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Inert Carbon Free Radicals. 12. Synthesis, Electronic Spectra, and Magnetic Properties of Stable Polymeric Polyradicals with Perchlorotriphenylmethyl Radical Units[1]

V. M. Domingo, J. Castañer,* J. Riera, and L. Fajarí

Departamento de Materiales Orgánicos Halogenados, Centro de Investigación y Desarrollo (CSIC), Jordi Girona 18-26, 08034 Barcelona, Spain

A. Labarta

Departamento de Física de Estado Sólido, Facultad de Física, Universidad de Barcelona, Avda. Diagonal 647, 08028 Barcelona, Spain

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Taking steric hindrance as a guiding principle for the design of high-spin organic polymers, four stable polymeric polyradicals [poly(perchloro-(4,4′-dimethyltriphenylmethyl)-α′,α″-diylidene) (ERHP, **5**), poly(perchloro-(4,4′-dimethyltriphenylmethyl)-α′,α″-diylidine) (ARHP, **4**), poly[(perchloro-(4,4′-dimethyltriphenylmethyl)-α′,α″-diylidene)tris(perchloro-*p*-xylene-α,α′-diylidene)] (ERCP, **10**), and poly[(perchloro-(4,4′-dimethyltriphenylmethyl)-α′-ylidyne-α″-ylidene)(perchloro-*p*-xylene-α-ylidyne-α′-ylidene)bis(perchloro-*p*-xylene-α,α′-diylidene)] (ARCP, **9**)] with a polymerization degree of 13−28 and high radical purities (about 90%) have been synthesized and characterized. These polymers are highly colored substances, while ARHP and ARCP are dark green, ERHP and ERCP are dark red, depending on the presence of triple bonds in the connecting bridges. The electronic spectra of ERHP and ERCP show evidence of the presence of degenerate or nearly degenerate states (SOMOs) caused by steric hindrance. The spin−spin interactions in all these polyradicals are governed by the nature and length of the connecting bridges. Thus, while with long bridges (ARCP and ERCP) the interactions are negligible, with short ones (ARHP and ERHP) stronger spin−spin interactions appear. While ARHP, with ethynylene bridges, shows strong intramolecular antiferromagnetic interactions, ERHP with vinylene ones, presents the characteristic magnetic behavior of a near degeneracy between its low- and high-spin states, as ascertained by SQUID magnetometry in the 4−300 K temperature range and ESR spectrometry in the 77−300 K temperature range. The magnetic behavior of these polyradicals agrees with their electronic spectral data.

Introduction

In recent years much interest has been directed toward the study and development of organic materials with unusual magnetic, electronic, and/or optical properties. Some of the best candidates for this type of materials are conjugated alkaromatic hydrocarbons with no classical Kekulé structures and possessing half-filled nonbonding molecular orbitals (NBMOs), however, they present an important drawback, i.e., the lack of stability. ESR spectroscopy has recently allowed the detection of some of these types of species, with high spin states at very low temperature and inert atmosphere.[2−4]

Furthermore, the synthesis of macromolecular compounds with high-spin states is desirable, where highly reactive carbenes[4] were replaced by stable spins. Recently, Iwamura[5] and Nishide[6] have introduced the new strategy of preparing conjugated polymers, in which stable radical centers such as nitroxyls[5] or galvinoxyls[6] are attached to the main chain as pendants. Our work is traced to the synthesis of such types of polymers, but placing stable perchlorotriphenylmethyl (PTM) radicals[7] not as pendants but as repeating units integrated in the polymer backbone. In this case the presence of a "narrow band" of degenerate quantum states will not

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(1) (a) For the sake of brevity the following acronyms have been used in the paper: PTM for (perchlorotriphenyl)methyl; TBAOH for tetrabutylammonium hydroxide; HHP for αH-homopolymer **2**; HCP for αH-copolymer **7**; ERHP for ethylenic radical homopolymer **5**; ARHP for acetylenic radical homopolymer **4**; ERCP for ethylenic radical copolymer **10**; and ARCP for acetylenic radical copolymer **9**. (b) In the sake of clarity, the nomenclature here used for highly chlorinated compounds is a most convenient extension of the IUPAC indicated hydrogen recommendations.

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(5) (a) Fujii, A.; Ishida, T.; Koga, N.; Iwamura H. *Macromolecules* **1991**, *24*, 1077. (b) Vlietstra, E. J.; Nolte, R. J. M.; Zwikker, J. W.; Drenth, W.; Meijer, E. W. *Macromolecules* **1990**, *23*, 946.

(6) (a) Nishide, H.; Yoshioka, N.; Inagaki, K.; Tsuchida, E. *Macromolecules* **1988**, *21*, 3119. (b) Nishide, H.; Yoshioka, N.; Kaneko, T.; Tsuchida, E. *Macromolecules* **1990**, *23*, 4487. (c) Abdelkader, M.; Drenth, W.; Meijer, E. W. *Chem. Mater.* **1991**, *3*, 598.

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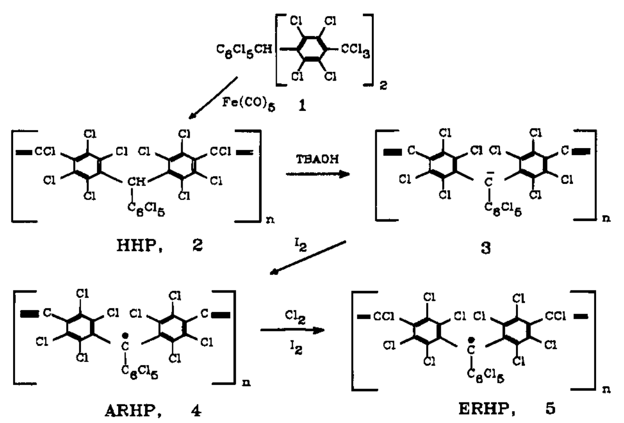
be obtained by molecular topology factors (Rajca,[2b] and Iwamura[4b]), but by steric hindrance which reduces the overlap between the interacting singly occupied orbitals according to the model of Müllen.[8] The effective exchange integral J, in the Heisenberg Hamiltonian, has been investigated by Müllen as a function of the overlap between adjacent π_a and π_b atomic orbitals, and it has been shown that the ferromagnetic alignment is favored for small overlaps between the adjacent singly occupied π-orbitals.[8] In the present case the steric hindrance will be caused by the bulkiness of the chlorine atoms in the α positions of the connecting bridges and those of the **ortho** positions of the phenyl rings. It is already known that the radicals of the perchlorotriphenylmethyl (PTM) series, with a propeller-like conformation and a high steric protection of the trivalent carbon by the six **ortho** chlorines, are some of the most stable radicals withstanding agressive chemical reagents and temperatures up to 200 °C;[7,9] some years ago two of us published the synthesis of two stable carbon biradicals of the PTM series: the perchloro-4,4′-vinylenebis(triphenylmethyl) (**14**) and the perchloro-4,4′-ethynylenebis(triphenylmethyl) (**13**) biradicals[10] with unexpected ESR and magnetic properties, and more recently one of us has published the synthesis of a stable carbon tetraradical with a pair of triplets.[11] Taking into account all this background, the aim of the present work is to synthesize polymeric polyradicals containing PTM units linked through vinylene or ethynylene (less hindered) conjugating bridges, such as poly(perchloro-(4,4′-dimethyltriphenylmethyl)-α′,α″-diylidene) (ERHP, **5**)[1] and poly(perchloro-(4,4′-dimethyltriphenylmethyl)-α′,α″-diylidyne) (ARHP, **4**). To study the influence of the distance between the radical centers on the spin−spin interaction, the synthesis of poly[(perchloro-(4,4′-dimethyltriphenylmethyl)-α′,α″-diylidene)tris(perchloro-p-xylene-α,α′-diylidene)] (ERCP, **10**) with a longer conjugating bridge will also be presented.

Results and Discussion

It is already known that the usual precursors of the PTM radicals are the corresponding αH-PTM derivatives;[7] consequently the first aim of this work would be the synthesis of the corresponding αH polymers, i.e., poly(αH-pentadecachloro-(4,4′-dimethyltriphenylmethane)-α′,α″-diylidene) (HHP, **2**) and poly[(αH-pentadecachlorotriphenylmethane-α′,α″-diylidene)tris(perchloro-p-xylene-α,α′-diylidene)] (HCP, **7**), which in turn can be obtained by reductive condensation of the corresponding bis(trichloromethyl) derivatives αH-nonadecachloro-4,4′-dimethyltriphenylmethane (**1**),[7f] alone or in admixture with perchloro-p-xylene (**6**).[12] These monomers have been obtained by known aromatic chlorination methods, based on the BMC chlorinating agent ($AlCl_3$, S_2Cl_2, SO_2Cl_2).[12]

Scheme 1



Synthesis of αH-Homopolymer (HHP, 2). The synthesis of macromolecular chlorocarbons by reductive condensation of bis(trichloromethyl) aromatic compounds by means of stannous choride or ferrous chloride in refluxing dioxane[13a,b] (and more recently with $Fe(CO)_5$ in refluxing benzene)[13c] has already been reported. Since the yields are better with $Fe(CO)_5$, this method has been used for the self-condensation of bis(trichloromethyl) compound **1**, yielding homopolymer HHP (**2**, Scheme 1) with a M_n = 22 600 (osmometry, $n \simeq 29$).[14]

The mechanism for the condensations with $Fe(CO)_5$ is controversial; up to now three possibilities have been suggested: (1) an initial oxidation process yielding an iron complex that loses CO and dimerizes;[15] (2) a radical intermediate;[15] and finally (3) a carbene intermediate.[16] To ascertain this mechanism, the dimerization of perchlorotoluene with $Fe(CO)_5$ in benzene in an ESR cavity has been performed. At 70 °C a strong and well-resolved seven-line spectrum (1:2:3:4:3:2:1) identical to that of the already reported perchlorobenzyl radical[17] has been observed. This suggests that, at least in the perchloroorganic chemistry, the mechanism is of radical character.

Synthesis of Copolymer HCP (7). The reductive condensation of a mixture of bistrichloromethyl compound **1** and perchloro-p-xylene[12] (**6**, molar ratio 1:4) with $Fe(CO)_5$ as in the preceding paragraph yielded perchloro-p-xylylene (23%)[18] and copolymer HCP (**7**) (Scheme 2). The amount of perchloro-p-xylylene isolated, and the elemental analyses indicate that the molar ratio of both monomers **1** and **6** in copolymer HCP

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[9] Ballester, M.; Veciana, J.; Riera, J.; Castañer, J.; Rovira, C.; Armet, O. *J. Org. Chem.* **1986**, *51*, 2472.

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[13] (a) Ballester, M.; Castañer, J.; Riera, J. *J. Am. Chem. Soc.* **1966**, *88*, 957. (b) Ballester, M.; Castañer, J.; Riera, J. *Synthesis and Properties of Alkaromatic Chlorocarbons;* 1968; ARL 68 (18), Clearinghouse, U.S. Department of Commerce (*Chem. Abstr.* **1969**, *70*, 46980t). (c) Fors, P.; Juliá, L.; Tura, J. M.; Sauló, J. *J. Polym. Sci. A. Polym. Chem.* **1992**, *30*, 2489.

[14] Preliminary attempts with inconclusive results (low $M_n \sim 3000$) were performed many years ago.[13b]

[15] Alper, H.; King, E. C. H. *J. Org. Chem.* **1972**, *37*, 2566.

[16] Coffey, C. E. *J. Am. Chem. Soc.* **1961**, *83*, 1623.

[17] Olivella, S.; Ballester, M.; Castañer, J. *Tetrahedron Lett.* **1974**, 587.

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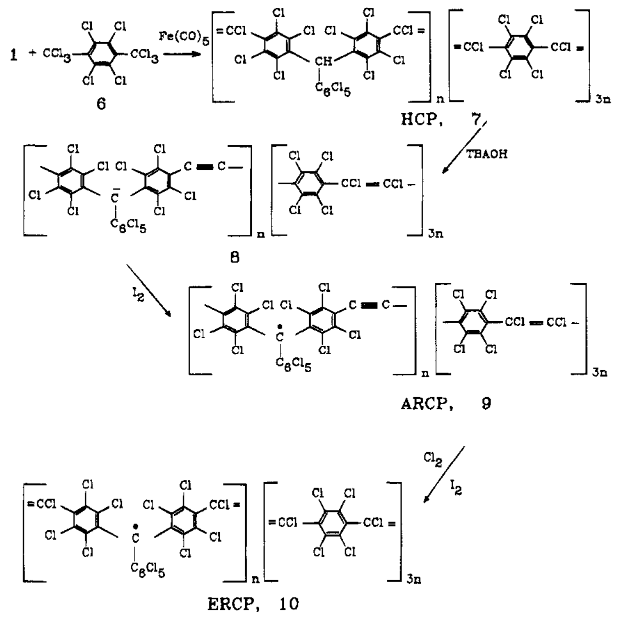
Table 1. Comparative IR and UV Spectral Data of *cis*-HHP, *trans*-HHP, HCP, PPX,[a] *cis*-11,[30] and *trans*-11[30]

	IR (cm^{-1})		UV nm (ϵ/n)[b] (see Figure 2)		
	C=C str	C−Cl str			
cis-HHP	1600 (w)	802 (m)	284 (8980)	313 (sh) (2950)	345 (sh) (680)
cis-**11**	1610 (w)	805 (s)	284 (5300)	304 (sh) (2130)	313 (sh) (635)
trans-HHP		815 (m) 800 (m)	297 (4450)	307 (4397)	
trans-**11**		825 (m) 800 (s)	298 (1885)	305 (2025)	
HCP	1605 (w)	820 (m) 807 (m)	283 (22270)	311 (sh) (10630)	342 (sh) (1330)
PPX[a]		835 (m)	285 (4000)	310 (2200)	

[a] PPX, poly(perchloro-*p*-xylene-α,α′-diylidene).[13a] [b] *n* = number of PTM units per molecule.

Scheme 2



is about 1:3.[19] The mean molecular weight was 22 200 (osmometry, n ≃ 13). The IR spectra of copolymer HCP and homopolymer HHP look very similar, with one significant difference: while HHP presents three strong bands (1365, 1320, 1290 cm^{-1}), in the aromatic C=C stretching region, HCP presents two medium bands (1345, 1300 cm^{-1}) and only one strong band (1320 cm^{-1}) in this region; this fact is an indication of the incorporation of $=CCl-C_6Cl_4-CCl=$ units in the copolymer, since poly(perchloro-*p*-xylenediylidene) presents a strong band (1325 cm^{-1}) in this region.[13a] A comparative study of the UV spectra of HHP and HCP polymers (Table 1) in the aromatic secondary band region of the highly chlorinated compounds (280−310 nm) shows that HCP exhibits a much higher absorptivity than HHP (per repeating unit). This fact can be rationalized taking into account the additivity of the absorbances[20] of the different chromophores of HCP due to the steric inhibition of resonance caused by the bulkiness of the chlorine atoms in the α and **ortho** positions.[21,22] The three $=CCl-C_6Cl_4-CCl=$ chromophore groups and one =CCl−αHPTM−CCl= group of HCP will give (Table 1) $\epsilon_{HCP(298)} = 4000 \times 3 + 8980 = 20\,980$ and $\epsilon_{HCP(311)} = 2200 \times 3 + 2950 = 9550$. These calculated data agree quite well with the experimental values ($\epsilon_{(298)} = 22\,270$, $\epsilon_{(311)} = 10\,630$) of the HCP copolymer, which confirms the validity of the assumed 1:3 ratio. The isolation of noticeable amounts of perchloro-*p*-xylylene (23%) coincides with the fact that this compound is also isolated in the reductive condensations of perchloro-*p*-xylene (**6**) with either $Fe(CO)_5$[13c] or $SnCl_2$[13a] and with the assumed 1:3 ratio.

This copolymerization has also been performed using $SnCl_2 \cdot 2H_2O$ as condensing agent. The same copolymer, HCP (**7**), was obtained. However, in this case perchloroheptafulvene[23,24] was isolated along with perchloro-*p*-xylylene. The mean molecular weight was 6380 (n ≃ 4). This low M_n, due possibly to the greater hydrogen-donor capability of dioxane as compared with that of benzene, led us to dispense with the use of $SnCl_2$ as condensing agent. The isolation of perchloroheptafulvene along with perchloro-*p*-xylylene, as a byproduct of this polymerization was quite unexpected. A study of the reaction conditions for the synthesis of perchloroheptafulvene has been performed.[24]

Synthesis of Polyradical Poly(perchloro-(4,4′-dimethyltriphenylmethyl)-α′,α″-diylidine) (ARHP, 4). It is already known that the immediate precursors of the PTM radicals are their corresponding carbanions (obtained from the αH-PTM derivatives by reaction with base) which are then oxidized with I_2 or chloranil.[7] Moreover, it is also known that *cis*- and *trans*-αH,α′H-triacontachloro-4,4′-vinylenebis(triphenylmethane) (**11**), when treated with base, in order to obtain the corresponding dicarbanions, undergo an easy dechlorination reaction affording perchloro-4,4′-ethynylenebis(triphenylmethide) (**12**),[10,25] the corresponding acetylenic dicarbanion which is then oxidized to the perchloro-4,4′-ethynylenebis(triphenylmethyl) biradical (**13**); this, in turn, is chlorinated to *trans*-perchloro-4,4′-vinylene-bis(triphenylmethyl) (**14**) the corresponding vinylene biradical[10] (Scheme 3). Taking these precedents into account, it was decided to perform first a study of the reaction of the αH-polymer HHP (**2**) with base.

(a) Spectroscopic Study of the Reaction of Polymer HHP (2) with an Excess of Tetrabutylammonium Hydroxide (TBAOH). The reaction was monitored by UV−vis spectroscopy. The results are summarized in Figure 1. The study of the evolution of the UV−vis spectrum

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(19) The UV−vis data of HCP and ERCP along with the magnetic susceptibility behavior of ERCP polyradical confirm this 1:3 ratio, as we shall see later.

(20) Ballester, M.; Riera, J.; Spialter, L. *J. Am. Chem. Soc.* 1964, *86*, 4276.

(21) (a) Ballester, M.; Castañer, J.; Codina, J. M.; Lluch, F. *Anal. Real Soc. Españ. Fis. Quim.* **1960**, *56B*, 197. (b) Ballester, M.; Rosa, J. *Tetrahedron* **1960**, *9*, 156. (c) Ballester, M.; Castañer, J. *Anales Real Soc. Españ. Fis. Quim.* **1970**, *66B*, 487. (d) Ballester, M.; Castañer, J.; Riera, J.; De la Fuente, G.; Camps, M.; *J. Org. Chem.* **1985,** *50*, 2287.

(22) See footnotes 15 and 16 in ref 13a.

(23) Identified by melting point and X-ray analysis. Roedig, A.; Försch, M. *Liebigs Ann.* **1978**, *804.*

(24) Domingo, V. M.; Castañer, J.; Riera, J.; Molins, E.; Mas, M. *J. Org. Chem.* **1994**, *59*, 4104.

(25) Ballester, M.; Castañer, J.; Ibañez, A. *Tetrahedron Lett.* **1974,** 2147.

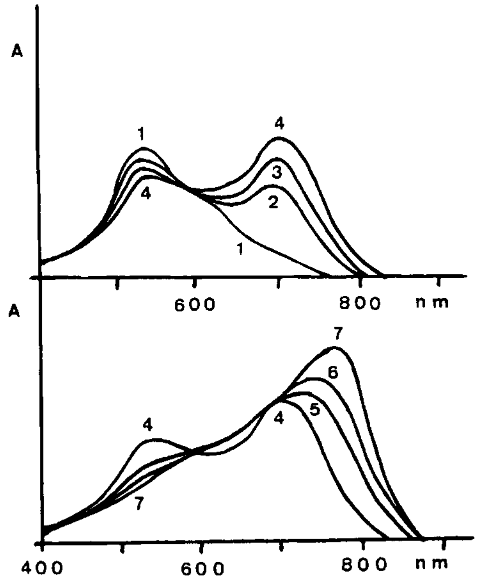
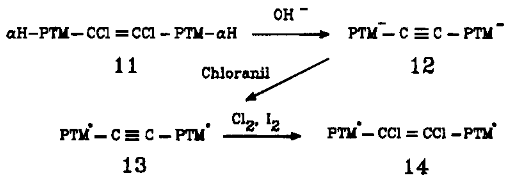


Figure 1. Monitoring by UV−vis spectroscopy of the reaction of HHP with TBAOH in THF. Top: curves 1−4 (1−30 min reaction time) formation of monoacetylenic PTM anions. Bottom: curves 4−7 (30 min−24 h reaction time) formation of diacetylenic PTM anions.

Scheme 3



shows three main steps: (1) A very fast (1 min) formation of a band at 533 nm (ϵ, 26 000), that can be attributed to a vinylenic PTM carbanion with negligible conjugation,[26] since PTM carbanions with no conjugating groups present a strong band in the interval 505−525 nm (ϵ, 25 000−35 000).[27]

(2) A slow decrease of the band at 533 nm and the rise of a new one at 700 nm (already observed as a shoulder in the 1 min spectrum). This new band reaches its maximum (ϵ, 30 100) around 30 min and can be attributed to a slow dechlorination process giving rise to a PTM carbanion bearing one ethynylene group, since perchloro-4,4′-ethynylenebis(triphenylmethide) (**12**) presents a similar UV−vis spectrum (λ max = 665 nm, $\epsilon/2$ = 41 400).[27c,d]

(3) From 30 min to 24 h, the band at 533 almost disappears, and a new one at 780 nm grows steadily up to ϵ = 42 050 and then it remains stable. This new absorption can be traced to the continuation of the dechlorination process yielding finally PTM carbanions with two vicinal ethynylene groups. The presence of a small shoulder at 700 nm in the UV−vis spectrum at 1 min reaction time indicates the impossibility of obtaining a PTM polyanion with purely vinylene bridges.

(b) Polyradical ARHP (4). In view of the preceding results it was decided to perform the reaction of polymer HHP (**2**) with TBAOH with a long reaction time (steady-state UV−vis spectrum, 70 h). The resulting acetylenic polyanion (**3**) was then oxidized with I_2 yielding polyradical ARHP (**4**, Scheme 1) as a dark-green solid insoluble in $CHCl_3$, characterized by elemental analysis and IR, UV−vis,[28] and ESR spectra. The anomalous magnetic behavior of polyradical ARHP did not allow the direct determination of its radical purity; however, this could be determined indirectly via its chlorination to polyradical ERHP (**5**, see later). The synthesis of ARHP was also attempted using powdered NaOH instead of TBAOH; however, this method was abandoned because of lower yields.

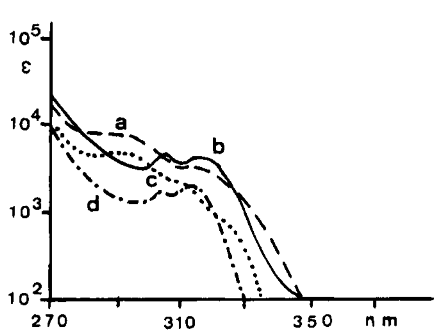


Figure 2. UV spectra of (a) *cis*-HHP (ϵ/n), (b) *trans*-HHP (ϵ/n), (c) *cis*-11 ($\epsilon/2$), (d) *trans*-11 ($\epsilon/2$).

Synthesis of Ethylenic Polyradical ERHP (5). It is known that the chlorination of acetylene biradical **13** with Cl_2 and I_2 done in darkness yields vinylene biradical **14** almost quantitatively.[10] When this chlorination is performed with acetylene polyradical ARHP (**4**), an almost quantitative yield of *trans*-vinylene polyradical ERHP (**5**) was obtained, which was characterized by elemental analyses and IR, UV−vis, ESR spectra, and GPC and osmometry measurements (Scheme 1). ERHP is a dark-red stable solid, soluble in $CHCl_3$ with a mean molecular weight M_n = 22 210 (osmometry, $n \simeq 28$).[14] ERHP presents normal paramagnetic behavior (see later) following the Curie−Weiss law, with a calculated radical purity of 91%. This result allows us to ascertain indirectly that the radical purity of the intermediate acetylenic polyradical ARHP is also 91% or higher.

Cis−Trans Configuration of the Vinylene Bridges of Polymers HHP and ERHP. The reduction of polyradical ERHP with ascorbic acid[29] gave a high yield of a polymer HHP which was identified by elemental analyses and IR and UV spectra. The comparative study of the IR and UV spectra of this Polymer and the original HHP, with those of dimers *cis*- (*cis*-**11**) and *trans*-αH,α′H-triacontachloro-4,4′-vinylenebis(triphenylmethane) (*trans*-**11**, Table 1 and Figure 2) show great similarities between the original polymer HHP and *cis*-**11** and between the polymer HHP obtained from ERHP and *trans*-**11**. These facts can be rationalized by assuming that the initial HHP polymer presents the vinylene groups with a configuration predominantly cis (*cis*-HHP), while the polymer derived from ERHP

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[26] Due to steric inhibition of resonance; for instance, vinylene biradical **14**[10] presents a UV−vis spectrum (per PTM unit) almost coincident with that of the PTM radical[7a] (see Table 3).

[27] (a) Ballester, M.; De la Fuente, G. *Tetrahedron Lett.* **1970**, 4509. (b) Ballester, M.; Pascual, I.; Torres, J. *J. Org. Chem.* **1990**, *55*, 3035. (c) Ballester, M.; Pascual. I.; Riera, J.; Castañer, J. *J. Org. Chem.* **1991**, *56*, 217. (d) Pascual, I. Doctoral Thesis, University of Barcelona, 1990.

[28] Because of its very low solubility only a qualitative UV−vis spectrum in tetrachloroethylene could be recorded.

[29] Ballester, M.; Riera, J.; Castañer, J.; Casulleras, M. *Tetrahedron Lett.* **1978**, 643.

[30] (a) Ibañez, A, Doctoral Thesis, University of Barcelona, 1972. (b) Ballester, M.; Castañer, J.; Riera, J. *Synthesis and Properties of Alkaromatic Chlorocarbons. Versatile Candidates for Thermostable, Inert Materials.* A.D. Report 1973, 763125. From US Govt. Rep. Announce, **1973**, *73 (16)*, 43 (*Chem. Abstr.* **1973**, *79*, 136646d). (c) Ballester, M.; Olivella, S. *Polychloroaromatic Compounds;* Suschizky, H., Ed.; Plenum Press: London, 1974; p 163.

presents a configuration predominantly trans (*trans*-HHP). Thus, while both cis compounds present a C=C stretching peak in the IR spectrum, this peak is absent (because of symmetry) in their trans isomers. Also it has been reported that the doublet at around 810 cm^{-1} in the IR spectrum of ethylenic perchloroaromatic compounds is characteristic of the **trans** configuration.[22] In view of the preceding considerations polyradical HPRD should also have a trans configuration, thus agreeing with the fact that it is already known that the chlorination of perchlorodiphenylacetylene yields *trans*-perchlorostilbene almost quantitatively.[31]

Synthesis of Poly[(perchloro-(4,4′-dimethyltriphenylmethyl)-α′-ylidyne-α″-ylidene)(perchloro-*p*-xylene-α-ylidyne-α′-ylidene)bis(perchloro-*p*-xylene-α,α′-diylidene)] (ARCP, 9). To ascertain the reaction conditions of HCP (7) with "TBAOH", it was decided to perform first, as before, an UV–vis spectroscopic study.

(a) Study of the Reaction of Polymer HCP with an Excess of TBAOH. The reaction was monitored by UV–vis spectroscopy. The study of the evolution of the UV–vis spectrum (very similar to Figure 1a) shows two main steps: (1) A fast (5 min) formation of a band at 525 nm (ϵ, 26 000) attributed, as before, to a vinylene–PTM carbanion with negligible conjugation.[26,27] (2) A slow decrease of the band at 525 nm and the rise of a new one at 685 nm (already observed as an asymmetry of the band at 525 nm). This band reaches its maximum (ϵ, 19 000) around 5 h, and then it remains stable. This band can be attributed, as before, to a PTM carbanion bearing one ethynylene group.[27c,d] There are three important factors to consider: (a) The dechlorination reaction is slower than in the case of HHP. (b) Unexpectedly, this dechlorination reaction stops when monoacetylenic PTM carbanions have been formed and no formation of a band around 780 nm is observed (see later); (c) The asymmetry of the band at 525 nm in the spectrum at 5 min reaction time (overlapping with the 685 nm band) indicates, also in this case, the impossibility of obtaining a PTM polyanion with purely vinylene bridges.

(b) Polyradical ARCP (9). In view of the preceding result it was decided to perform the reaction of polymer HCP (**7**) with TBAOH with a long reaction time (stabilization of the UV–vis spectrum; 24 h). The resulting polyanion **8** was then oxidized with I_2 or chloranil yielding a dark-green solid soluble in $CHCl_3$, characterized as polyradical ARCP (**9**, Scheme 2) with only one triple bond for each PTM unit, by elemental analyses, IR, UV–vis, and ESR spectra. As for ARHP, the anomalous magnetic behavior of ARCP did not allow the direct determination of its radical purity; however, this could be determined via its chlorination to polyradical ERCP (**10**, see later).

Synthesis of Ethylenic Polyradical ERCP (10). The chlorination of polyradical ARCP (**9**) with Cl_2 and I_2 yielded polyradical ERCP (**10**, 83%) as a red stable solid, characterized by elemental analyses, IR, UV–vis, and ESR spectra, and GPC and osmometry measurements (Scheme 2). ERCP presents normal paramagnetic behavior (see later) following the Curie–Weiss law, with a calculated radical purity of 86.6% for a comonomer ratio 1:3 as already estimated. This allows us to ascertain that the radical purity of polyradical ARCP is 86.6%, or higher. The mean molecular weight of ERCP is 19950 (osmometry, n ≃ 12).

Table 2. Osmometry and GPC Data of Polymers HHP, HCP, ERHP, and ERCP

	osmometry		GPC (monomodal distribution)		
	M_n	n^a	M_n	M_w	polydisp
HHP	22 600	≈29	8 750	17 740	2.03
ERHP	22 120	≈28	8 250	13 350	1.62
HCP	22 200	≈13	10 120	23 890	2.36
ERCP	19 950	≈12	11 020	22 040	2.00

[a] n = mean number of repetitive units in the polymer.

Molecular Weights, Thermal Stability, and Electrical Conductivity Data. The osmometry and GPC data of polymers are summarized in Table 2.

The similarity of the molecular weights of the αH-polymers HHP and HCP, as compared with their polyradical counterparts ERHP and ERCP, respectively, shows that within the precision of the technique, polymer degradation has not occurred during the radicalization processes.

The GPC data with a monomodal distribution (a single peak) and a polydispersity around 2 for all the polymers obtained indicate the presence of homogeneous polymers with rather narrow molecular weight distributions. The fact that higher molecular weights have not been obtained with this polymerizaton technique can be traced to solubility problems (insolubility of the higher polymers in the refluxing benzene used as reaction solvent).

The thermal stability of polymers has been determined by TGA and in some cases by direct heating to air. While the αH-polymers HHP and HCP withstand temperatures of up to 450 °C (TGA; IR) polyradicals ARHP, ERHP, ARCP, and ERCP undergo appreciable decomposition around 220 °C (TGA, IR).

The conductivity measurements on compressed pellets of the aforesaid polymers do not show differences between the αH-polymers and their polyradical counterparts. All them behave as insulators with conductivity values below 10^{-12} (or 10^{-7}) S cm^{-1} (the sensitivity limits of the two electrometers used).

Ultraviolet–Visible Spectra. PTM radicals can be classified into two principal groups according to electronic interactions: The first group assembles those PTM mono- and polyradicals with negligible electronic interactions, due to steric inhibition of resonance.[7,9,10] The second one assembles those PTM mono- and polyradicals with noticeable electronic interactions.[7c,9,32]

(a) Ethylenic polyradicals ERHP and ERCP. The PTM radicals belonging to the first group (more than 35 have been published) show UV–vis spectra very similar to that of the PTM radical.[7a] Table 3 presents the spectral data of some of these radicals along with those of ERHP and ERCP polyradicals. The great similarity of the whole spectra of ERHP and ERCP, with this group of PTM radicals indicates that these polymeric polyradicals present independent half-filled nonbonding molecular orbitals (NBMOs) with negligible electronic interaction through, and with, the vinylene bridges. This is due to the steric hindrance (overlapping) between the bulky vinylene chlorines and those in the aromatic positions vicinal to the bridges. In this connection, it must be pointed out that steric inhibition

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(31) Ballester, M.; Castañer, J.; Riera, J.; Armet, O. *J. Org. Chem.* **1986**, *51*, 1100.

(32) Ballester, M.; Riera, J.; Castañer, J.; Rodríguez, A.; Rovira, C.; Veciana, J. *J. Org. Chem.* **1982**, *47*, 4498.

Table 3. Comparative UV–Vis Spectral Data of Nonconjugated PTM Radicals (Red Radicals)

PTM[a] nm (ϵ)	382 (37 200)	562 (1200)	ERCP[e] (ϵ/n) 1:0	389 (16 520)	565 (509)
PTBT[b] nm (ϵ/2)	386 (37 400)	560 (1350)	ERCP[e] (ϵ/n) 1:1	389 (23 030)	565 (709)
14[c] nm (ϵ/2)	388 (37 250)	563 (1170)	ERCP[e] (ϵ/n) 1:2	389 (29 540)	565 (910)
EPTM[d] nm (ϵ/2)	385 (36 900)	562 (1215)	ERCP[e] (ϵ/n) 1:3	389 (36 040)	565 (1110)
ERHP nm (ϵ/n)	390 (37 800)	566 (1240)	ERCP[e] (ϵ/n) 1:4	389 (42 550)	565 (1310)

[a] Perchlorotriphenylmethyl (PTM) radical.[7a] [b] Perchloro-α,α,α′,α′-tetraphenylbi-p-tolyl-α,α′-ylene biradical (PTBT).[7a] [c] Perchloro-4,4′-vinylenebis(triphenylmethyl) biradical (**14**).[10] [d] 1,2-Ethylenebis(4-tetradecachlorotriphenylmethyl) biradical.[9] [e] Calculated molar absorptivities (ϵ_{389} and ϵ_{565}) depending on the comonomers ratio for experimental values A_{389} L g^{-1} = 21.8 and A_{565} L g^{-1} = 0.650 (mol wt of the repetitive units: 783.75, 1092.45, 1709.85, and 2018.55, respectively).

Table 4. Comparative UV–Vis Spectral Data of Conjugated PTM Radicals (Green Radicals)

PTM–NH$_2$[a] nm (ϵ)	PPF[b] nm (ϵ)	**13**[c] nm (ϵ/2)	ARHP, nm (A)[28]	ARCP (ϵ/n)
390 (32 100)	388 (6 150)	385 (26 200)	392 (0.767)	388 (28060)
	460 (1 330)	435 (11 350)	453 (0.572)	442 (15440)
	498 (1 170)	460 (13 950)		
553 (2 680)	573 (2 030)			
598 (5 030)	622 (5 080)	637 (20 650)	670 (0.556)	650 (3570)

[a] 4-Aminotetradecachlorotriphenylmethyl radical.[32] [b] Perchloro-9-phenylfluorenyl radical (PPF).[7c] [c] Perchloro-4,4′-ethynylenebis(triphenylmethyl) biradical (**13**).[10]

Table 5. ESR Spectral Data of Polyradicals and Related Radicals

	solid state		isotropic solution (Me-THF)			glassy matrix; Me–THF; 77 K			
compounds	*g*	ΔH$_{pp}$(G)	*g*	ΔH$_{pp}$ (G)	a$_{\alpha C}$ (G)	*g*	ΔH$_{pp}$ (G)	*D* (G)	*R* (Å)
PTM	2.0024	5.0	2.0026	2.6	29.5[a]	2.0026	5.8		
14[27c]			2.0027	4.1	13.9[b]	2.0027	4.7	18.9	11.3
13[27c,d]			2.0027	2.7	28.3[c]	2.0026	3.6	18.7	11.3
ERCP	2.0027	6.1	2.0026	3.2		2.0026	7.2	55	7.9
ERHP	2.0019	21.0	2.0027	5.6		2.0026	2.6		
ARCP	2.0029	4.9	2.0026	3.8		2.0027	5.0		
ARHP	2.0031	6.0	2.0029	2.4		2.0026	4.4		

[a] Solvent CCl$_4$.[7a] [b] Solvent CHCl$_3$.[10] [c] Solvent CCl$_4$.[10]

of resonance by chlorine atoms in vinyl–aromatic chlorocarbons[21,22] and in the vinylene biradical **14**, analogue of ERHP (Table 3) have already been reported.[10] The almost constant value of the molar absortivities per PTM unit (ϵ/n) of the characteristic radicals bands C and D around 388 and 560 nm respectively allow us:

(1) To ascertain that the radical purity of ERHP homopolymer is around 100% (Table 2, $\epsilon \sim 37\,000$ and ~1200 versus ϵ 37 800 and 1240 for ERHP) in good agreement with the magnetic data (see later).

(2) To confirm the correctness of the 1:3 ratio assumed for the ERCP copolymer since, its molar absortivities (ϵ_{390} and ϵ_{560}) agree with the normal values ($\epsilon \sim 37\,000$ and ~ 1200 versus 36 040 and 1110 for ERCP) when the 1:3 ratio is adopted (Table 3).

(b) Acetylenic Polyradicals ARHP and ARCP. The UV–vis spectra of the PTM radicals belonging to the second group differ from those of the first group by the appearance of new UV–vis absorptions due to more extended π–p electronic interactions. Table 4 presents the spectral data of some of these PTM radicals along with those of the ARHP and ARCP polyradicals.

A comparative study of these spectral data shows that while the conjugation bands of ARHP and ARCP polyradicals differ markedly from those of PTM–NH$_2$[32] and perchloro-9-phenylfluorenyl radical PPF[7c] (different conjugating systems), they are similar to those of acetylenic biradical **13**,[10] thus confirming the acetylenic character of the connecting bridges in ARHP and ARCP polyradicals.

Electron Spin Resonance. Polyradicals ARCP and ERCP present ESR spectra with a rather broad single line spread out over a wide range of magnetic field (Table 5). The *g* values and the line width either in solid state or in isotropic solution are similar to those of PTM radical. This indicates that the spins in the polymers behave as independent spins with small dipolar spin–spin interactions. Such behavior is due to length of the connecting bridges between the radical (PTM) units. The lack of a noticeable conjugation through these bridges, due to steric interactions (see UV–vis) makes the spins independent in these polymers. However, the extended wings in the ESR spectra and the small broadening of the line, that prevent the detection of the ^{13}C satellites, suggest a rather small dipole–dipole interaction.

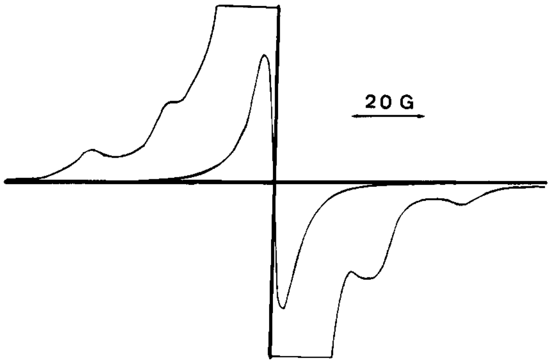

Figure 3. Triplet interactions in the ESR spectrum of ERCP polymer (in methyl–THF at 77 K).

Unexpectedly when the ESR spectrum of polyradical ERCP was recorded in a Me–THF glassy matrix at 77 K, a fine structure corresponding to a triplet state was observed (Figure 3). The zero-field splitting parameter *D* found was 55 G. From this datum, an electron–electron distance of r = 7.9 Å was calculated.[33,34a] Since the electron–electron distance between two PTM radi-

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(33) So, H.; Belford, L. *J. Am. Chem. Soc.* **1969**, *91*, 2392.

(34) (a) Ballester, M. *Química Orgánica Física, Fundamentos y Espectrometrías;* Pirámide, Ed.; Madrid, 1978; p 422. (b) *Ibid.*; p 429. (c) Ballester, M.; Pascual, I.; Carreras, C.; Vidal-Gancedo, J. *J. Am. Chem. Soc.* **1994**, *116*, 4205.

cals linked by a single *trans*-dichlorovinylene bridge (the minimun possible distance) is about 12 Å,[35] the triplet interaction observed cannot be due to the presence of vicinal PTM units. The low intensity of these lines permits the assumption that this interaction can be made through the space between PTM units put together occasionally by the random structural folding of the polymeric chain. As expected, the line width of these polymers increases with decreasing temperature, this being characteristic of the presence of anisotropic dipolar interactions.

Although polyradicals ARHP and ERHP with shorter connecting bridges between PTM units (ethynylene or *trans*-dichlorovinylene, respectively) must behave in a different way, surprisingly acetylenic polyradical ARHP presents an ESR spectrum (solid state and isotropic solution) with a single line whose *g* value and line width are also similar to those of PTM radical and the preceding ERCP and ARCP polyradicals, and no triplet lines are observed at 77 K. This apparent absence of strong dipole–dipole and exchange interactions does not agree with the anomalous magnetic behavior (see later), since although the spin concentration of ARHP has been estimated indirectly to be at least 91%, the magnetic susceptibility at room temperature is only 59% of the theoretical value, and decreases with the temperature (14% at 4.2 K). With regard to the above inconsistency, we must take into account that the dimeric analogue, the acetylene biradical **13**, also presents an anomalous magnetic behavior (about 50% of theory at room temperature).[10] However the ESR spectrum of **13** in a glassy matrix at 77 K shows the fine structure corresponding to a triplet with a zero-field splitting parameter *D* value of 18.7 G (electron–electron distance of 11.3 Å).[27c,d] The anomalous behavior of acetylene biradical **13** can be rationalized by assuming that a strong spin–spin exchange interaction gives rise to spin coupling into a singlet diamagnetic ground-state species[10] in thermal equilibrium with a triplet species. A similar reasoning can be used to rationalize the magnetic ESR behavior of acetylene polyradical ARHP. Here the strong spin–spin exchange interaction gives rise to antiferromagnetic spin coupling with formation of diamagnetic dimeric vicinal units with the intercalation of isolated PTM radical units. This explanation agrees with the low paramagnetism of polyradical ARHP, and the absence of triplet absorptions in the glass matrix ESR spectrum, since in this polymer the PTM radical units are isolated and separated by long diamagnetic bridges formed by spin–spin antiferromagnetic coupling of the vicinal radicals. A similar explanation has been suggested by Tsuchida[36] in order to explain the ESR, UV–vis, and magnetic behavior of polyacetylene with galvinoxyl radicals as pendants.

Finally polyradical ERHP, unlike the preceding polymers, showed distinct features in its ESR spectra. At room temperature in either solid or dilute ($<10^{-4}$ M) isotropic solution, ERHP displays a broad asymmetric signal with a line width at least twice that of the preceding polyradicals, due most probably to strong intramolecular dipole–dipole and exchange interactions, similar to those already observed in the vinylene biradical **14**,[10] where the observed α-^{13}C coupling constants are half the value of those of PTM radical.[7a] When the spectrum of ERHP was recorded in a Me-THF glassy matrix at 77 K, its line width was about half the value found at room temperature in solution (5.6 G vs 2.6 G). A similar effect was found by Iwamura for a strongly interacting nitroxide triradical (14 vs 4.5 G).[37] However, although the glassy matrix spectrum of vinylene biradical **14** shows the characteristic fine structure due to the triplet-state transition $\Delta Ms = 1$,[35] the corresponding fine structure does not appear in the spectrum of polyradical ERHP. This fact can be rationalized as follows: In a polyradical with an average of 28 radical units,[38] the great number of allowed $\Delta Ms = 1$ transitions, results in lowering the intensity and consequently become unobservable because they are scattered along a broad magnetic range and blurred by the electronic random noise. No signals corresponding to the "forbbiden" $\Delta Ms = 2$ transition could be observed in any of the polymeric polyradicals studied here. This is not an unexpected result since recently Ballester[34c] has reported that this "forbbiden" transition was not observed in the majority of the biradicals of the perchlorotriphenylmethyl series (PTM) studied in that paper (11 versus 1).

Table 6. Magnetic Data of Polymeric Polyradicals ERHP, ERCP, ARHP, and ARCP

	χ_{dia} cm^3 g^{-1} ($\times 10^6$)[a]	C_{emu}[b]	θ[b] (K)	μ_{eff}[b] (μ_{BM})	μ_{eff} 300 K
ARHP	−0.544				1.33
ERHP	−0.525	0.341	−5.1	1.65	1.61
ARCP	−0.525	0.282	−3.9	1.50	1.49
ERCP	−0.523	0.323	−2.2	1.61	1.56

[a] Calculated from Pascal's systematics.[39] [b] Calculated by linear regression of the 100–300K data according the Curie–Weiss law.

Magnetic Susceptibility. The molar magnetic susceptibilities (χ_M per radical unit) of ethylene (ERCP, ERHP) and acetylene (ARCP, ARHP) polyradicals were measured for powder samples in the temperature range 4.2–300 K and at a magnetic field of 20 kOe. The experimental data were corrected ($\chi_M - \chi_{\text{dia}} = \chi'_M$) for the diamagnetic susceptibility of the samples and the holder (see Table 6). The diamagnetic contribution of the molecules were estimated using Pascal's constants.[39] The results are plotted in terms of the effective magnetization in Bohr magnetons, μ_{eff} (μ_{BM}), per radical unit as a function of the temperature (Figure 4).

It has been found that polyradicals ERCP, ERHP, and ARCP present a similar qualitative magnetic behavior. They obey the Curie–Weiss law $\chi_M - \chi_{\text{dia}} = N\beta^2\mu^2/3K(T - \theta)$ in the range 100–300 K (see Table 5 and Figure 4) with almost constant μ_{eff} values approaching 1.73 μ_{BM} at room temperature. The high μ_{eff} values calculated for ERCP (1.61) and ERHP (1.65) according to the Curie–Weiss law indicate a radical purity of 87 and 90 ± 5% respectively, in accordance with their UV–vis data (see before) and with the comonomer ratio 1:3 assumed for HCP. They also show the absence of strong ferro-

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(35) The ESR spectrum in a methyl–THF glassy matrix at 77 K of vinylene birradical **14** has been recorded. A zero-field splitting parameter $D = 18.9$ G was found and a spin–spin distance of 11.3 Å was then calculated. This value agrees with that calculated by Ballester of about 12 Å, from structural data.[34b]

(36) Yoshioka, N.; Nishide, H.; Tsuchida, E. *Mol. Cryst. Liq. Cryst.* **1990**, *190*, 45.

(37) Ishida, T.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 4238.

(38) ~10 radical units if the presence of some defects in the chain (<10%) are taken into account (see later).

(39) Hellwege, K.; Hellwege A. Landolt-Börnstein II; *Diamagnetic Susceptibility*; Springer-Verlag: Berlin, 1977; Vol. 16, p 1.

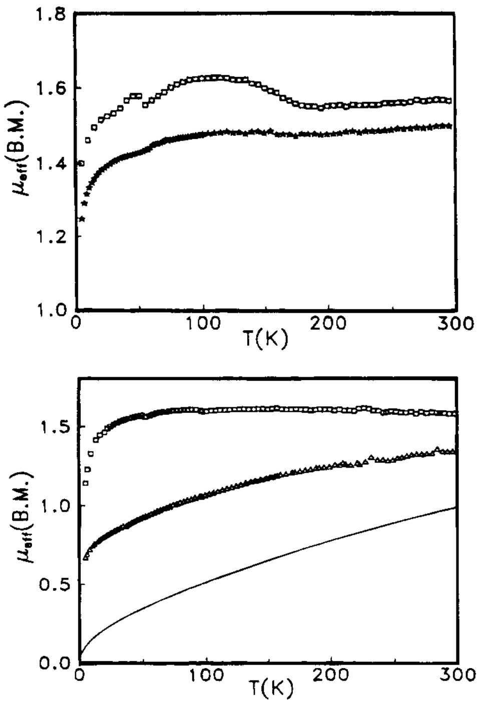

Figure 4. Thermal variation of μ_{eff} (μ_{BM}) for polymeric polyradicals. Top: □ ERCP, ★ ARCP Bottom: □ ERHP, △ ARHP, — theoretical curve for an infinite Heisenberg chain of spin $S = 1/2$ with antiferromagnetic coupling.[40]

magnetic interactions, due probably to the high spin–spin distance (>11 Å). Below 100 K all these polyradicals present weak antiferromagnetic interactions as revealed by the decreasing of the μ_{eff} values in lowering temperatures and by the small negative values of the Curie–Weiss constants θ calculated from the Curie–Weiss law in the range 100–300 K (see Table 6). The rather low value of μ_{eff} in ARCP (1.50) as compared with that of the related ERCP (1.60) is attributed to the partial presence of triple bonds in the former, which cause some antiferromagnetic coupling of the spins and therefore a low μ_{eff} value (see the ESR section before). The μ_{eff} plot of ERCP presents at around 100 K a maximum value (Figure 3) suggesting the existence of a weak intrachain ferromagnetic coupling. This fact accords with the ESR data that show the existence of weak triplet bands (see ESR section). Ethylene polyradical ERHP has no ferromagnetic interactions, showing a near degeneracy between its low- and high spin states; these facts do not agree with the predictions of Müllen[8] mentioned in the Introduction.

Acetylenic polyradical ARHP (precursor of the ERHP) presents a different and abnormal magnetic behavior. It does not follow the Curie–Weiss law in the studied range of temperatures (4.2–300 K), and consequently a direct determination of its radical purity is not possible. Its μ_{eff} at room temperature is only 1.33 μ_{BM} (much lower than that of ERHP obtained from it), and it decreases when the temperature lowers (0.65μ_{MB} at 4.2 K, Figure 4). Consequently, in accordance with the observed π–π interactions in the UV–vis spectrum at room temperature, its ground state is most probably diamagnetic. This behavior is characteristic of a strong antiferromagnetic coupling that is attributed to the presence of the acetylene bridges, between the PTM units. The comparison between the plot μ_{eff} versus T for ARHP and the theoretical curve calculated for an infinite Heisenberg chain of spins $S = 1/2$ with antiferromagnetic coupling[40] indicates a similar qualitative behavior for an integral exchange constant, $J \approx -187$ cm^{-1} (Figure 4). However a general uplift of the experimental curve is observed. This is probably due to the presence of a residual paramagnetic component (isolated PTM radical units and the contribution of the unpaired radical units corresponding to finite chains with an odd number of centers). These facts confirm the assertion given in the ESR section for the spectral behavior of ARPH.

Although the radical purity of the ERHP, ERCP, ARHP, and ARCP, as ascertained by UV–vis spectroscopy and magnetic susceptibility measurements is very high (over 90%) the presence of a small amount of defects in the radical chains cannot be discounted. However, in polymers ERHP and ERCP, where the magnetic measurements follow the Curie–Weiss law with a qualitative similar behavior, the presence of defects (maximum amount 10%, which means radical chains with an average of 8–9 units) do not invalidate the assertion of being polymers with "independent spins with rather small dipole–dipole interactions"; in other words the paramagnetic behavior observed is an intrinsic property of the dichlorovinylene PTM polyradical structure rather than a consequence of defects.

As far as ARHP, chemical precursor of ERHP, is concerned, its anomalous magnetic behavior cannot be attributed to the presence of defects (maximum amount 10%) since the magnetic susceptibility curve is controlled by the high M_w fractions (Heisenberg chain) and not by the low M_w fractions, which would present a higher paramagnetic component and consequently a susceptibility maximum at low temperatures.

Conclusions

PTM polyradicals ERHP, ARHP, ERCP, and ARCP are new stable "quasi" 1D-paramagnetic or antiferromagnetic materials with no electrical conductivity. The structure of the connecting bridges in these polyradicals modulates their magnetic behavior. Although the ESR data of the ERHP polymer show small electronic interactions, and its UV–vis spectroscopic data indicate the presence of almost degenerate states caused by steric hindrance, its magnetic behavior does not fit with the Müllen theory ("the small overlapping of adjacent orbitals favours ferromagnetic interactions"),[8] since only a paramagnetic behavior with small antiferromagnetic interactions is observed. In the case of acetylenic polyradical ARHP, apparently the absence of steric hindrance in the acetylene bridge and the adequate topology of the PTM unit (para substitution), gives rise to the strong antiferromagnetic interactions detected by its magnetic susceptibility behavior. Unexpectedly the ARCP copolymer, with longer bridges between the radical units, shows weak ferromagnetic interactions due to triplet interactions; this suggests not only that, in the design of high-spin polyradicals, the "pure connectivity" must be taken into account but also that the "three-dimensional structure" plays a decisive factor, as indicated by Miller[41a] and Lathi.[41b] The experimental work described here opens up the potential to synthesize

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(40) Bonner, J. C.; Fisher, M. E. *Phys. Rev.* **1964**, *135*, A640.

(41) (a) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994,** *33*, 385. (b) Lathi, P. M.; Ling, C.; Yoshioka, N, Rossitto, F. C.; van Willigen, H. *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **1993**, *233*, 17.

other stable PTM polyradicals with other topologies and to test other models of approaching organic ferromagnets.

Experimental Section

General Methods. Perkin-Elmer 682, Perkin-Elmer Lambda Array 3840, Bruker WP 80 SY, and Varian E109E spectrometers were used for IR, UV–vis, ^{1}H NMR, and ESR spectroscopy, respectively. The routine magnetic susceptibilities were measured with a Varian 4-in. magnet with constant-force caps operating at 11 kOe, and a Cahn RG electrobalance. More precise data were collected with a SHE SQUID magnetometer operating in a field strengh of 20 kOe. The thermogravimetric analyses were carried out with a Perkin-Elmer TGS-2 system, under N_2 (40 cm^3 min^{-1}). The conductivity measurements were performed by the Van der Pauw[42] method with a 0–900 V electrical source (sensitivity 10^{-7} S cm^{-1}); more precise data were taken with a PAR 136 digital electrometer with applied voltages corresponding to electric fields from 10^4 to 2.5×10^5 V·m^{-1} (sensitivity 10^{-12} S cm^{-1}); the measurements were carried out on powder samples, compressed into pellets under pressures exceeding 4×10^7 Pa. The osmometric measurements were performed with a V. P. Knauer osmometer Model 7311. The GPC measurements were carried out on a Waters Ass. instrument with a Polymer Laboratories gel column with an exclusion range 10^3–10^4 Å, with 50 μL (0.2% w/v) samples at a flow rate of 0.5 mL min^{-1}. The working-up of the polyradicals was performed in darkness. Since the locations of the IR peaks of highly chlorinated compounds differ markedly from their nonchlorinated counterparts they are included in this section, although weak peaks in the region 1300–400 cm^{-1} are not given.

Detection of Perchlorobenzyl Radical in the Reaction of Perchlorotoluene with Fe(CO)$_5$. A solution of a small amount of perchlorotoluene in anhydrous benzene was poured into a RSE quartz tube and degassed by three freeze–pump–thaw cycles. A drop of Fe(CO)$_5$ was added under argon and sealed. The ESR tube was heated at 70 °C in the cavity of an ESR spectrometer. The characteristic spectrum of perchlorobenzyl was detected with high intensity and resolution.[17]

Poly(αH-pentadecachloro-(4,4′-dimethyltriphenylmethane)-α′,α″-diylidene) (HHP, 2). Fe(CO)$_5$ (10 mL) was slowly added to a refluxing solution of αH-nonadecachloro-4,4′-dimethyltriphenylmethane[7f] (**1**, 5.00 g, 5.39 mmol) in purified benzene (100 mL), under argon. After 1 h of refluxing more Fe(CO)$_5$ (10 mL) was added and the refluxing was continued (3 h more).

The resulting reaction mixture was cooled and filtered.

(a) The solid separated was washed with aqueous HCl and with water, then dried, and purified through silica gel in CHCl$_3$. The resulting solid resin (3.5 g) was digested with refluxing ethyl ether. The insoluble white material was characterized as HHP (fraction A, 3.02 g, 71%); TGA, stability >450 °C; IR (KBr) 2935 (w), 1600 (w), 1535 (w), 1365 (s), 1320 (s), 1290 (s), 1140 (s), 802 (m), 710 (m), 695 (m), 655 (m), 506 (m) cm^{-1}; UV (CHCl$_3$, calcd for $C_{21}HCl_{15}$): λ_{max} 284, 313 (sh), 345 (sh) nm (ϵ 8980, 2950, 680), ^{1}H NMR (CHCl$_3$) δ 7.06–6.82 complex signal; osmometry (CHCl$_3$, 35 °C) M_n found 22 600, calcd for $n = 29$, M_n 22 768; GPC (CHCl$_3$, 35 °C, polystyrene standard): $M_n = 8750$, $M_w = 17\,740$, polydispersity = 2.03 (monomodal distribution); conductivity ($\sigma_{RT} < 10^{-12}$ S cm^{-1}). Anal. Calcd for $(C_{21}HCl_{15})_n$: C, 32.1; H, 0.1; Cl, 67.8. Found: C, 32.1; H, 0.2; Cl, 67.7.

The ethereal extract, evaporated to dryness (0.051 g), was not investigated since it presented carbonylic and aliphatic impurities (IR).

(b) The benzene solution was evaporated to dryness in vacuo, and the residue, dissolved in CHCl$_3$, was washed with aqueous HCl and with water, dried, and evaporated. The green residue was purified through silica gel (CHCl$_3$), and the white solid resin obtained was digested with refluxing ethyl ether. The insoluble material was identified as polymer HHP (fraction B, 0.861 g, 20%). TGA, stability >450 °C; IR and ^{1}H NMR (CHCl$_3$) very similar to HHP (fraction A); osmometry (CHCl$_3$, 35 °C) M_n found 6600, calcd for $n = 8$, M_n 6280; GPC (CHCl$_3$, 35 °C, polystyrene standard), $M_n = 3300$, $M_w = 5250$, polydispersity = 1.59 (monomodal distribution). Anal. Calcd for $(C_{21}HCl_{15})_n$: C, 32.1; H, 0.1; Cl, 67.8. Found: C, 32.2; H, 0.2; Cl, 67.4.

Poly[(αH-pentadecachloro-(4,4′-dimethyltriphenylmethane)-α′,α″-diylidene)tris(perchloro-*p*-xylene-α,α-diylidene)] (HCP, 7). *(1) With Fe(CO)$_5$ as Condensing Agent.* A mixture of perchloro-*p*-xylene[12] (**6**, 4.70 g, 10 mmol) and αH-nonadecachloro-4,4′-dimethyltriphenylmethane[7f] (**1**, 2.40 g, 2.6 mmol) in purified benzene (130 mL), was polymerized with Fe(CO)$_5$ (10 mL + 10 mL) as in the preceding paragraph.

(a) The precipitate was filtered and treated as before yielding copolymer HCP (fraction A, 3.1 g, 59%). TGA, stability > 450 °C; IR (KBr) 1600 (w), 1535 (w), 1345 (m), 1320 (s), 1300 (m), 1150 (s), 825 (m), 815 (m), 802 (m), 710 (s) cm^{-1}; UV (CHCl$_3$, calcd for $(C_{21}HCl_{15})(C_8Cl_6)_3$): λ 283, 311 (sh), 342 (sh) nm (ϵ 22 270, 10 630, 1330); ^{1}H NMR (CHCl$_3$) δ 7.06–6.82 complex signal; osmometry (CHCl$_3$, 35 °C) M_n found: 22 200, calcd for $(C_{21}HCl_{15})_n(C_8Cl_6)_{3n}$ $n = 13$, M_n 22 247; GPC (CHCl$_3$, 35 °C, polystyrene standard) $M_n = 10\,120$, $M_w = 23\,890$, polydispersity = 2.36 (monomodal distribution); conductivity $\sigma_{RT} < 10^{-12}$ S cm^{-1}. Anal. Calcd for $(C_{21}HCl_{15})_n(C_8Cl_6)_{3n}$: C, 31.6; H, 0.1; Cl, 68.4. Found: C, 31.6; H, 0.1; Cl, 68.4.

The ethereal extract was evaporated to dryness giving a residue (0.112 g), which by sublimation (100 °C, 0.01 mmHg) yielded perchloro-*p*-xylylene[18] (0.010 g) identified by its melting point and IR spectrum. The residue was impure copolymer HCP (0.100 g) identified by IR spectrum.

(b) The benzene solution was treated as in the preceding reaction, but the digestion was performed with pentane affording copolymer HCP (fraction B, 0.876 g, 17%) identified by elemental analysis and IR and ^{1}H NMR spectra. Osmometry (CHCl$_3$, 35 °C), M_n found 7900, calcd for $(C_{21}HCl_{15})_n(C_8Cl_6)_{3n}$ $n = 5$ $M_n = 8557$. GPC (CHCl$_3$, 35 °C, polystyrene standard), $M_n = 3920$, $M_w = 7690$, polydispersity = 1.96 (monomodal distribution). Anal. Calcd for $(C_{21}HCl_{15})_n(C_8Cl_6)_{3n}$: C, 31.6; H, 0.1; Cl, 68.4. Found: C, 31.8; H, 0.2; Cl, 68.5.

The pentane solution, evaporated to dryness, gave a residue (1.00 g) which by sublimation (100 °C, 0.01 mmHg) afforded perchloro-*p*-xylylene[18] (0.83 g, 23%) identified by its melting point and IR spectrum. The residue (0.050 g) was identified as impure copolymer HCP (IR spectrum).

(2) With SnCl$_2$ as Condensing Agent. A mixture of perchloro-*p*-xylene (**6**, 0.63 g, 1.40 mmol), αH-nonadecachloro-4,4′-dimethyltriphenylmethane (**1**, 0.33 g, 0.35 mmol), SnCl$_2$·2 H$_2$O (5 g, 22 mmol) and purified dioxane (40 mL) was refluxed under argon and in darkness (4.5 h).

The reaction mixture was poured into aqueous 2 N HCl, and the resulting precipitate was filtered and dissolved in CHCl$_3$, and the clear solution was washed with aqueous HCl and with water, dried, and evaporated. The resulting resin (0.618 g) was purified through silica gel (CHCl$_3$) and digested with refluxing ethyl ether. The final solid was identified as polymer HCP (0.400 g, 63%). IR (KBr) 1600 (w), 1535 (w), 1345 (s), 1320 (s), 1300 (m), 1150 (s), 825 (m), 815 (m), 802 (m), 710 (s) cm^{-1}; ^{1}H NMR (CHCl$_3$) δ 7.06–6.82 complex signal; osmometry (CHCl$_3$) M_n found: 6380, calcd for $(C_{21}HCl_{15})_n(C_8Cl_6)_{3n}$ $n = 4$, M_n 6846. Anal. Calcd for $(C_{21}HCl_{15})_n(C_8Cl_6)_{3n}$ C, 31.6; H, 0.1. Found: C, 31.5; H, 0.2.

The ethereal extract was evaporated and the residue (0.152 g) submitted to column chromatography yielding the following:

(a) From hexane: A mixture of perchloro-*p*-xylylene[18] and perchloroheptafulvene[23,24] (0.070 g) that was separated by a complex crystallization–sublimation process.

(b) From CHCl$_3$: impure HCP (0.048 g) containing carbonylic impurities (IR spectrum).

Polyradical poly(perchloro-(4,4′-dimethyltriphenylmethyl)-α′,α″-diylidyne) ARHP (4). *(1) With NaOH and I$_2$.* A mixture of polymer HHP (**2**, 0.069 g), powdered NaOH (0.17 g), and DMSO (4 mL) was stirred under argon and in darkness

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[42] Wieder, H. H. *Laboratory Notes on Electrical and Galvanomagnetic Measurements, Materials Science Monographs*; Elsevier: Amsterdam, 1979; Vol. 2.

(24 h). The dark-blue solution was filtered on a sintered-glass funnel, poured over I_2 (0.124 g), and left undisturbed (1 h).

The brown reaction mixture was poured into water, and the resulting precipitate was filtered, washed with water, and dried (0.055 g). The dark-green solid was digested with refluxing $CHCl_3$ yielding an insoluble fraction (0.043 g, 62%) identified as polyradical ARHP (see next paragraph). Anal. Calcd for $(C_{21}Cl_{13})_n$: C, 35.3. Found: C, 35.4.

The $CHCl_3$ extract (0.008 g, 11%) presented an IR spectrum almost identical to that of the insoluble fraction.

(2) With TBAOH and I_2. TBAOH (40% in water, 4.5 mL) was added to a solution of homopolymer HHP (M_n 22 590, 1.320 g, 1.68 mmol) in a mixture of purified THF (200 mL) and DMSO (20 mL), and the resulting dark blue-violet solution was stirred in the dark at room temperature and under argon. The reaction was monitored by UV−vis spectroscopy until no more evolution of the UV−vis spectrum (total formation of triple bonds) was observed (70 h). Then I_2 (5.0 g, 39 mmol) was added, and the stirring was continued (3 h).

The resulting suspension was poured into water (400 mL), and the precipitate filtered, washed with water and with acetone, digested with refluxing ethyl ether, and finally dried yielding a dark green solid insoluble in $CHCl_3$ (1.173 g, 97%) characterized as polyradical ARHP; TGA, stable up to 220 °C; IR (KBr) 1520 (w), 1425 (w), 1320 (s), 1250 (m) 1220 (m), 1182 (m), 730 (m), 705 (s), 670 (m), 650 (m), 422 (m) cm^{-1}; UV−vis[28](C_2Cl_4) λ 392, 453, 670 nm (A 0.767, 0.572, 0.556); ESR and magnetic susceptibility (see Results and Discusion). Conductivity: $\sigma_{RT} < 10^{-7}$ S cm^{-1}. Anal. Calcd for $(C_{21}Cl_{13})_n$: C, 35.3; H, 0.00; Cl, 64.7. Found: C; 35.0; H, 0.1; Cl, 64.6%.

Polyradical Poly(perchloro-(4,4′-dimethyltriphenylmethyl)-α′,α″-diylidene) ERHP (5). A slow stream of dry Cl_2 was passed through a mixture of the polyradical ARHP (0.552 g), I_2 (0.187 g), and purified CCl_4 (250 mL) at room temperature in darkness. The end point was monitored by UV−vis spectroscopy (1 h).

Evaporation of the solvent yielded a red residue (0.750 g) which was purified through silica gel ($CHCl_3$) and digested with refluxing ethyl ether to give finally polyradical ERHP (0.590 g, 97%) soluble in $CHCl_3$; TGA, stable up to 220 °C; IR (KBr) 1505 (w), 1320 (f), 1255 (w), 1170 (m), 815 (f), 725 (m), 700 (f), 485 (m) cm^{-1}; UV−vis ($CHCl_3$) (calcd for $(C_{21}Cl_{15})_n$): λ 282, 341 (sh), 371, 390, 503, 566 nm (ϵ 9080, 6250, 19 120, 37 800, 1170, 1240); ESR and magnetic susceptibility (see results and discussion); osmometry ($CHCl_3$, 35 °C) M_n found: 22210, calcd for $(C_{21}Cl_{15})_n$ $n = 28$ units M_n 21 945; GPC ($CHCl_3$, 35 °C, polystyrene standard) M_n = 8250, M_w = 13 350, polydispersity = 1.62 (monomodal distribution). Conductivity $\sigma_{RT} < 10^{-12}$ S·cm^{-1}. Anal. Calcd for $(C_{21}Cl_{15})_n$: C, 32.1; Cl, 67.9. Found: C, 32.1; H, 0.1 ; Cl, 67.6.

Reversion of Polyradical ERHP (5) to HHP (2). Ascorbic acid (0.015 g, 0.084 mmol) was added to a solution of polyradical ERHP (0.011 g, 0.014 mmol) in moist THF (4 mL), and the mixture was stirred (2 h). The color of the solution changed from red to yellowish-white.

The reaction mixture was poured into water, and the precipitate which formed was filtered, washed with ethyl ether, and dried to give polymer *trans*-HHP (0.009, 82%) identified by IR and UV spectra. IR (KBr) 2935 (w), 1535 (w), 1365 (s), 1320 (s), 1290 (s), 1145 (s), 815 (m), 800 (m), 700 (s), 680 (m), 480 (m) cm^{-1}; UV (THF) calcd for $(C_{21}HCl_{15})_n$ λ 297, 307 (ϵ, 4450, 4397) nm.

Poly[(perchloro-(4,4′-dimethyltriphenylmethyl)-α′-ylidyne-α″-ylidene)(perchloro-*p*-xylene-α-ylidyne-α′-ylidene)-bis(perchloro-*p*-xylene-α,α′-diylidene)] (ARCP, 9). *(1) With TBAOH and Chloranil in THF−DMSO.* TBAOH (40% in water, 2 mL, 3 mmol) was added to a solution of copolymer HCP (**7**, M_n = 22 200, 1.35 g, 0.70 mmol) in a mixture of purified THF (130 mL) and DMSO (13 mL) that was stirred under argon and in darkness. The reaction was monitored by UV−vis spectroscopy until no more evolution of the UV−vis spectrum was observed (24 h). Then *p*-chloranil (1.1 g, 4.47 mmol) was added, and the stirring was continued (4 h).

The resulting dark solution was concentrated, and the residue treated with water and with acetone, yielding a dark green residue that was digested with refluxing ethyl ether to give polyradical ARCP (1.290 g, 96%). This compound was extracted with refluxing $CHCl_3$ (100 mL) yielding the following:

(a) A soluble fraction which was purified through silica gel and, after digestion with refluxing ethyl ether, gave polyradical ARCP (soluble fraction, 1.046 g, 78%) dark green powder. TGA, stable up to 220 °C; IR (KBr) 1600 (w), 1570 (w), 1550 (w), 1510 (w), 1320 (s), 1160 (s), 1120 (s), 1070 (s), 815 (m), 705 (s), cm^{-1}; UV ($CHCl_3$, calcd for $(C_{21}Cl_{13})(C_8Cl_6)_3$) λ 288, 370 (sh), 388, 442, 650 nm (ϵ 25 280, 16 540, 28 060, 15 440, 3570); ESR and magnetic susceptibility (see Results and Discussion). Conductivity: $\sigma_{RT} < 10^{-7}$ S cm^{-1}. Anal. Calcd for $(C_{21}Cl_{13})_n(C_8Cl_6)_{3n}$: C, 32.9; Cl, 67.1. Found: C, 32.8; Cl, 67.1.

(b) An insoluble fraction, identified as polyradical ARCP (insoluble fraction, 0.147 g, 11%) by IR spectrum (very similar to that of the soluble fraction). Anal. Calcd. for $(C_{21}Cl_{13})_n(C_8Cl_6)_{3n}$: C, 32.9. Found: C, 32.6.

(2) With TBAOH and I_2 in THF−DMSO. The preceding reaction was repeated (HCP, 0.050 g, TBAOH, 0.1 mL, THF, 10 mL, DMSO, 1 mL) but using I_2 (0.090 g, 0.71 mmol) as oxidizing agent.

Polyradical ARCP (0.042 g, 84%) was obtained which was identified by IR and UV−vis spectra, both almost identical to those of the preceding reaction.

(3) With "TBAOH" and Chloranil in THF. A great amount of TBAOH (40% in water, ≈20-fold excess) was added, under argon and in darkness, to a solution of HCP (0.057 g, 0.033 mmol) in THF (2.5 mL), and the resulting dark blue-violet solution was stirred at room temperature for 24 h. Then chloranil (0.25 g, 1.02 mmol) was added, and the stirring continued (4 h).

Elimination of the solvent gave a residue which was washed with water and with acetone, and digested with refluxing ether to give ARCP (0.050 g, 90%) identified by elemental analysis and IR and UV−vis spectra.

Poly [(perchloro-(4,4′-dimethyltriphenylmethyl)-α′,α″-diylidene)tris(perchloro-4-xylene-α,α″-diylidene)] (ERCP, 10). Chlorination of polyradical ARCP (**9**, 0.342 g) with Cl_2 and I_2 (0.120 g) in CCl_4 was performed as in the synthesis of ERHP, yielding polyradical ERCP (0.285 g, 83%), red powder. TGA, stable up to 220 °C; IR (KBr) 1600 (w), 1570 (w), 1550 (w), 1510 (w), 1320 (s), 1160 (s), 815 (m), 705 (f), cm^{-1}; UV−vis ($CHCl_3$) (calcd for $(C_{21}Cl_{15})(C_8Cl_6)_3$) λ 280, 389, 565 nm (ϵ 25 600, 36 010, 1110); osmometry ($CHCl_3$, 35 °C) M_n found 19 950, calcd for $(C_{21}Cl_{15})_n(C_8Cl_6)_{3n}$ $n = 12$, $M_n = 20\,530$; GPC ($CHCl_3$, 35 °C, polystyrene standard) M_n = 11 020, M_w = 22 040, polydispersity = 2.00 (monomodal distribution); ESR and magnetic susceptibility (see Results and Discusion). Conductivity ($\sigma_{RT} < 10^{-7}$ S cm^{-1}). Anal. Calcd for $(C_{21}Cl_{15})_n(C_8Cl_6)_{3n}$: C, 31.6; H, 0.0; Cl, 68.4. Found: C, 31.8; H, 0.1; Cl, 68.2.

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