n-Alkyl Group-Substituted Poly(*m*-aniline)s: Syntheses and Magnetic Properties

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ABSTRACT: Preparation of *n*-alkyl group-substituted derivatives of poly(*m*-aniline) that we have proposed as a possible organic ferromagnetic polymer has been attempted. We started from the syntheses of the monomers, *n*-alkyl-substituted *m*-bromoanilines (R = methyl, ethyl, hexyl, dodecyl, and hexyloxy groups). The approximate solubilities of the methyl, ethyl, and hexyloxy group-substituted polymers in *N*-methyl-2-pyrrolidone (NMP) were nearly equal to that of poly(*m*-aniline). On the other hand, hexyl- and dodecyl-substituted polymers have high solubilities in the conventional organic solvents such as acetone, dichloromethane, and so forth. The ferromagnetic spin correlation was observed in the polymer oxidized by $NOBF_4$ in the temperature range above 50 K. The average total spin quantum number was determined to be 1.0 at 2 K. Moreover, in all polyradical samples, a weak antiferromagnetic interaction between spin clusters was observed at very low temperatures probably due to a conformational change in the present poly(*m*-aniline) derivatives.

1. Introduction

Over the last few decades, organic ferromagnets have been the subject of controversy. However, in the last few years, a number of organic ferromagnets have been found successfully.[1−7] At this point, it may be safely said that organic ferromagnetism is no longer an unrealistic proposition.

The organic ferromagnets so far prepared are classified into (i) organic radical crystals,[1−5] unexceptionally consisting of nitroxide radical molecules, and (ii) charge transfer complexes;[6,7] we are aware of only C_{60} and tetrakis(dimethylamino)ethylene (TDAE) complexes. Unfortunately, the ferromagnetic phase transition has still not been observed in polymer-based materials in spite of many researches since the 1960s. Nevertheless, turning to the oligomeric approach toward organic ferromagnetic polymer, it is well-known that the spins located on *m*-phenylcarbene oligomers[8,9] possess ferromagnetic spin alignment from the topological correlation between localized spins, as first pointed out by Mataga.[10] This observation still suggests that we can prepare polymer-based organic ferromagnets.

We have proposed poly(*m*-aniline)[11,12] shown in Figure 1 that could have a spin-parallel alignment in the polymer skeleton analogous to that of oligo(*m*-phenylcarbene). In the previous papers,[13,14] we have reported a local ferromagnetic interaction among unpaired spins of poly(*m*-aniline) in its cation-radical form. This polymer has a relatively high molecular weight; however, it is insoluble in usual organic solvents possibly due to partial cross-linked structures. It is considered that good solubility is indispensable for a polymer alignment, which is important to a high-spin state throughout the bulk as well as to a better handling. Moreover, the solubility of poly(*m*-aniline) in various organic solvents enables the processing of films and fibers, etc., of poly(*m*-aniline) from solution. These films

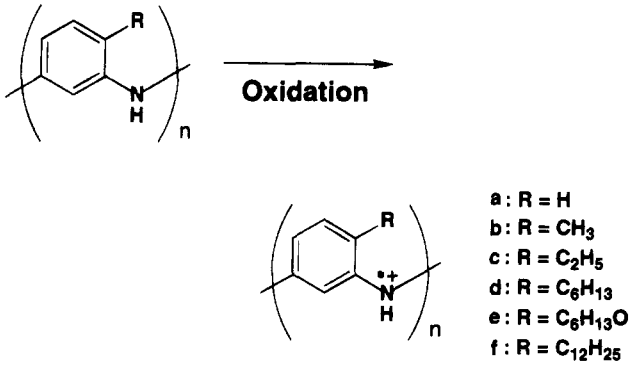

Figure 1. *n*-Alkyl group-substituted poly(*m*-aniline)s.

or fibers make it possible for the polymer to be transformed into polyradical form by suitable oxidizing agents (or dopants). Hence, we designed here a poly(*m*-aniline) derivative in order to make the polymer soluble in the usual organic solvents by introducing a long *n*-alkyl group into the phenyl ring. Several substituted polymers (Figure 1, **a**−**f**) were synthesized for investigating the difference of solubility by the length of *n*-alkyl chains introduced. In this paper, we report the results of (i) syntheses of *n*-alkyl group-substituted poly(*m*-aniline)s, (ii) characterization of these newly synthesized polymers, and (iii) magnetic properties of the polyradical generated on *n*-dodecyl-substituted poly(*m*-aniline).

2. Syntheses of the Monomers (4c−e, 7)

The monomers **4a**−**f** (shown in Figure 2) were required in order to obtain the polymers (**a**−**f**). Monomers **4a** and **b** are commercially available. We tried to synthesize the others (**4c**−**f**) by following Scheme 1. However, we were not able to obtain monomer **4f** by this scheme, as described later. Hence, we synthesized monomer **7**, which also leads to polymer **f** after Ullmann condensation, as outlined in Scheme 2. Herein, *p*-ethylnitrobenzene (**2c**), *n*-hexylbenzene (**1d**), *p*-(hexyloxy)-nitrobenzene (**2e**), and *n*-dodecylbenzene (**1f**) were employed as the starting products.

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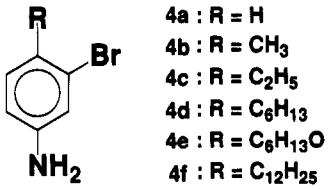
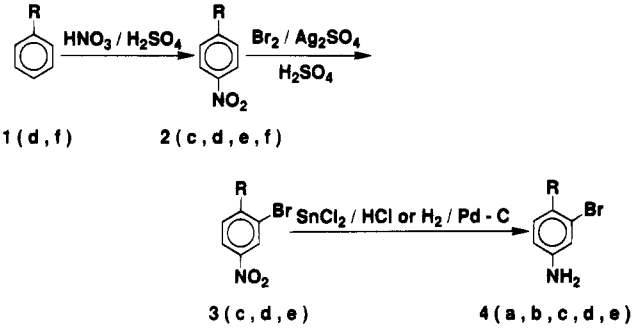
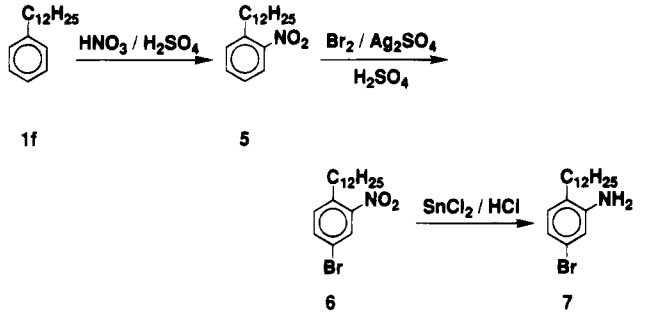


Figure 2. Monomers toward synthesis of poly(*m*-aniline) derivatives.

Scheme 1



Scheme 2



The ortho/para ratio after the nitration of *n*-alkylbenzenes (**1d,f** → **2d,f**) was nearly unity irrespective of the length of the *n*-alkyl groups, as studied by Baas and Wepster.[15] In the bromination process (**2c,d** → **3c,d**), the reaction did not proceed by the usual method utilizing Fe catalyst but by the Derbyshire and Waters method,[16] in which the reaction was carried out in sulfuric acid in the presence of silver sulfate. The **2e** → **3e** conversion was easily done by mixing with Br_2, probably because of the ortho–para orientation by the *n*-hexyloxy group. However, we failed to cause the bromination into the position ortho to the *n*-dodecyl group of *p*-*n*-dodecylnitrobenzene (**2f**) although every method to the best of our knowledge was tried. This result is remarkable when compared with the nitration of *n*-alkylbenzene, in which there is no dependency on the length of the *n*-alkyl group. As a result, we succeeded in the bromination into the position para to the *n*-dodecyl group of *o*-*n*-dodecylnitrobenzene (**5**) with the Derbyshire and Waters method. Finally, the target monomers were obtained from **3c**–**e** and **6** by the usual method employing stannous chloride or the catalytic hydrogenation. The ^1H NMR spectra were recorded with a JEOL FT-NMR Model FX 90A spectrometer, and chemical shift values are given in parts per million (ppm) relative to internal tetramethylsilane (TMS). The Fourier-transformation infrared (FT-IR) spectra were obtained with a JASCO A-302 FT-IR spectrometer.

***p*-Alkylnitrobenzene (2d,f) and *o*-Dodecylnitrobenzene (5).** A mixed acid reagent (sulfuric acid (12 mL, 97 wt %) and nitric acid (9 mL, 70 wt %)) was gradually added into the ice-cooled alkylbenzenes (about 20 g). The mixture was stirred for several hours at *ca.* 50 °C. The reaction was monitored by TLC. The products of nitration were three-times extracted with 60 mL of *n*-hexane, and the resulting organic layer was dried over $MgSO_4$. The solvent was evaporated, and the products were separated by column chromatography on silica gel (CH_2Cl_2/*n*-hexane = 1/10). The average yield was around 90%. The average ratio of *o*-alkylnitrobenzene/*p*-alkylnitrobenzene was nearly unity.

2d. ^1H NMR ($CDCl_3$): δ 0.90 (t, 3H), 1.32 (br, 6H), 1.60 (m, 2H), 2.73 (t, 2H), 7.33 (m, 2H), 8.16 (dd, 2H).

2f. Anal. Calcd for $C_{18}H_{29}NO_2$: C, 74.18; H, 10.03; N, 4.81. Found: C, 74.20; H, 9.91; N, 4.60. ^1H NMR ($CDCl_3$): δ 0.88 (t, 3H), 1.28 (br, 20H), 2.72 (t, 2H), 7.32 (d, 2H), 8.12 (d, 2H).

5. ^1H NMR ($CDCl_3$): δ 0.88 (t, 3H), 1.26 (br, 20H), 2.87 (t, 2H), 7.37 (m, 3H), 7.86 (dd, 1H).

3-Bromo-4-alkylnitrobenzenes (3c,d). The bromination of *p*-alkylnitrobenzenes was done according to the Derbyshire and Waters method.[16] 3-Bromo-4-alkylnitrobenzenes (**3c,d**) (0.03 mol) and bromine (0.03 mol) were dissolved in a mixture of 29 mL of sulfuric acid (97 wt %), and 4 mL of distilled water and silver sulfate (0.03 mol) was then added all at once. The reaction mixture was stirred vigorously for several hours, after which the color of the mixture changed from that of bromine to the pale yellow of silver bromide. The resulting solution was diluted with distilled water or NaOH aqueous solution. After suction filtration, the organic layer was extracted with CH_2Cl_2, then washed with 10% sodium bisulfite aqueous solution, and dried over $MgSO_4$. After column chromatography on silica gel (eluent: *n*-hexane), if necessary, the solvent was evaporated and the product was obtained as a pale brown solid. The average yield was around 70%.

3c. Yield: 81%. Anal. Calcd for $C_8H_8NO_2Br$: C, 41.77; H, 3.50; N, 6.09; Br, 34.73. Found: C, 41.20; H, 3.36; N, 6.28; Br, 36.03. ^1H NMR ($CDCl_3$): δ 1.28 (t, 3H), 2.88 (q, 2H), 7.36 (t, 1H), 8.12 (dd, 1H), 8.40 (d, 1H).

3d. Yield: 70%. ^1H NMR ($CDCl_3$): δ 0.90 (t, 3H), 1.36 (br, 8H), 2.82 (t, 1H), 7.36 (d, 1H), 8.08 (dd, 1H), 8.38 (d, 1H).

3-Bromo-6-dodecylnitrobenzene (6). The synthetic method was the same as that for compounds **3c,d**. Yield: 75%. ^1H NMR ($CDCl_3$): δ 0.90 (t, 3H), 1.28 (br, 20H), 2.84 (t, 2H), 7.24 (m, 1H), 7.64 (dd, 1H), 8.04 (dd, 1H).

3-Bromo-4-(hexyloxy)benzene (3e). Bromine (0.13 mol) was added to *p*-(hexyloxy)nitrobenzene (0.07 mol) in a flask equipped with a gas trap maintained at 30 °C, with stirring. The reaction mixture was stirred overnight and finally solidified. The solid was extracted with *n*-hexane, washed with distilled water, and dried over $MgSO_4$. Evaporation of the solvent left a slightly reddish white solid. The product was recrystallized from ethanol to give white needles. Yield: 70%. ^1H NMR ($CDCl_3$): δ 0.92 (t, 3H), 1.40 (br, 6H), 1.88 (m, 2H), 4.14 (t, 2H), 6.96 (d, 1H), 8.20 (dd, 1H), 8.46 (d, 1H).

3-Bromo-4-alkylanilines (4c,d). The reduction of the corresponding nitro compounds (**3c,d**) was carried out by the use of (i) the usual method with stannous chloride for **4c** and (ii) the catalytic hydrogenation for **4d**.

(i) The nitro compound (4 mmol) dissolved in ethanol was added quickly into a hot (*ca.* 50 °C) mixed solution (ethanol 5 mL, concentrated HCl 5 mL) of stannous chloride with stirring. As the temperature decreased, the white solids were deposited. The resulting mixture was made alkaline enough so as not to deposit inorganic white colloids and extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried over $MgSO_4$. After column chromatography on silica gel (CH_2Cl_2/*n*-hexane = 1/2), if necessary, the solvent was evaporated and the product was obtained as a light yellow liquid.

(ii) An ethyl acetate solution of the nitro compound was degassed repeatedly and then vigorously stirred with Pd on carbon under H_2 gas overnight until the solution becomes colorless. The resulting amine is obtained as a pale yellow liquid by filtering off the catalyst, washing the residue with CH_2Cl_2, and evaporating the solvent. The average yield was around 80%.

4c. Yield: 69%. Anal. Calcd for $C_8H_{10}NBr$: C, 48.02; H, 5.04; N, 7.00; Br, 39.94. Found: C, 48.08; H, 5.01; N, 7.00; Br, 39.98. ^1H NMR ($CDCl_3$): δ 1.16 (t, 3H), 2.64 (m, 2H), 3.52 (s, 2H), 6.52 (dd, 1H), 6.84 (d, 1H), 6.96 (d, 1H). FT-IR (KBr, cm^{-1}): 3437, 3352, 2967, 2930, 2821, 1621, 1496, 1306, 1265, 1030, 875, 852, 820, 680.

4d. Yield: 90%. Anal. Calcd for $C_{12}H_{18}NBr$: C, 56.26; H, 7.08; N, 5.47; Br, 31.19. Found: C, 56.09; H, 7.21; N, 5.46; Br, 30.94. ^1H NMR ($CDCl_3$): δ 0.89 (t, 3H), 1.33 (br, 8H), 2.60 (t, 2H), 4.18 (s, 2H), 6.54 (dd, 1H), 6.91 (m, 2H). FT-IR (KBr,

cm^{-1}): 3422, 3349, 2956, 2927, 2856, 1620, 1496, 1296, 1260, 1029, 877, 819, 678.

3-Bromo-4-(hexyloxy)aniline (4e). The synthetic method was the same as that for **4d**. However, the resulting product was column chromatographed on silica gel (eluent: CH_2Cl_2). The solvent was evaporated to give a reddish brown solid. Yield: 65%. Anal. Calcd for $C_{12}H_{18}NOBr$: C, 52.95; H, 6.66; N, 5.15; Br, 29.36. Found: C, 52.86; H, 6.66; N, 5.16; Br, 29.47. ^1H NMR ($CDCl_3$): δ 0.90 (t, 3H), 1.36 (br, 6H), 1.69 (m, 2H), 3.38 (s, 2H), 3.86 (t, 2H), 6.68 (m, 3H). FT-IR (KBr, cm^{-1}): 3414, 3313, 2951, 2850, 1626, 1500, 1469, 1270, 1225, 1073, 862, 801, 780, 670.

3-Bromo-6-dodecylaniline (7). The synthetic method was the same as that for **4c**. Yield: 82%. Anal. Calcd for $C_{18}H_{30}NBr$: C, 63.52; H, 8.88; N, 4.12; Br, 23.48. Found: C, 63.36; H, 8.68; N, 4.08; Br, 23.68. ^1H NMR ($CDCl_3$): δ 0.90 (t, 3H), 1.28 (br, 20H), 2.40 (t, 2H), 3.60 (br, 2H), 6.84 (m, 3H). FT-IR (KBr, cm^{-1}): 3473, 3380, 2925, 2853, 1618, 1491, 1288, 1256, 886, 847, 798, 771, 722, 678.

3. Synthesis of the Polymers (a–f)

Poly(*m*-aniline) and its derivatives were synthesized from the monomers (**4a–e**, **7**) using copper(I) iodide and potassium carbonate on the basis of the Ullmann condensation reaction, which is the only reaction which forms meta-linked arylamines. The synthesis of poly(arylamine)s has been described in our previous papers.[11,17,18] In addition to the previous results, there were some new findings. Although the reaction of monomer **f** was continued for 3 days, an increase in the yield was not observed compared with that of the 1-day reaction. The average yield was 50% irrespective of the kind of monomer. While we employed nitrobenzene as the solvent throughout the present work, diphenyl ether, which is a useful solvent for the Ullmann condensation reaction, was also used for the polymerization of monomer **7**. However, only the oligomeric products that could not be isolated were obtained and there is no definite explanation of this result. The electron spin resonance (ESR) measurement of these synthesized polymers did not detect any typical ferromagnetic impurities such as transition metal oxide.

Procedure of Polymerization. A typical procedure is as follows. A flask equipped with a nitrogen gas inlet, a thermometer, and a reflux condenser was evacuated and backflushed with nitrogen gas. Then the monomer (20 mmol), potassium carbonate (10 mmol), and copper(I) iodide (0.6 mmol) were put in the flask. Nitrobenzene (15 mL) was used as a solvent. Although most of the mixture did not dissolve, the color of the solution became transparent orange. Under a nitrogen-gas flow, the mixture was heated to *ca.* 210 °C for 24 h. During the reaction, the mixture became black and almost homogeneous. After cooling to room temperature, *n*-hexane was added into the flask to dissolve the oligomers produced and unreacted materials. The mixture was filtered and washed with methanol. In order to remove the catalyst and the neutralizing agent, the residue was washed with 6 M aqueous HCl and methanol. This washing procedure was repeated several times. The resulting reddish black solid was then isolated by filtration and dried under dynamic vacuum for 24 h.

4. Characterization of the Polymers (a–f)

4.1. Solubility. The approximate solubility of the newly synthesized poly(*m*-aniline) derivatives **b–f** and the unsubstituted poly(*m*-aniline) **a** was obtained using the method similar to that of Angelopoulos et al.[19] *N*-Methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), and dichloromethane were used for the solubility test. The highest solubility of the polymers (**a–f**) for NMP reached our expectations. The *n*-dodecyl-substituted polymer (**f**) was fairly soluble in every solvent. This is an accurate reflection of the longest *n*-alkyl group. Solubility of polymers **a–e** for DMSO or DMF lie in between those for NMP and dichloromethane. Moreover, polymers **a–c** were hardly soluble in dichloromethane. The weights of the polymers (**a–f**) dissolved in NMP were as follows: (**a**) unsubstituted, ~0.58; (**b**) methyl, ~0.72; (**c**) ethyl, ~0.87; (**d**) *n*-hexyl, ~11; (**e**) *n*-hexyloxy, ~0.81; (**f**) *n*-dodecyl, ~22 (g/100 g of NMP). This clearly shows that the longer the *n*-alkyl group, the higher the solubility of the polymer in NMP becomes. Here, we should notice the unexpected difference between *n*-hexyl and *n*-hexyloxy substituents. It is well-known that high solubility for many organic solvents is obtained by introducing relatively short *n*-alkoxy groups into phenyl rings of polyaniline (poly(*p*-aniline)).[20] However, the present results contradict those so far obtained about solubilization of polyaniline.

4.2. Gel Permeation Chromatography (GPC). The average molecular weights of the polymers (**a–f**) were evaluated by gel permeation chromatography (GPC) [polystyrene standard, 0.01 M LiBr/NMP solution as eluent]. The GPC system consists of a main column (Shodex, KD80M), pump (Shimadzu, LC-3A), oven (Shimadzu, SPD-6AV), and UV–vis detector (Shimadzu, C-R4A). LiBr/NMP (0.01 M) was used as the eluent, monitored by UV absorption at 310 nm. A calibration curve was obtained with polystyrene standards (TOSOH, TSK standard polystyrene).

The distribution curve for each polymer shows a single peak and no shoulder, indicating that (i) oligomeric portions are excluded by washing of as-polymerized polymers and (ii) the synthesized polymers (**a–f**) have a single molecular structure. The mass-average molecular weight ($\bar{M}_w$) for the present polymers (**a–f**) was as follows: (**a**) unsubstituted, 4100; (**b**) methyl, 2200; (**c**) ethyl, 4100; (**d**) *n*-hexyl, 7900; (**e**) *n*-hexyloxy, 9800; (**f**) *n*-dodecyl, 18 000. The degrees of polymerization ranged from 50 to 100. In conclusion, the difference of the substituents of the monomers (**4a–e**, **7**) does not effect the polymerization by the Ullmann condensation reaction from 50 to 100.

4.3. Fourier Transform-Infrared (FT-IR) Spectroscopy. The spectra of the unsubstituted poly(*m*-aniline) (**a**) have been described in the previous paper.[11] Here we concentrate on the spectra of monomer **7** and polymer **f**, because the other polymers (**b–e**) showed similar spectra, as shown in Figure 3. The two peaks at 3482 and 3392 cm^{-1} in Figure 3a are assigned to the N–H stretching of the primary amine, and the broad band above 3000 cm^{-1} in Figure 3b corresponds to the new N–H stretching of the secondary amine. A series of peaks around 2900 cm^{-1} in Figure 3b indicates that the polymer contains long alkyl-chain substituent. Two small peaks at 2360 and 2340 cm^{-1} in both spectra are due to extrinsic CO_2. Although the bands observed in the C–H out-of-plane deformation region are usually assigned to the substituted benzene, it is known that the bands of the poly-substituted benzene do not have a high enough accuracy for the assignment. However, we should notice the two peaks at 750 and 700 cm^{-1} appear in all the substituted polymers (**b–f**), probably indicating the 1,2,4-substitution.

4.4. Ultraviolet–Visible (UV–Vis) Spectroscopy. The UV–vis spectra of the polymers (**a–f**) were recorded in NMP, DMSO, DMF, and dichloromethane solutions. Ultraviolet–visible (UV–vis) spectra were measured with a Shimadzu UV-365 spectrophotometer.

Solvatochromism was not observed for these solutions, showing dark blue with a reddish tint. All the spectra in DMSO solution are shown in Figure 4. These consist

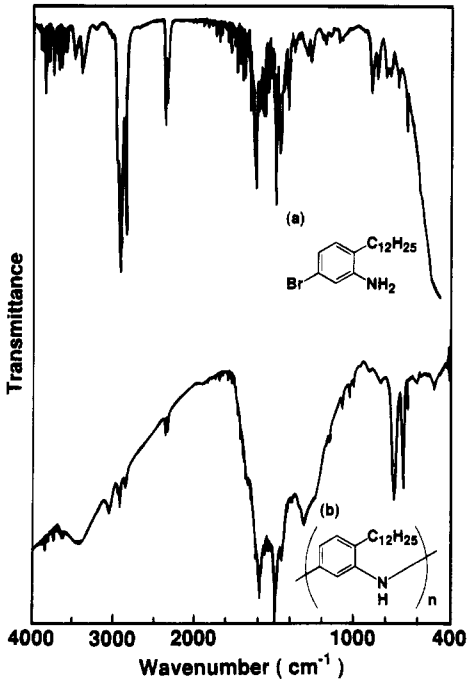


Figure 3. FT-IR spectra of (a) 3-bromo-6-dodecylaniline and (b) *n*-dodecyl-substituted poly(*m*-aniline).

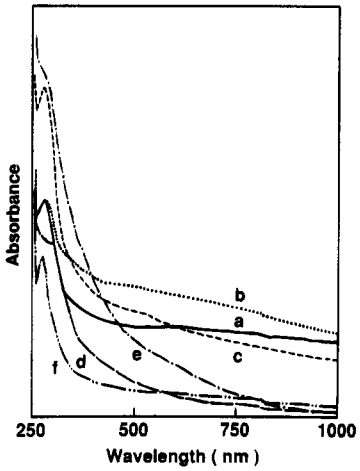


Figure 4. UV–vis spectra of (a) unsubstituted and (b) methyl-, (c) ethyl-, (d) hexyl-, (e) hexyloxy-, and (f) dodecyl-substituted poly(*m*-aniline)s in DMSO.

of only one band near 250 nm that is assigned to the $\pi-\pi^*$ transition of the phenyl ring. Although the broad band near 600 nm has been assigned to the absorption by the nitrogen-quinone groups as in usual polyaniline (poly(*p*-aniline)),[21] the corresponding band was never observed in the polymers (**a**–**f**) in every solvent used. Hence, this fact shows that the present polymers have a different structure from polyaniline (poly(*p*-aniline)), which always contains the nitrogen-quinone structure, except for the leucoemeraldine form. Let us stress again here that we designed the synthesis route in order to obtain the strictly meta-linked polyaniline which was described in earlier studies.[11,17] Moreover, it has been theoretically concluded that the nitrogen-quinone form of poly(*m*-aniline) inevitably generates the unpaired electron on the phenyl ring and hence this quinoid form is less stable than the benzenoid one,[12] justifying no observation of the nitrogen-quinone band near 600 nm. Considering these points, it is strongly suggested that the present polymers have the linkage of poly(*m*-aniline).[22]

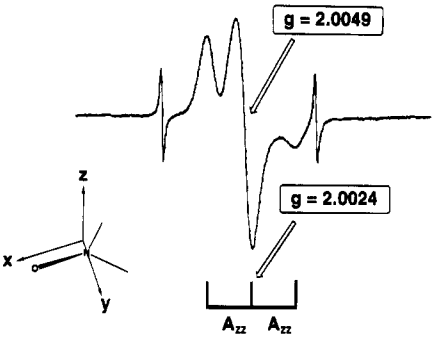


Figure 5. ESR spectrum with an anisotropic hyperfine structure for the MCPBA-treated *n*-dodecyl-substituted poly(*m*-aniline). A_{zz} designates the principal value for the *z*-direction of the hyperfine coupling tensor.

Table 1. *g* values and spin concentrations (N_s in spins·g^{-1}) of the polyradical samples of *n*-dodecyl substituted poly(*m*-aniline)

Sample	*g* value	N_s
Pristine	2.0034	6.3×10^{18}
I	2.0047	5.0×10^{19}
N	2.0030	2.4×10^{19}
M	2.0049	2.6×10^{19}

5. Polyradicals of *n*-Dodecyl-Substituted Poly(*m*-aniline)

5.1. Generation of the Polyradical of *n*-Dodecyl-Substituted Poly(*m*-aniline). In order to examine the magnetic properties of *n*-alkyl chain-substituted poly(*m*-aniline)s, we have generated the polyradical on *n*-dodecyl-substituted poly(*m*-aniline), since that is the most soluble one. The polymer was treated with three kinds of oxidizing agents (I_2, MCPBA (*m*-chloroperbenzoic acid), and $NOBF_4$). These oxidation processes were performed in the liquid phase (dichloromethane for I_2 and MCPBA; acetone for $NOBF_4$) under high-purity N_2 gas. The samples thus obtained were labeled I, M, and N according to the utilized oxidizing agents I_2, MCPBA, and $NOBF_4$. After the evaporation of the solvent and dynamic vacuum drying, the spin concentration of each polyradical sample was determined at room temperature by the ESR measurements. The results are shown in Table 1. All the samples contain 10 times as many radical spins as the pristine sample. The *g* values of sample N and the pristine polymer show that the radical spins generated are mainly located on nitrogen atoms. The *g* value (2.0047) of sample I becomes larger than that of the pristine polymer, which probably reflects the influence of iodine atoms (for example, the *g* value of the I_2^- anion radical is 2.1561[23]).

The ESR spectrum with the typical anisotropic hyperfine structure for randomly oriented nitroxide radicals[24] was detected in sample M, as shown in Figure 5. The fact that this spectrum is derived from a nitroxide radical center is also supported by the *g* value (2.0049). The principal value of the hyperfine coupling tensor takes a value similar to that of the diaryl nitroxide molecule (for example, 23.8 G for diphenyl nitroxide[25] and 24.6 G for di-*p*-anisyl nitroxide[26]) rather than of dialkyl nitroxide (for example, 31.78 G for di-*tert*-butyl nitroxide[27]). In addition, Rassat and his co-workers[2] have employed MCPBA as a powerful reagent for conversion of secondary amines into nitroxides. Judging from the above, it is suggested that, as shown in Figure 6, poly(*m*-aniline) is converted into poly(*m*-phenylene nitroxide). This has also been investigated by Iwamura et al.[28] through oligomer model studies.

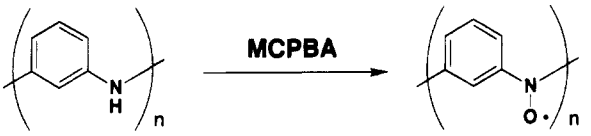


Figure 6. Conversion of poly(*m*-aniline) into poly(*m*-phenylene nitroxide).

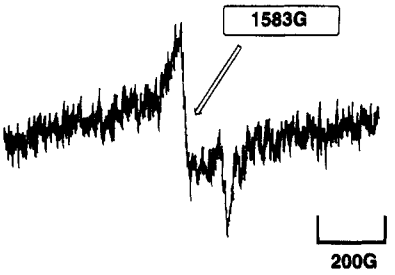


Figure 7. Half-field resonance ($\Delta m_s = \pm 2$) observed in the iodine-treated *n*-dodecyl-substituted poly(*m*-aniline) at 2.6 K.

5.2. Magnetic Properties of the Generated Polyradical. The electron spin resonance (ESR) spectra at the *X* band were recorded with a Varian E-112 spectrometer equipped with an Oxford Instruments liquid-helium-flow cryostat at 10–260 K and with a JEOL JES-RE-2X spectrometer at room temperature. The sample was packed into a 4.75 mm o.d. quartz tube. The sample tube was evacuated down to less than 10^{-4} Torr for 2 h and then charged with high-purity helium gas (99.9999%) as a heat medium for temperature-dependent measurements up to 10 Torr before sealing. The determination of the *g* value and the magnetic field calibration were performed using a Mn^{2+}/MgO solid solution as a reference, and in order to determine the spin concentration $CuSO_4 \cdot 5H_2O$ was used as a standard. The 100 kHz field-modulation width was kept less than 25% of the peak-to-peak line width (ΔH_{pp}).

The ESR signals consist of a usual $\Delta m_s = \pm 1$ signal and a forbidden $\Delta m_s = \pm 2$ signal (half-field resonance). The latter weak signal appeared gradually under 50 K in all the samples, as shown in Figure 7. The $\Delta m_s = \pm 1$ signals of samples other than M are of almost Lorentzian type in the whole temperature range, judging from the ratio $\Delta H_{1/2}/\Delta H_{pp}$, where ΔH_{pp} and $\Delta H_{1/2}$ are defined as the peak-to-peak line width and the outside half-height line width of the ESR peak, respectively. The observed ratios are within 2.4 ± 0.3, while Gaussian and Lorentzian line shapes have the values 1.92 and 2.40, respectively. The temperature dependence of ΔH_{pp} in the range 10–240 K is shown in Figure 8. The ΔH_{pp} of each sample remains nearly constant down to 50 K and increases gradually under 50 K probably because the motional narrowing is suppressed at very low temperature. The *g* value of each sample remains almost the same in the whole temperature range.

The magnetization and the magnetic susceptibility were measured using an Oxford Instruments Faraday-type magnetic balance. The magnetic susceptibility was recorded in the temperature range 2–260 K under the constant magnetic field of 10 kG. A quartz cell was stuffed with the sample (*ca.* 70 mg), and several drops of liquid paraffin were dropped into the cell as a binder. The correction of the diamagnetism originating from the quartz cell and liquid paraffin was carried out in a standard manner.[29]

The data from the temperature dependence of magnetic susceptibility were analyzed on the basis of

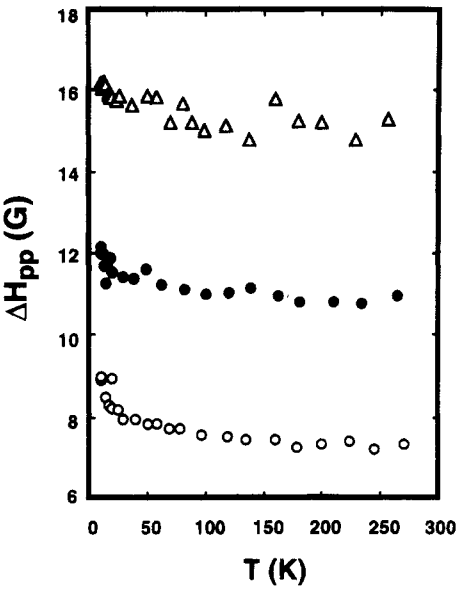


Figure 8. Temperature dependence of peak-to-peak line width (ΔH_{pp}) for *n*-dodecyl-substituted poly(*m*-aniline); (○) pristine polymer; (△) iodine-treated polymer; (●) $NOBF_4$-treated polymers.

conventional Curie–Weiss law:

$$\chi = \chi_{dia} + C/(T - \Theta) \quad (1)$$

where χ_{dia} stands for the diamagnetic susceptibility, *C* is the Curie constant, and Θ is the Weiss temperature. In accordance with eq 1, the $1/(\chi - \chi_{dia})$ vs *T* plot in the 2–260 K region showed a good linear relationship with the Weiss temperature (Θ) of zero within the experimental error for the samples I, M, and the pristine polymer. However, the plots for the sample N cannot be represented by a single line (Figure 9). The straight line below 50 K passes through the origin, whereas the line above 50 K, when extrapolated, has a positive Weiss temperature of 10.5 K, indicating that the radical centers feel ferromagnetic interaction in such a temperature region.

The χT vs *T* plots of samples I, M, and N and the pristine polymer are shown in Figure 10. In the polyradical generated by $NOBF_4$ (sample N), the product χT continued to increase with decreasing temperature down to 50 K. This indicates that ferromagnetic interaction between radical spins works in this polyradical sample. The χT–*T* plots of the other samples were rather horizontal and curved gradually downward at temperatures lower than 20 K. The decrease of χT was also observed under 20 K in the sample N. This suppression at lower temperatures shows that magnetic interaction in the present polyradical samples turned on the weak antiferromagnetic coupling.

The magnetization curves of each sample at 2 K are given in Figure 11. Although these magnetization curves do not show the hysteresis, the saturation tendency of the magnetization is obvious in all the curves at high magnetic field. The theoretical magnetization curves with the spin quantum number $S = {}^1/_2$, 1, and ${}^3/_2$ are also shown in Figure 10 on the basis of the following formula:

$$M(H,T) = M_S B_J(Jgm_B H/k_B T) \quad (2)$$

where M_S is the saturation magnetization, $B_J(x)$ is the Brillouin function, *g* is the Landé factor, m_B is the Bohr

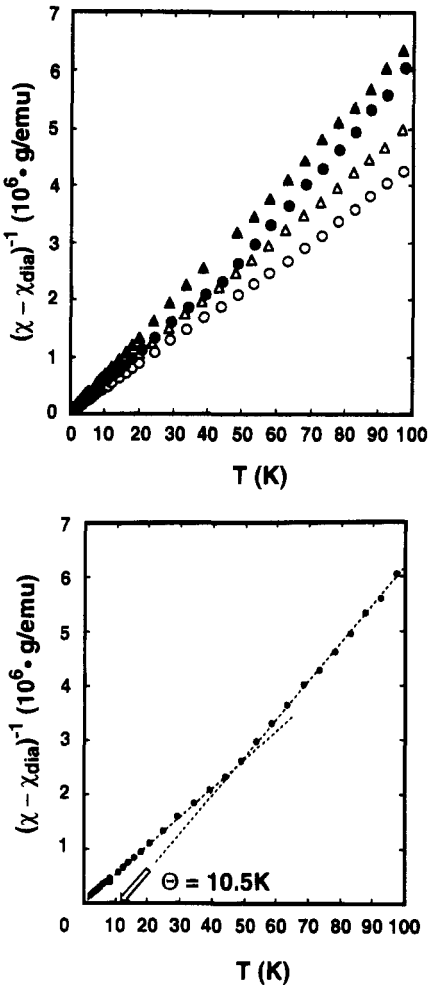


Figure 9. $1/(\chi - \chi_{dia})$ plots for *n*-dodecyl-substituted poly(*m*-aniline); (○) pristine, (△) iodine-treated, (●) NOBF4-treated, and (▲) MCPBA-treated polymers. The same plot for the $NOBF_4$-treated polymer is shown again in the lower panel. The straight line down to 50 K gives a positive intercept (10.5 K).

magneton, J (=L + S) is the angular momentum quantum number, and k_B is the Boltzmann constant. Here g was assumed to be 2 for simplicity and the orbital angular momentum quantum number L was neglected as in usual organic radicals. The S value for the polyradical generated by $NOBF_4$ (sample N) is estimated to be unity, which suggests that a small "spin cluster" was formed due to ferromagnetic interaction between the contiguous radical centers. Although the magnetization curves at 4 K were also measured, the data points were deviated upward from the curves at 2 K in all the samples. This result indicates that the antiferromagnetic interaction exerted between the radical centers (for the samples I, M, and the pristine polymer) and the spin clusters (for the sample N) formed in a higher temperature region than 20 K.

Let us consider here the reason why the weak antiferromagnetic interaction between the radical centers in the present polyradical sample was apparently observed at very low temperatures. We introduced long alkyl substituents into poly(*m*-aniline) in order to make it soluble in the usual organic solvents. Although the side chain does not substantially influence the electronic properties of the poly(*m*-aniline), the conformation of the polymer does change through steric repulsion between the polymer main chain and the side chain. As a result of the steric hindrance due to the side chains, the main chain is considered to prefer nonplanar and sometimes even helical conformations. In fact, the recent *ab initio* calculations about diphenylamine derivatives showed that in the diphenylaminium cation radical the optimized torsion angle between two adjacent phenyl rings takes a comparatively large value, and this radical is energetically stable for torsional motion around the equilibrium structure.[30] Hence, the helical conformation can be realistic for the present polyradicals. This conformational torsion weakens the π-conjugation along the main polymer chain and, furthermore, the ferromagnetic interaction through topology of the conjugated polymers.

Based on these points, the observed weak antiferromagnetic interaction between the spin clusters at very low temperatures can be explained from the frustration between through-bonds and through-space interactions. When through-space interaction does not exist, the more extensive ferromagnetic correlation than the obtained results must be observed in the present sample from the theoretical prediction. However, the above-mentioned torsional conformation of the polymer chain leads to weakening of the ferromagnetic interaction through topology of the conjugated chain (through-bond interaction). Moreover, the through-space antiferromagnetic interactions, which may be enhanced as the superexchange interaction supported by a counteranion such as I_3^- or BF_4^-, can appear simply because the relative distances of the radical centers located with several lattice spacings are shortened periodically by the helical conformation. Finally, as the motional narrowing is really suppressed at such low temperatures, the through-space interaction becomes comparable with the through-bond interaction and the alignment of the radical spins along the polymer chain can be frustrated by simultaneous exertion of these interactions. This frustration usually leads to the spin reduction due to quantum fluctuation.[31] The different magnetic behavior between the samples I and N probably lies in the difference of the molecular sizes of I_3^- (or I_5^-) and BF_4^-, which is convoluted into the polymer chain.

6. Conclusions

We have reported the results of the synthesis of *n*-alkyl-substituted poly(*m*-aniline) and a series of characterizations of the products. There are six major findings in the present study.

(i) The solubility of the newly synthesized polymer product increases dramatically according to the increase in the length of *n*-alkyl substituent. Solubility for organic solvents of methyl- and ethyl-substituted poly(*m*-aniline)s remains unchanged. The solubility of *n*-dodecyl-substituted poly(*m*-aniline) in NMP amounts to about 18 wt % and the polymer is also soluble in the usual organic solvents such as acetone, dichloromethane, and so forth.

(ii) The mass-average molecular weight determined by GPC ranges from 2200 (the ethyl-substituted polymer) to 18 000 (the *n*-dodecyl-substituted one). Judging from the distribution of the molecular weight, it is possible that the synthesized polymer has a single molecular structure.

(iii) From the spectroscopic measurements (FT-IR and UV–vis), it is strongly suggested that the present polymers have the meta-linkage like poly(*m*-aniline) and the *n*-alkyl groups are incorporated in the polymer skeleton.

(iv) We generated the polyradical on *n*-dodecyl-substituted poly(*m*-aniline) by the treatment with I_2,

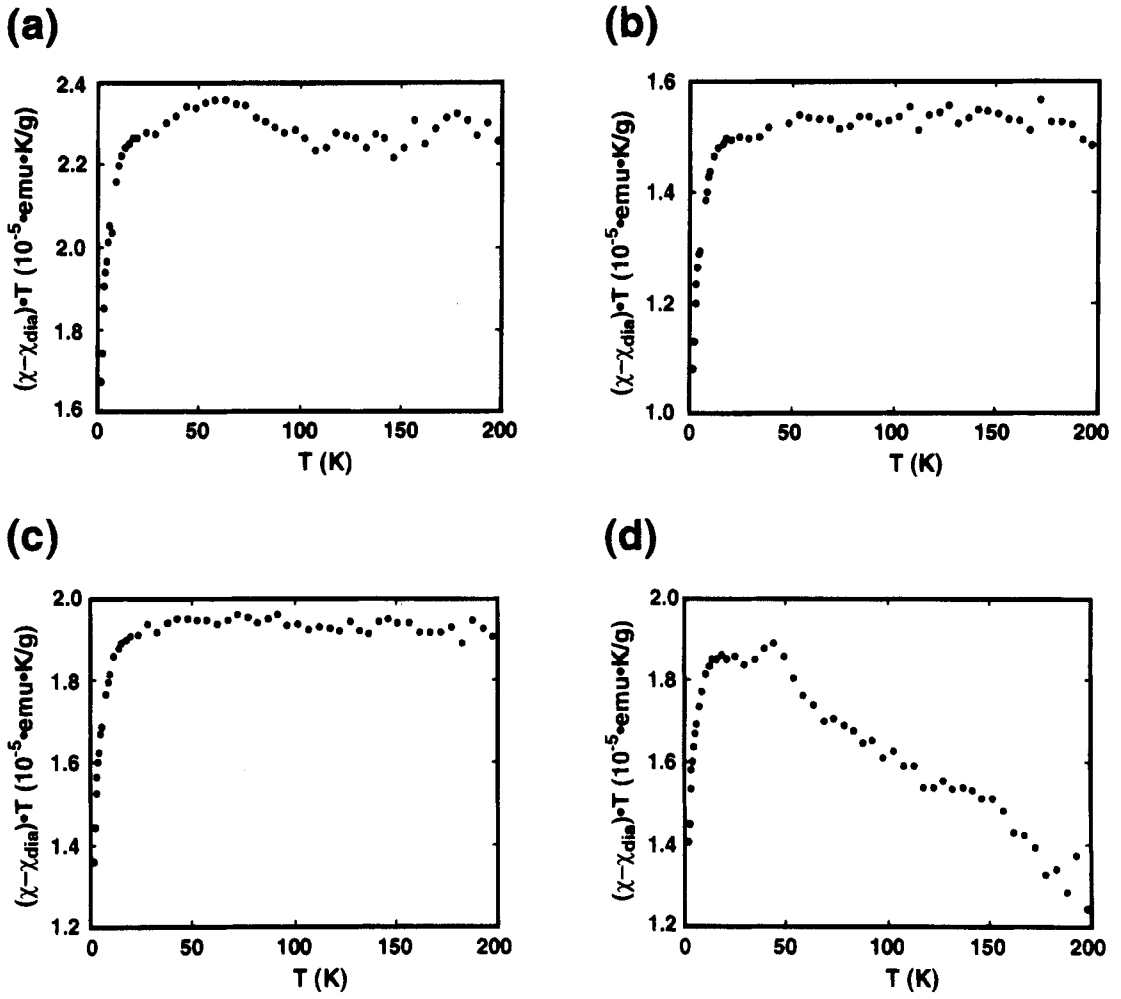


Figure 10. χT vs T plots for n-dodecyl-substituted poly(m-aniline): (a) pristine, (b) MCPBA-treated, (c) iodine-treated, and (d) $NOBF_4$-treated polymers.

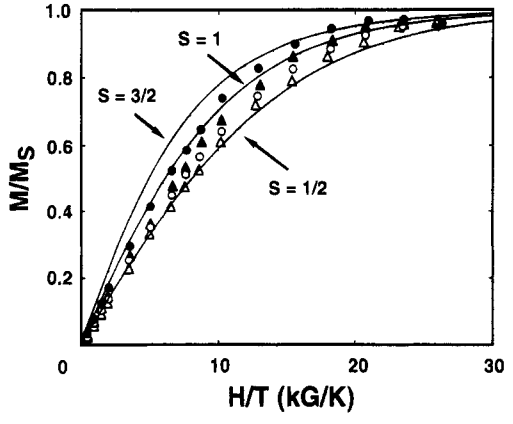


Figure 11. Theoretical and experimental magnetization curves for n-dodecyl-substituted poly(m-aniline) at 2 K; (○) pristine, (△) iodine-treated, (●) $NOBF_4$-treated, and (▲) MCPBA-treated polymers.

MCPBA, and $NOBF_4$. In particular, when treated with MCPBA, the pristine polymer is converted into poly(m-phenylene nitroxide).

(v) The polyradical sample oxidized by $NOBF_4$ showed a ferromagnetic correlation between the radical centers at a temperature higher than 50 K and the average spin quantum number was estimated to be unity even at 2 K.

(vi) In all the polyradical samples a weak antiferromagnetic interaction between so-called spin clusters was observed at very low temperatures, probably because the through-space antiferromagnetic interaction induced by conformational change in the present polymer with bulky substituents became comparable with the through-bond ferromagnetic interaction, which usually leads to the spin reduction due to quantum frustration.

We are now trying to prepare films of the synthesized poly(m-aniline) derivatives, making the most of high solubility. Furthermore, a theoretical study of the magnetic frustration phenomena of helical polymers is in progress and will be reported elsewhere.

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