MAGNETIC POLYMERS

Introduction

Typical behavior of small molecules or metal ions with unpaired electrons is that of a paramagnet, ie, magnetic interactions within the large ensemble of electron spins are negligible and a large external magnetic field is required to even partially align the electron spins. For ferromagnetism and other technologically useful types of magnetism, the quantum mechanical exchange interaction between electron spins is a prerequisite (1). In a ferromagnet, the exchange interactions within a three-dimensional structure align the spins in one direction, producing a large magnetic moment in magnetic domains of more than 10^4 electron spins, even in the absence of external magnetic field. The strength of this exchange interaction determines the *Curie temperature* (T_C), that is, the temperature above which the magnetic ordering is destroyed and the material becomes paramagnetic (1). (Analogously, T_C is referred to as ferrimagnetic Curie temperature in ferrimagnets).

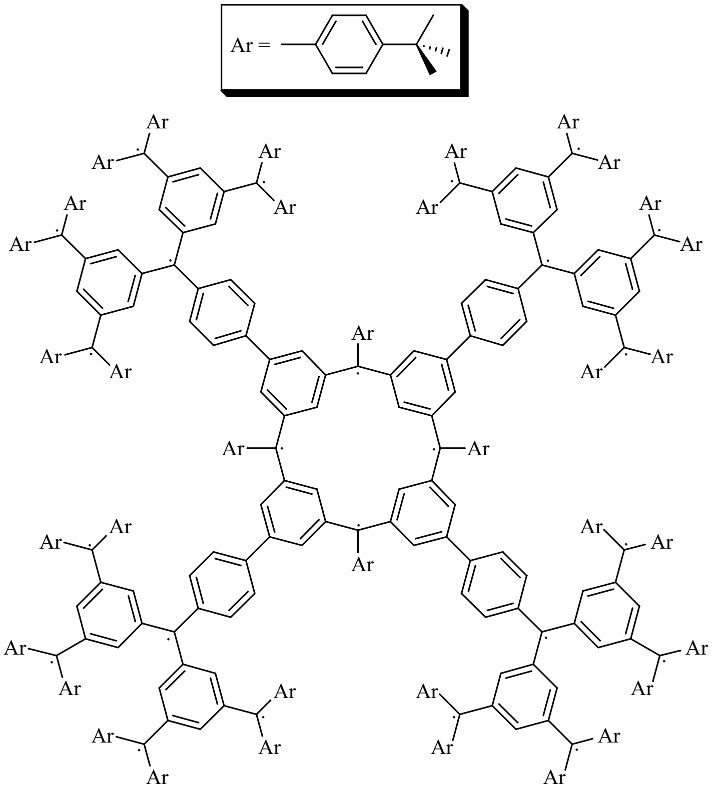
Traditional magnetic materials are based upon metals (and metal ions) with partially filled *d*- and *f*-shells, ie, selected metals, metal alloys, and ceramics. Composite materials such as organic polymers filled with small metallic or inorganic magnetic particles fall into similar category (2).

The relatively recent magnetic materials, in which organic radicals function as the source of electron spin, are organometallic magnets and organic magnets. In organometallic magnets, the exchange interaction occurs between organic radicals or radical anions and metal ions. Many of such materials may be viewed as one-, two-, or three-dimensional coordination polymers (3–5). In organic magnets, based upon molecular solids of organic radicals (or radical ions), exchange interactions occur between molecules with unpaired electrons. Because such through-space interactions are inherently weak, the T_C's for organic ferromagnets are typically below 2 K, with the exception of the C_{60}-TDAE [TDAE = tetrakis(dimethylamine)ethylene] radical ion salt which has $T_C = 16$ K (6–8).

Organic polymers, in which exchange interactions between radicals are mediated by π-conjugated system, provide an alternative approach to organic magnets. As early as 1968, Mataga proposed few structures for plausible one- and two-dimensional "ferromagnetic" polymers, based upon cross-conjugated diphenylcarbenes and triphenylmethyls (9). Studies of numerous model diradicals (and dicarbenes) established the importance of connectivity of π-system mediating exchange interaction between the radicals. For two radicals linked through *m*-phenylene, triplet (spin multiplicity, $2S + 1 = 3$, for $S = 1$, where S is the total spin quantum number) ground state is found, as long as the π-system is approximately planar. The energy gap (ΔE_{ST}), between the singlet excited state and the triplet ground state, exceeds RT at room temperature in several diradicals. The analogous p- or o-connectivity leads to the singlet ground state, ie, pairing of two spins-1/2 (10,11). Such pairwise exchange interactions leading to the triplet and singlet ground states are referred to as ferromagnetic coupling and antiferromagnetic coupling, respectively. Strong ferromagnetic couplings ($\Delta E_{ST} > RT$), when extended in a three-dimensional network, could lead to ferromagnetism at room temperature (10). This goal was recently brought a step closer by discovery of magnetic ordering in a highly cross-linked conjugated organic polymer (12), which is described in the next section.

One of the measures of progress toward magnetic polymers is the average value of S in the ground state of the paramagnetic macromolecule. (For n ferromagnetically coupled spin-1/2, $S = n/2$). Several problems need to be addressed in synthesis of such conjugated polymers. Connectivity between the radicals within the π-system of the macromolecule must be strictly controlled; typically, the head-to-tail polymerization provides adequate connectivity for ferromagnetic coupling. However, even a single head-to-head (or tail-to-tail) connection may result in spin pairing (or interruption of exchange interaction) and, consequently, low value of average S will be obtained. Analogously, a severe out-of-plane twist of the π-system may interrupt exchange coupling or change ferromagnetic coupling to antiferromagnetic coupling. This particular problem is amplified by the need for sterically hindered groups in the macromolecule to prevent radicals from dimerization or other chemical decomposition pathways of radicals. The placement of sterically bulky groups and overall connectivity of the π-system should allow for significant delocalization of spin density from radicals to the linking π-system; this is a prequisite for a significant through-bond exchange interactions, including ferromagnetic coupling between the neighboring radicals. The chemical yield for generation of radicals must be near quantitative or, if radical monomers are used for polymerization, the radicals should survive polymerization conditions intact.

It is clear that the synthesis of magnetic polymers poses an extreme challenge for polymer science and organic chemistry, especially in view of the fact that the ultimate goal is a macromolecule with large number (10^4 or more) of interacting radicals (12). Not surprisingly, until late 1990s, the highest values of S in organic molecules and polymers were attained for strictly monodisperse organic molecules, eg, polyarylmethyl **1** with $S = 10$, prepared by laborious multistep syntheses (13–15) (Fig. 1). Even though stable triplet ground state ($S = 1$) diradicals



(1)

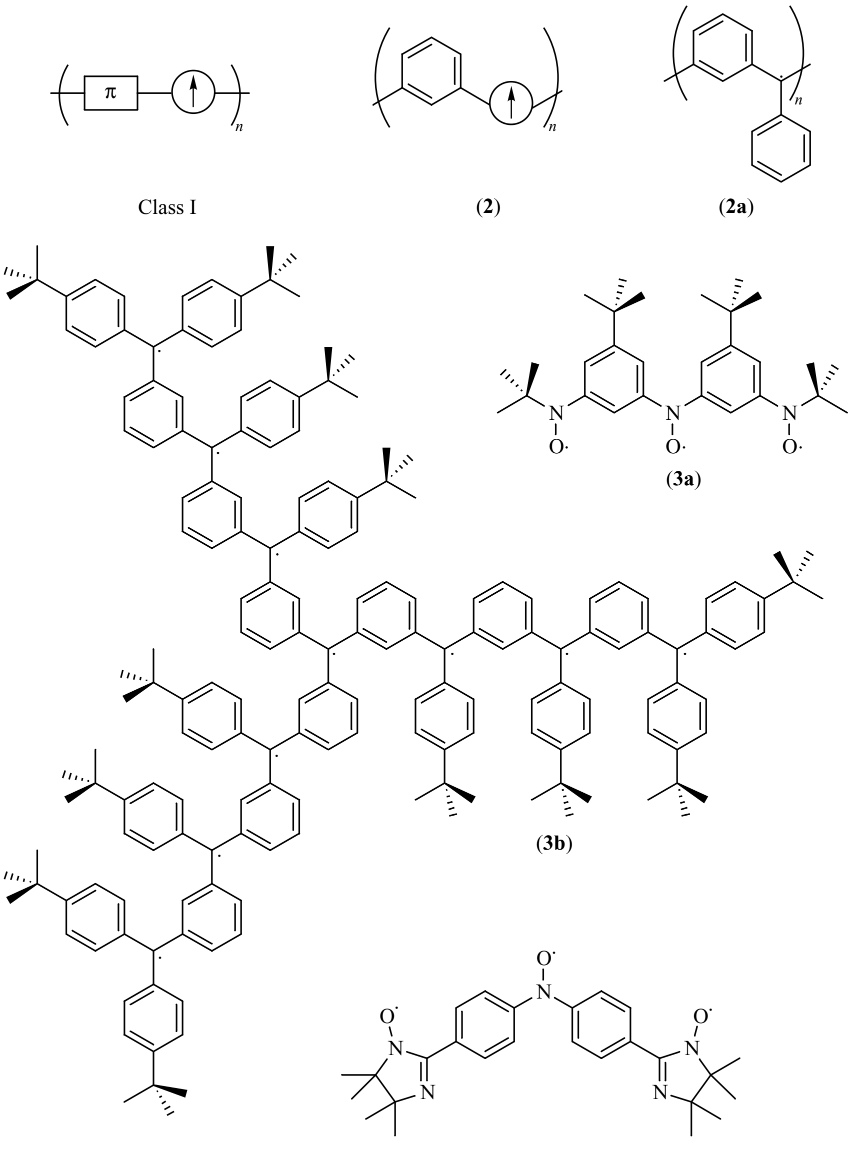
Fig. 1. Dendritic-macrocyclic polyradical **1**.

are well known, most of the reported "magnetic" polymers did not even reach $S \approx 1$, ie, a ferromagnetic coupling of two spin-1/2 radicals on average. Spurious reports of "ferromagnets" showing hystereses at room temperature in organic polymers with radical concentration on the order of 1% radical/unit or less are ignored in this review; magnetic behavior of such "magnetic" polymers has been shown to be associated with metal purities (16).

Two limiting approaches have been developed for connectivity between the radicals within conjugated polymers: Class I polyradicals, in which the radicals are within the π-system mediating exchange interactions, and Class II polyradicals, in which radicals are pendant groups attached to the conjugated polymer backbone.

Class I Polyradicals

The discussion of Class I polyradicals is focused on conjugated polymers **2** in which *m*-phenylene groups are employed to attain through-bond ferromagnetic coupling (Fig. 2). They are by far the most important of all organic polymers studied for their magnetic properties.



Class I (**2**) (**2a**) (**3a**) (**3b**) (**3c**)

Fig. 2. Selected linear and branched neutral polyradicals with *m*-phenylene-like connectivities.

Linear polyarylmethyl polymer **2a** was prepared from the corresponding hydrocarbon with degree of polymerization (DP) of about 30. Magnetic studies showed an average value of $S \approx 2$; the radical concentration was not determined (17). The star-shaped model molecules had much higher values of S, eg, $S = 5$ for **3b**; oligoradicals **3** could be much better characterized compared to polymers **2** (Fig. 2) (18). Extension of star-shaped connectivity to dendrimers was not successful in improving the values of S (19).

While moderately sterically hindered polyarylmethyls can be handled in solution at low temperatures, the isoelectronic aminium radical cations and boride radical anions may offer stability at room temperature. However, such highly charged species may exist as complicated, medium-dependent oligomeric aggregates in solution. It is not uncommon that such intermolecular dimers and oligomers are diamagnetic, leading to overall very low radical concentrations. Nevertheless, the general idea of generating spin carrying polyradical polyions connected via *m*-phenylenes (or other ferromagnetic couplers) has attracted considerable interest ("polaronic ferromagnet") (20) (Fig. 3).

Electron spin resonance (ESR) spectra for disodium diboride (**4**) suggest triplet ($S = 1$) ground state or near degeneracy between the singlet and the triplet states; however, the resonance positions are highly solvent and counterion dependent (21). Such a complicated behavior for a simple diradical suggests that this system is not a promising candidate for magnetic polymers.

Bushby reported several aminium-based polymers (22). Polyamine **5a** ($M_w > 10^4$, GPC) was prepared by Suzuki reaction based polymerization, and then p-doped with antimony pentachloride. The resultant polyaminium polymer **5b** had radical concentration of ~0.5 radical/unit and an average value of $S \approx 4$ (22). The ferromagnetic coupling was rather weak, as expected for extended exchange pathway of *m*-phenylene with two *p*-phenylene spacers (Fig. 3).

ESR studies of numerous model aminium-based small monodisperse oligomers, eg, **6** and **7**, were reported in the past few years (Fig. 3) (23,24). For dications and trications, $S = 1$ and $S = 3/2$ states were detected (25–32). The $S = 3/2$ and $S = 1$ ground states for **6a** and **7b** were determined via spin nutation spectroscopy and magnetization study, respectively (Fig. 3) (24,32). For selected di- and trications bearing *p*-phenylenediamino-based radical cations, preliminary measurements of magnetic susceptibility using Evans NMR method suggested the low spin ground states ($S = 0$ and $S = 1/2$), though detailed studies with respect to medium and concentration effects for these highly charged species are needed (25–28). The $S = 1$ and $S = 3/2$ states were also detected for di- and trications derived from ylids **8a** and **8b**, respectively (Fig. 3) (33). There were reports of functionalized poly(*m*-aniline)s oxidized to the corresponding polyaminiums and polynitroxides; however, only values of $S \leq 1$ were obtained and, typically, radical concentrations were poor (34,35).

The radical cation based polymers and oligomers described in the previous section may be viewed as possessing very compact radical ions, centered on boron or nitrogen. An alternative approach is to use short, readily dopable fragments of π-system, which are linked together with *m*-phenylene couplers into a conjugated polymer. The representative examples of such polymers and oligomers, reported by Dougherty and co-workers, are p-doped polyacetylene-based **9**, p-doped heterocyclic-based **10**, and electrochemically n-doped fuchsone-based **11** (36,37) (Fig. 4). Polymers **9** and **10** (DP = 15–30) and polydisperse oligomer **11** (DP ≈ 7) were obtained using polymerizations based upon Suzuki coupling or Wittig reaction. For **9** and **10**, chemical p-doping (I_2 or AsF_5) gave polyradicals with very low radical concentrations (0.002–0.18 radical/unit) and an average value of $S = 1/2$ to 3, at low temperatures. Studies of model oligomers, *m*-phenylene connected bithiophenes and bipyrroles, revealed that radical cations form diamagnetic dimers, as expected from previous reports on conducting polymers and oligomers by Miller

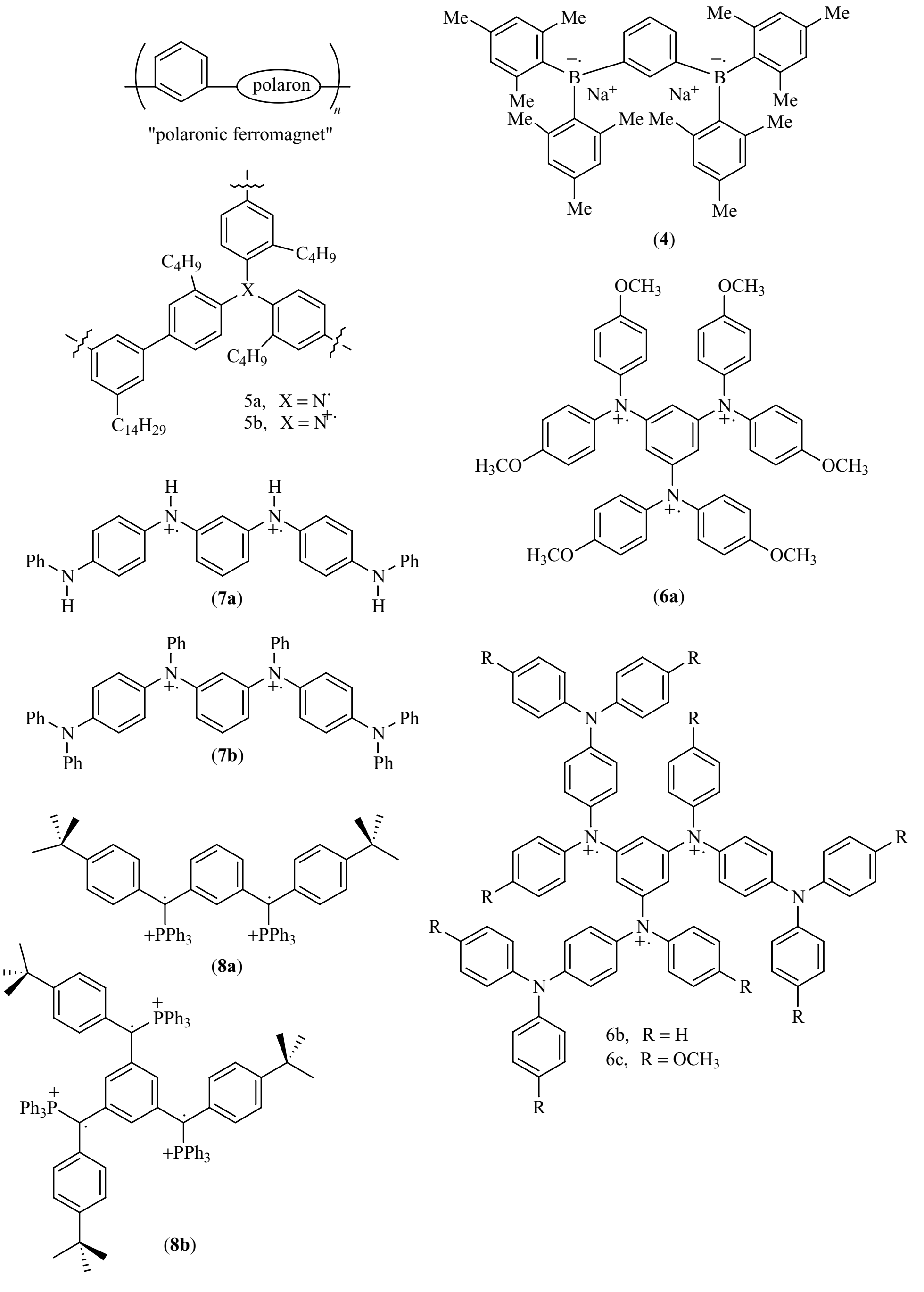
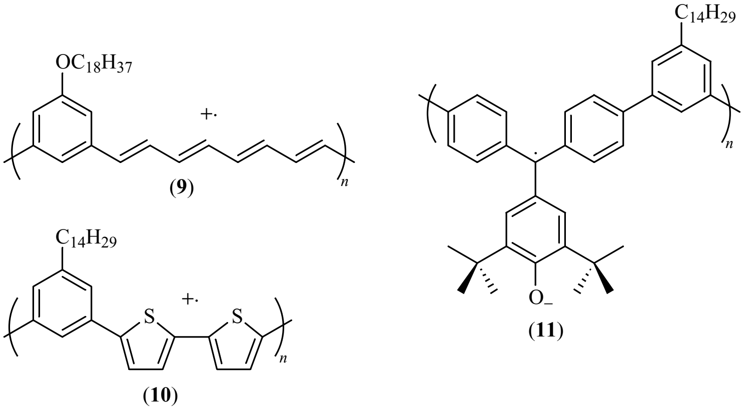


Fig. 3. Selected boron- and nitrogen-centered polaronic polyradicals.



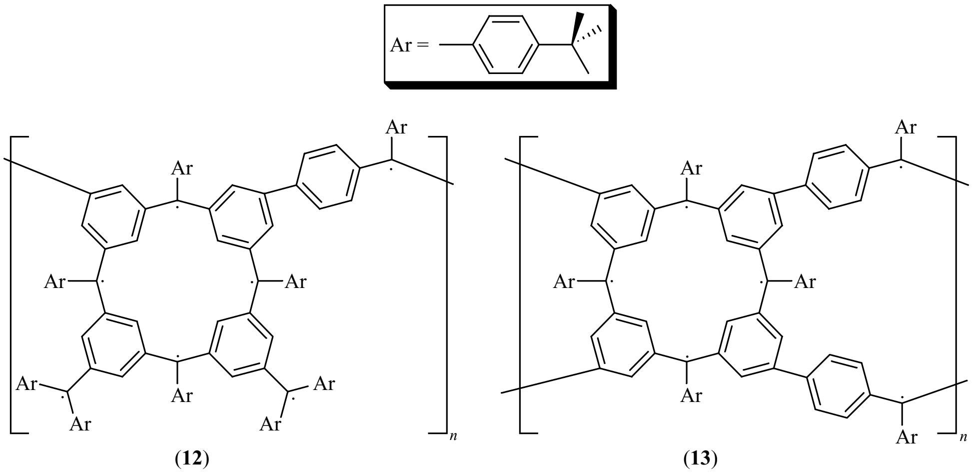
(9) (10) (11)

Fig. 4. Selected polaronic polyradicals with delocalized polarons.

and co-workers (38); this behavior is detrimental to attaining high concentration of radicals or large values of S in p-doped polymers (39). For oligomer **11**, better-controlled electrochemical n-doping is allowed to reach radical concentrations of 0.5 radical/unit. Average values of $S \approx 2$ are reasonable in view of DP and radical concentration for **11**; the temperature dependence of magnetic moment vs temperature is also consistent with the expected strength of ferromagnetic coupling in this oligomer. Overall, oligomer **11** and Bushby's polymer **5b** are perhaps the most promising systems for "polaronic ferromagnet."

Considering difficulties involved in efficient generation and characterization of polyradicals based upon radical ions, neutral radicals remain the most appealing source of spin. Further improvements in through-bond ferromagnetic coupling in polymers were guided by the studies on model monodisperse polyarylmethyls (40). In polymers **12** and **13**, calix[4]arene macrocycles are linked with bis(biphenylene)methyls (Fig. 5). Polymer **12**, which was obtained from the corresponding poly(arylmethylether) with $M_{\mathrm{w}} = 30$ kDa (MALS), had radical concentration of 0.4–0.6 radical/triarylmethyl and an average $S \approx 18$. The branching and/or cross-linking of calix[4]arene macrocycles lead to further improvements in value of S. Polymers **13**, which were obtained from the benzene soluble fractions of the corresponding poly(arylmethylether)s with $M_{\mathrm{w}} = 300$–500 kDa, had an average $S > 40$ (41). Magnetic properties of polymers **13**, which were prepared from benzene insoluble fractions of the poly(arylmethylether)s, depended on polymerization time beyond the gel point. When polymerization is stopped near the gel point, polymer **13** had $S = 600$–1500; for longer polymerization time $S = 3000$–7000 was obtained. The radical concentrations for polymers **13** were approximately 0.5 radical/triarylmethyl (12).

For the first time in a conjugated organic polymer, magnetic properties beyond simple paramagnetism were observed in polymer **13**. The onset of magnetic ordering is observed near the temperature of 10 K for a typical sample with $S \approx 5000$. Overall, the magnetic properties of polymer **13** are between insulating spin glasses and blocked superparamagnets, but closer to spin glasses. The soft magnetic behavior in polymer **13** is similar to the known small molecule based organic magnets, though the ordering temperature in polymer **13** is relatively high (6–8).



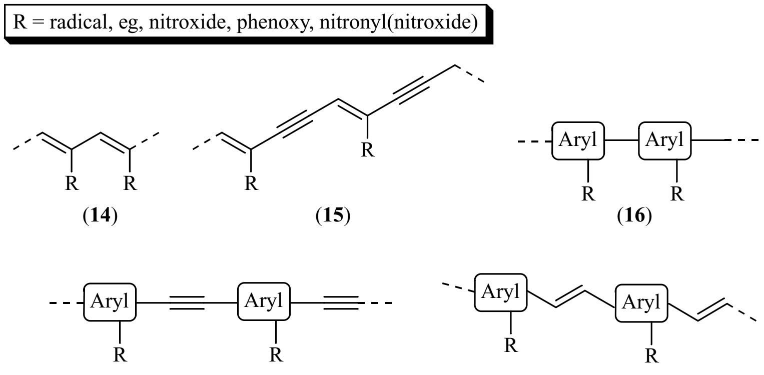
(12) (13)

Fig. 5. Calix[4]arene-based polyarylmethyl polymers.

Class II Polyradicals

Conjugated linear polymers, bearing multiple radicals as pendant groups, include several common π-systems as their conjugated backbones. Polyacetylene **14**, polydiacetylene **15**, various poly(arylene)s **16**, poly(aryleneethynylene)s **17**, and poly(arylvinylene)s **18** are among the leading examples (Fig. 6). Neutral stable radicals, such as phenoxyl, nitroxide, and nitronyl(nitroxide), are the most common pendant groups. Regioselective, typically head-to-tail, polymerizations are employed to attain the connectivity of the π-system, which is compatible with the ferromagnetic coupling. One of the advantages of pendant polymers is relatively straightforward synthesis.

Polyacetylene-based pendant polyradicals **14** were reported in late 1980s and early 1990s, as summarized in a recent review by Nishide and Kaneko (42). In



(14) (15) (16)

(17) (18)

Fig. 6. Polymers bearing radical pendants.

polyacetylenes, connectivity of non-Kekule π-system compatible with ferromagnetic coupling may be obtained by the attachment of conjugated pendant radical at the every other carbon of the polyene backbone (Fig. 6). Molecular weights (reported as either M_n or M_w) for many of such polymers were in the 10–100 kDa range, even for relatively bulky pendant groups, eg, galvinoxyl and diarylnitroxide. Although the radical concentrations were above 0.5 radical/unit in selected polymers, no ferromagnetic coupling was observed in any of the polyacetylene-based polymers (42). Most likely, severe out-of-plane twisting of the polyacetylene backbone, caused by the bulky radical pendants, prevents any significant exchange interactions (42). The magnetic properties of polymers **14** were compatible with $S = 1/2$ paramagnets (ie, independent, noninteracting spins-1/2).

Poly(diacetylene)-based polymers **15** (Fig. 6) were also studied but even for well-designed examples, such as polymers of 2-chloro-5-butadiynylphenyl *tert*-butylnitroxide, only low concentration of intact radicals were obtained, resulting in predominantly $S = 1/2$ paramagnetic behavior (43).

Availability of regioselective methods for polymerization of 3-substituted thiophenes and the efficient π-conjugation in the resultant polymers suggest that polythiophenes with radical pendant groups at 3-position are especially promising candidates for attaining polyradicals with $S > 1/2$ (44). Recently, three syntheses of poly[3-(3′,5′-di-*tert*-butyl-4′-oxyphenyl)thiophene] (**16a**) were reported (45–47) (Fig. 7). The $FeCl_3$-mediated and the Ni-catalyzed polymerizations of 3-(3′,5′-di-*tert*-butyl-4′-trimethysiloxyphenyl)thiophene and 2,5-dibromo-3-(3′,5′-di-*tert*-butyl-4′-trimethysiloxyphenyl)thiophene as monomers, respectively, gave polymers with M_w of 13 kDa (light scattering). However, the resultant polythiophenes lacked regioregularity and the magnetic characterization of corresponding polyradicals was lacking (45). Analogous $FeCl_3$-mediated polymerizations of 3-(3′,5′-di-*tert*-butyl-4′-methoxyphenyl)thiophene and 3-(3′,5′-di-*tert*-butyl-4′-methyloxymethoxyphenyl)thiophene gave only short oligomers (DP $\approx$ 6). Although the regioregularity was attained, the magnetic characterization of the corresponding polyradical (value of S, exchange interactions, yield of radicals) was not reported (46). Most recent $FeCl_3$-mediated polymerizations of 3-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)thiophene gave polythiophenes with $M_n \approx 10$ kDa (GPC) and regioregularity reaching 96%. Although the radical concentration of 0.3 radical/unit was rather low, the average value of $S \approx 1$ was determined at cryogenic temperatures. Numerical fitting of the magnetic susceptibility data indicated a modest ferromagnetic coupling, which is comparable to that in a triplet ground state diradical with $\Delta E_{ST}/R \approx 100$ K (47). Similarly prepared poly(3-phenylgalvinoxylthiophene) (**16b**) had $M_n > 10$ kDa (GPC) and head-to-tail content of about 90% (Fig. 7). An excellent radical concentration of 0.9 radical/unit was attained but only $S = 1/2$ paramagnetic behavior was found (48). This is compatible with almost complete localization of spin density on the galvinoxyl moiety in the model monoradical **19** (48) (Fig. 7). Polythiophenes **16a** and **16b** doped with iodine showed a modest electrical conductivity (10^{-5} S·cm^{-1}) (47,48).

Another recent example of pendant poly(arylene) is poly(1,3-phenylene) (**16c**) (Fig. 7) (49). The Pd-catalyzed polymerization of *N*-*tert*-butyl-2,4-dibromoaniline and 1,3-phenylenebis(trimethylene boronate) gave poly(1,3-phenylene) with the DP of about 18 (GPC); oxidation of pendant secondary *tert*-butyl amine groups to the corresponding nitroxides yielded polymer **16c** with the radical concentration of

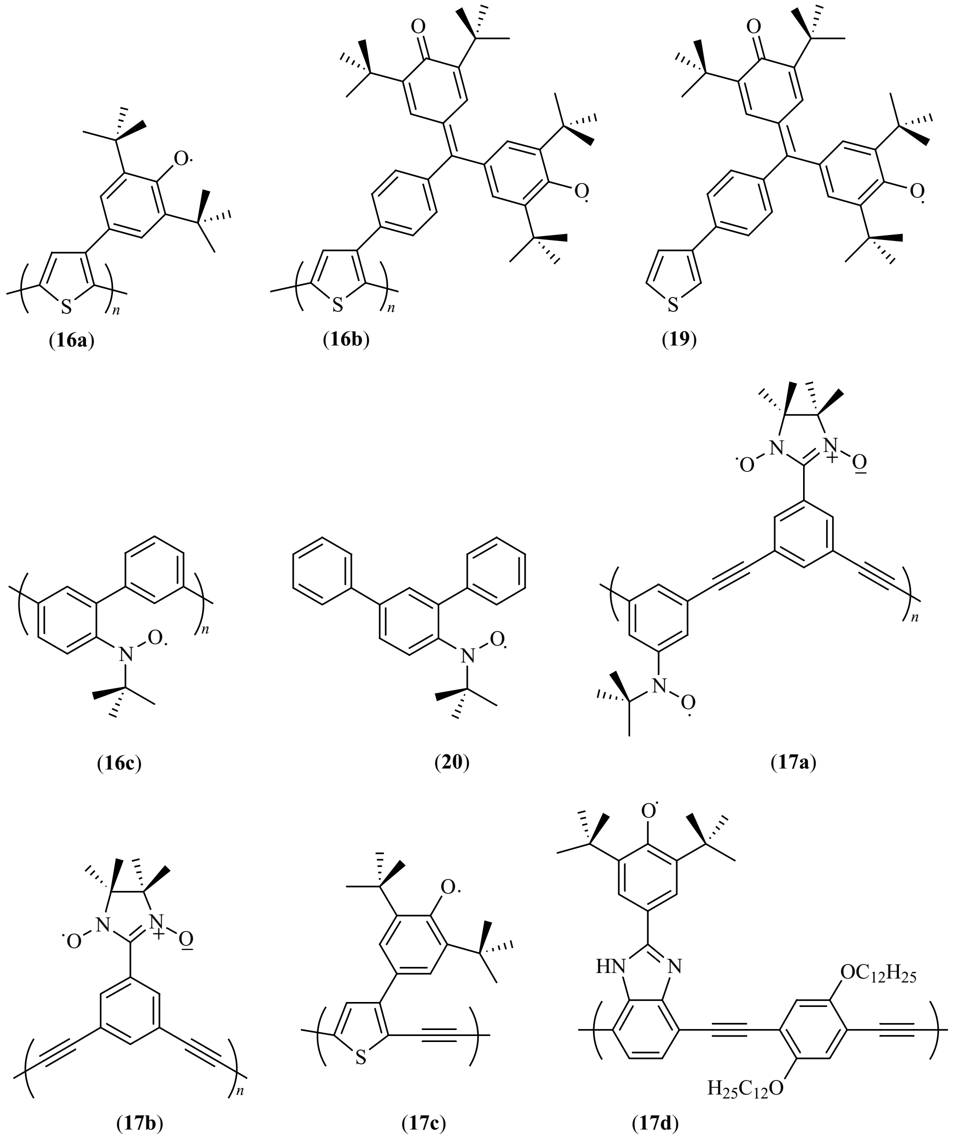


Fig. 7. Selected poly(arylene)s and poly(aryleneethynylene)s bearing radical pendants.

0.8 radical/unit. The X-ray crystallographic analysis of the model monoradical, *N*-*tert*-butyl-*N*-(2,4-diphenylphenyl)nitroxide (**20**) (Fig. 7), showed that the dihedral angle between the nitroxide moiety and the adjacent benzene ring is about 70°. This suggested that out-of-plane twisting of the pendant group might explain the failure to detect ferromagnetic coupling in polymer **16c** (49).

Various poly(aryleneethynylene)s **17** were recently reviewed by Miura (34). Because of mild reaction conditions for Pd-catalyzed C(*sp*)—C(*sp*^{2}) couplings, the polymerizations leading to poly(1,3-phenyleneethynylene)s **17a** may be carried out with selected radical monomers, based upon stable radicals such as nitroxides and nitronyl(nitroxides) (Fig. 7). Even with the M_n values of 1–10 kDa and radical concentrations of about 0.8 radical/unit, no ferromagnetic coupling was detected (34). Similarly, the oxidative C(*sp*)—C(*sp*) couplings can be carried out on nitronyl(nitroxide) monomers, leading to poly(phenylenediethynylene)s with nitronyl(nitroxide) pendants **17b** (Fig. 7) (34,50). Poly(aryleneethynylene)s with phenoxyl-based pendant radicals **17c** and **17d** were prepared by polymerization of the corresponding phenol-based monomers, followed by oxidation of pendant phenols to phenoxyls (Fig. 7) (51,52). The M_n values of 1–10 kDa (GPC) were reported for the pendant-phenol polymers; however, no meaningful magnetic characterization was described for the corresponding polyradicals **17c** and **17d** (51,52).

Nishide and Kaneko reviewed numerous linear head-to-tail linked poly(1,4-phenylenevinylene)s and poly(1,2-phenylvinylene)s with pendant phenoxyls, nitroxides, galvinoxyls, and nitronyl(nitroxides) (42). For most of their polymers, molecular weights were in the 1–10 kDa range, radical concentrations were at about 0.5+ radical/unit level, and, most importantly, magnetic susceptibility measurements on neat powders revealed ferromagnetic couplings (42). The best example of such polymer was phenoxyl-based poly(1,2-phenylvinylene) (1,2-PPV) (**18a**) reported by Nishide and Lahti (53) (Fig. 8). Polymer **18a** had DP $\approx$ 17, radical concentration of $\sim$0.7 radical/unit, and an average value of $S \approx 2$ (53). For both polymer (**18b**) and the corresponding model triplet ground state diradicals (**21** and **22**), ferromagnetic couplings were measured; eg, $\Delta E_{ST}/R \approx 70$ K in **21** became only about 9 K in **22** (Fig. 8) (53). This suggested that polymer **18a** is very sensitive to defects, ie, pendant groups missing phenoxyl radical are likely to interrupt the through-bond ferromagnetic coupling.

In an attempt to increase the strength of ferromagnetic coupling, 1,2-PPV with 3,5-bearing phenoxyl radical pendants **18b** was prepared (Fig. 8). However, only oligomers with DP $\approx$ 4 and radical concentration of 0.5 radical/unit were obtained; their average value of $S \approx 1$ was disappointingly low (54). Although *m*-phenylene adequately mediates ferromagnetic coupling between phenoxyls (55), the model tetraradical **23** with the $S = 2$ ground state could not be prepared; magnetic studies of **23** revealed the radical concentration and an average value that are both similar to that of polymer **18b** (Fig. 8) (55).

Branched topologies of PPV backbone provide increased values of DP and S, compared to their linear chain counterparts. Branched polymer **24** had DP $\approx$ 70, radical concentration of 0.6 radical/unit, and an average value of $S \approx 7/2$ (Fig. 8) (56). Polymer **25** had $M_w \approx 32$ kDa (LS, 90 phenolic units), radical concentration of 0.4 radical/unit, and an average value of $S \approx 5$ (Fig. 8) (57).

Phenoxyl-based 1,2-PPVs, such as **18a**, **24**, **25**, are the most effective in mediating ferromagnetic coupling among all pendant polymers. Although the values of S for the best Class II polyradicals are still rather modest, their cross-linking via controlled incorporation of macrocycles should provide a very promising approach toward magnetic polymers (12,41,58). Another interesting course of study involves polaronic pendant polymers, as illustrated by model compounds **26** and **27**. Sugawara and co-workers prepared numerous model di- and triradicals that consist of a neutral radical(s) attached to a radical cation π-system (59–61). For example, in triradical **26**, the neutral nitronyl(nitroxide) pendants are connected

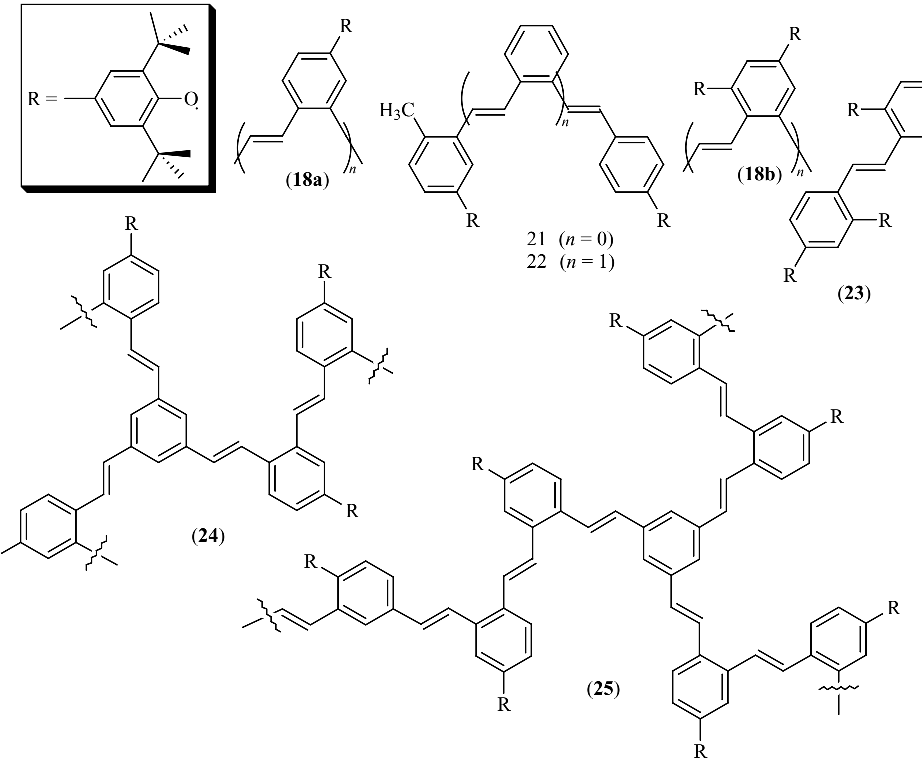
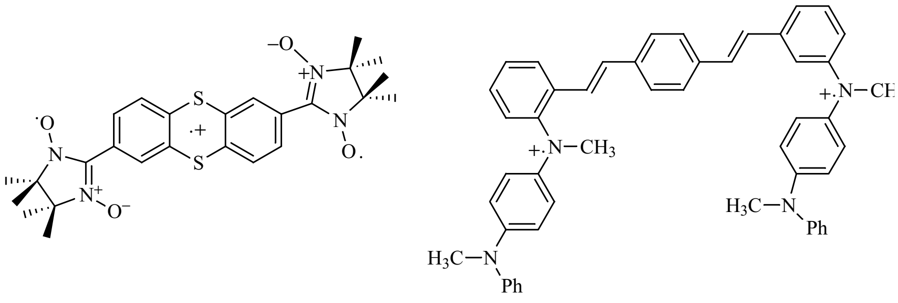


Fig. 8. Selected poly(1,2-phenylenevinylene)s bearing phenoxyl pendants.

to the polaronic (radical cation) thianthrene backbone (59). An alternative design was illustrated by van Meurs and Janssen; eg, in diradical **27**, the polaronic (radical cation) pendants are attached to the neutral 1,4-PPV backbone (62) (Fig. 9).



(26)

(27)

Fig. 9. Model triradical and diradical for polaronic pendant polymers.

Outlook

Among numerous designs for magnetic polymers explored so far, only a recently prepared highly cross-linked polyarylmethyls **13** showed magnetic ordering. The temperature of about 10 K, below which magnetic ordering was found, is relatively high among organic magnets. This suggests that the polymer approach to organic magnetism is very promising.

For a practical organic polymer magnet, both chemical stability and magnetic ordering at ambient conditions are important. However, polyarylmethyl-based polymer **13** has to be handled below 170 K and under oxygen-free atmosphere. Analogues of polymer **13**, where arylmethyls are replaced with ambient stable radicals, may provide the desired stability. Increase in temperature for magnetic ordering by more than an order of magnitude will require novel designs for magnetic polymers.

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