene.[9,10,12]

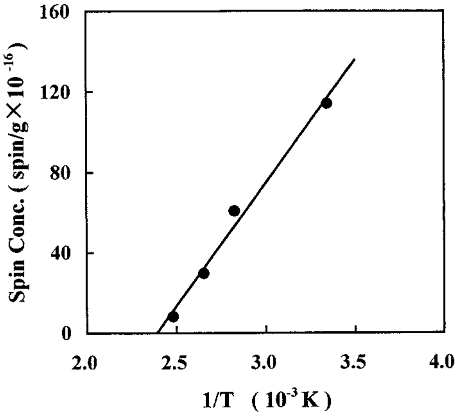


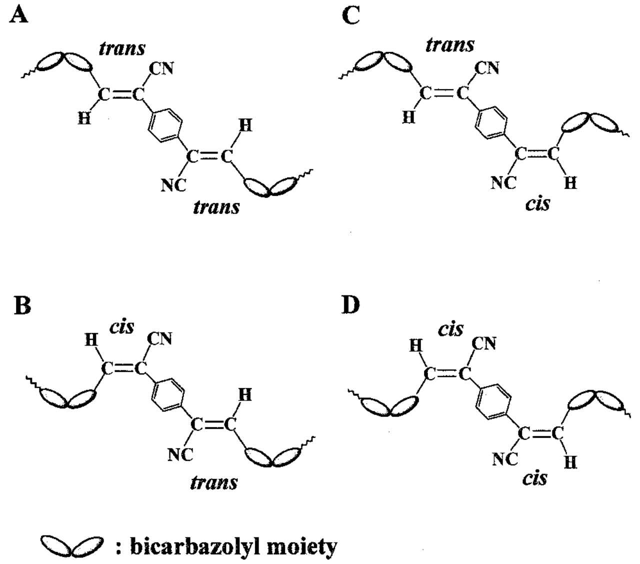
Figure 3. Plot of the spin concentrations of the PCPVi polymer against reciprocal temperature, $1/T$ (10^{-3} K), above room temperature.

Figure 2 shows temperature dependence of the intensity of the ESR spectra in the insoluble fraction. It is clear that the spectral intensity rapidly decreases with increasing temperature, especially in the higher temperature range between 299 and 403 K, although the spectral change was reversible in the temperature range from 330 to 77 K. However, such a rapid decrease of the radical concentration has not been observed up to date in the nonsubstituted polyacetylene since the unpaired electrons stabilized in the cis or trans conjugated sequences are known to be very stable at relatively high temperatures.[9,10,12,13]

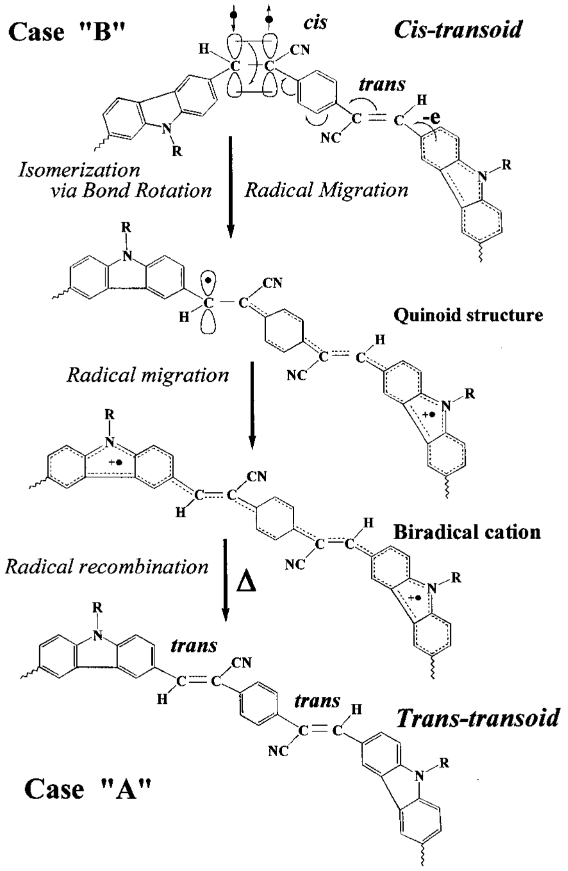
Figure 3 shows the temperature dependence of the spin concentrations observed above room temperature. The results clearly indicate that the unpaired electrons are not due to thermal electrons generated by the thermal treatment; i.e., the electrons are not correlated with electrical conducting electrons. Because the plot yields a straight line, the temperature dependence clearly obeys the Curie rule.[10a]

Origin of Radicals. Scheme 3 shows possible geometrical isomers concerning the two double bonds. Scheme 4 shows the possible bond scission mechanism in the case of the isomer: “B” (or its equivalent “C”) by

Scheme 3. Possible Geometrical Isomers of PCPV



Scheme 4



way of the π-bond rotation with respect to the cyanovinylene bond where cis and trans configurations regarding the two double bonds are depicted as one of three possible geometrical isomers. Let us consider the case "B" in detail as the so-called cis−transoid form; one cis double bond is rotationally broken to generate two π-radicals as the biradicals. The π-radicals may move around along the conjugated chain in order to meet an unpaired electron taking one electron from the carbazolyl nitrogen. This radical migration leads to the formation of a quinoid structure as a stable structure at lower temperature. Therefore, wider delocalization of the spin density due to formation of the radical cation may be created over the bicarbazolyl moiety to contribute to the motional narrowing of the line width in the observed ESR spectra. As an evidence, some of the resulting π-radicals may be localized along the polymer chain to some extent, although the quinoid structure is depicted as the extreme molecular structure. The molecular chain may also be distorted so that the spin density can be localized on the restricted molecular moiety in the main chain. Similar nitrogen radical cations may be also created on another side of the main chain in order to generate a similar quinoid structure. The resulting biradical cation may be called bipolaron, which is stable at lower temperature as shown in Figure 2. It is also necessary, however, to explain why the rapid disappearance of the radical cations takes place even at relatively lower temperature compared with that in the case of other polyacetylenes.[9,10,12,13] The resulting bipolaron can be recombined to generate a new trans C═C bond by which the "A" trans−trans isomer is lead as the more stable form within the higher temperature domain. At lower temperature the cis structure can be considered as stable geometrical isomers since still high concentration of unpaired electrons can be observed as shown in Scheme 4. In other words, the thermal treatment of PCPVi induces the *quinoid-to-trans isomerization*, occurring at higher temperature. It is noteworthy that such a recombination between radical cations does not occur easily during the Knoevenagel condensation since we can detect strong ESR signals from both the pristine PCPV polymer and the model compound. The unpaired electrons may be similar to the case of the cis−transoid units observed in monosubstituted polyacetylenes,[9,10,12] although behavior on their thermal stability is completely opposite. Furthermore, the line width of the ESR signal did not increase appreciably even when heating to 403 K (see Figure 2). This unambiguously indicates that no cross-linking is induced in the PCPVi polymer by such a thermal treatment under vacuum at ca. 10^{-3} Torr, because, usually, cross-linking resulted in the increase of the ESR line due to the destruction of the planar conjugation sequences.[14]

It is also reasonable to assume that more than two intermolecular biradicals may ferromagnetically interact with each other in order to generate ferromagnetic spin microdomains as one of the useful promising application. In this case we cannot expect to observe a strong ESR signal from the PCPV polymer because of the formation of magnetic spin domains which do not allow the penetration of the microwaves. Such a formation of magnetic domains may explain why the ESR signal intensity does not increase according to the Boltzmann distribution, when cooled below the room temperature, as partly shown in Figure 2.

^{13}C NMR. Figure 4 shows the CP MAS ^{13}C NMR spectra of the insoluble fraction PCPVi and solution ^{13}C NMR of the soluble fraction PCPVs. The spectral assignments were made by comparison with those for the model compound (see Scheme 1) and on the basis of previous studies.[6−8] In the case of the PCPVi fraction, TOSS pulse sequences were used to suppress the spinning sidebands in the solid state so that each peak intensity loses its reliability.[12] The peaks at 15.4, 24.3, 30.9, and 44.5 ppm were assigned to those of CH_{3a}, CH_{2b}, CH_{2c-g}, and NCH_2 carbons of the side chain. The broad peak with a shoulder observed at 119.5 ppm was

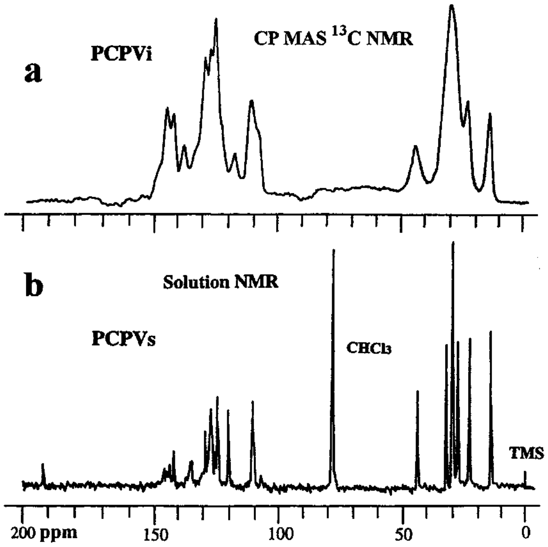


Figure 4. ^{13}C NMR spectra of PCPV: (a) CP MAS ^{13}C NMR spectrum of the insoluble fraction, PCPVi, and (b) ^{13}C NMR spectrum of the soluble fraction, PCPVs, observed at 30 °C in $CHCl_3$ solution.

ascribed to the carbons of the carbazole nucleus, i.e., C_1, C_5, C_7, C_8, and C_{11}, and the shoulder is due to C_{14} and C_{15} carbons. The small signal observed at 119.7 ppm may be due to C_{12}, C_{4a}, and/or C_{4b} carbons. The multiplet observed at 125.3−129.3 ppm was attributed to C2, C3, C4, and/or C6 carbons. The small peak may be also assigned to C_{13} carbon. The two peaks observed at 141.3 and 143.8 ppm were ascribed to C_{8a}, C_{9a}, and/or C_{10} carbons. As could be expected, both the NMR spectral shapes of the insoluble and soluble fractions of the PCPV polymer may be considered to be nearly the same. The insolubility of PCPVi may be ascribed to the rather high molecular weight and the stiffness of the backbone which the polar functions such as cyano group and/or bicarbazolyl moieties induce strong molecular aggregation as has been conjuctured.[8,15−19] The aggregation was clearly evidenced by wide-angle X-ray (WAX) diffraction of the PCPVi polymer because of formation of a pseudohexagonal structure,[18] e.g., poly(phenyl)acetylene,[17] poly(*p*-methylphenyl)acetylene,[16] and poly(alkyl propiolate)s.[15,19] This study will be the subject of a forthcoming paper.

^{1}H NMR. Figure 5 shows the ^{1}H NMR spectrum of the PCPVs observed at 30 °C in $CDCl_3$ solution. The peaks observed between ca. 0.95 and 1.9 ppm were easily assigned to the seven alkyl groups in the side chain. The signal observed at ca. 4.18 ppm was attributed to the two protons of the *N*-CH_2 group. Peaks at ca. 7.5 ppm were due to the aromatic $C-H_1$ and CH_{14} or 15 protons. The peak at ca. 7.8 ppm was ascribed to the $=CH_{10}$ vinyl proton of the main chain.[8] The five peaks observed at 7.85, 8.0, 8.2, 8.48, and 8.7 ppm were ascribed to the CH_8, CH_2, CH_7, CH_4, and CH_5 protons, respectively. The peaks observed at 10.03 and 10.01 ppm were attributed to the unreacted CHO moieties (see Scheme 1). It should be noted that the formyl protons were observed as two peaks with a different peak ratio. The signal at 10.01 ppm was attributed to the unreacted monomer remaining in the soluble fraction. A previous study of the PCPV copolymer by the infrared method has shown that the end groups of the macromolecular chains are exclusively constituted by aldehyde moieties.[7] Thus, the peak at 10.03 ppm was attributed to the oligomer chain ends. The relative intensities of the CHO signals (at 10.03 and 10.01 ppm) and that of the *N*-CH_2 group (at 4.18 ppm) allow the calculation of the DPn = $2n + 1$. The integral lines give 1.00 for 2H (CHO) and 7.81 for 4nH ($N-CH_2$ repeating units) + 4H ($N-CH_2$ end groups); n was then equal to 2.9 and DPn = 6.8. This calculation leads to a value around 3 as n.

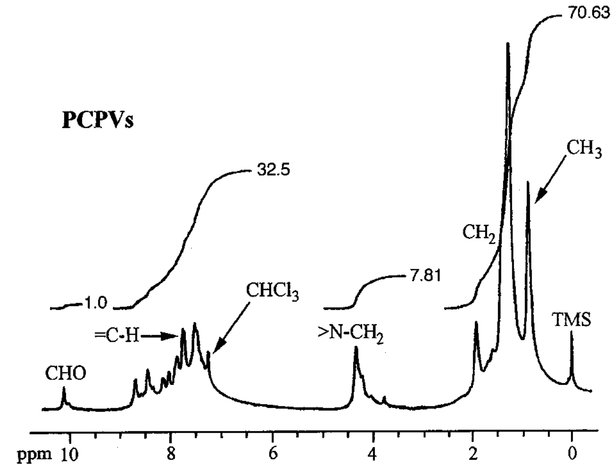


Figure 5. ^{1}H NMR spectrum of the soluble fraction of the PCPV polymer observed at 30 °C in $CDCl_3$ solution together with the integration ratios.

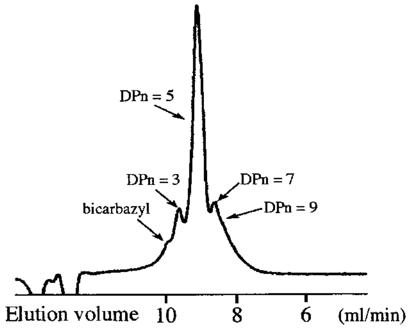


Figure 6. SEC chromatogram of the soluble low molecular weight PCPVs observed using THF as an eluent.

It should be noted that the observed ^{1}H NMR spectrum of PCPVs has an extremely broadened baseline with wider line widths unlike the ordinary spectrum; e.g., the baseline is extending to very higher magnetic field more than TMS signal at 0 ppm. The observed increase in each line width and baseline may be explained by not only the so-called magnetic dipole−dipole (DD) interaction between the polymer protons and the unpaired electrons but also the slower molecular motion of the resulting trans structure having planar π-conjugated sequences,[20] though the contribution ratio is difficult to quantitatively estimate.

The size exclusion chromatography (SEC) analysis (Figure 6) shows the signals corresponding to the remaining monomer and that of the oligomers in the soluble fraction PCPVs and lead to a value close to 5. Thus, it may be considered that the SEC results are not so much far from those obtained by NMR analyses. However, the resolution of the spectrum for the oligomers fraction is not as good as we could expect. This can be explained by the presence of the unpaired electrons that we observed by the ESR methods mentioned above. This peak broadening precludes any differentiation between isomers.

Conclusions

A donor−acceptor alternating copolymer, poly[bicarbazolylene-*alt*-phenylenebis(cyanovinylene)], was prepared through the Knoevenagel condensation. THF-soluble low molecular weight fraction and the insoluble fraction were characterized in detail in order to determine their structures, using solid and solution NMRs and ESR spectroscopies. No difference was found in the structure of the two fractions. The insolubility of the insoluble fraction may be ascribed to the fairly large molecular weight of the polymer associated with the stiffness and aggregation of the backbone due to polar substituents such as cyano and/or carbazolyl groups. The PCPV polymers showed strong ESR signals from radicals stabilized in the main chain, even at room temperature. The origin of the radicals observed in the PCPV polymer was explained by scission of the vinylic double bonds, although the observed radicals are not neutral ones but radical cations formed from the nitrogen atoms of the carbazole nuclei. The concentration of the radical cations was found to rapidly decrease with increasing the temperature up to 403 K. The disappearance of the radical cations was interpreted by their recombination so generating a new trans double bond from a cis originated structure. This trans configuration was proposed as the more thermally stable form. The poly[bicarbazolylene-*alt*-phenylenebis(cyanovinylene)] can be considered as a new conjugated material similar to polyacetylenes with respect to the mobile unpaired electrons.

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