研究報告

Ferromagnetic and Ferrimagnetic Behaviors of Pyrolyzed Organic Molecules Containing Nitrogen Atoms

by

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ABSTRACT

Organic material exhibiting a novel ferromagnetic behavior were obtained by the pyrolysis of the mixture of o, m, p-phenylenediamine (PDA) and 2, 4, 6-triphenoxy-1, 3, 5-triazine (TPTA) at 500-1000°C. The content of ferromagneticlike part was largest in the sample prepared at 600°C. The larger values of spin concentration N_s (1.18×10^{19} spins/g) and saturation magnetization M_s (6.24×10^{-1} emu $\cdot$ G/g) have been found in the product obtained from TPTA/m-PDA than those from TPTA/o-PDA and TPTA/p-PDA. Ferrimagnetic behavior was observed in the material obtained by the pyrolysis of TPTA/BG (benzoguanamine), TPTA/melamine (M), M/-PDA and BG/m-PDA containing nitrogen atoms. The results are tentatively discussed in terms of parallel spin orientation of nitrogen radicals.

Key Words : Organic Ferromagnet, Electron Spin resonance, Susceptibility, Pyrolyzed Organic Compound

1. Introduction

Since the ferromagneticlike behaviors were found in the organic compounds synthesized by two research groups^{1, 2)} in 1987, organic ferromagnets have attracted great interest from both experimental and theoretical points of view, because they can be ferromagnets in which both 3d and 4f electrons do not play a major role as the origin of spins contrary to the materials composed of transition and/or rare earth elements. Several organic materials prepared either by chemical synthesis or pyrolysis have been found to exhibit a novel magnetic behavior similar to ferromagnetic.³⁻⁸⁾ The yield and reproducibility of the preparation of the ferromagnetic material, however, were in most cases relatively low.

Ovchinnikov and Spector have proposed two-dimensional ferromagnetic polyradicals based on the graphite-net motif, in which some carbon atoms in a graphite net are substituted by nitrogen N.³⁾ Dixon and Miller have suggested that the derivatives from triazines may give a high spin state.⁹⁾ However, the experimental study of the preparation of such organic ferromagnets containing N atoms is very few.

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In this article, we attempt to obtain ferromagnetically aligned radicals by the pyrolysis of the mixture of the triazine derivatives and phenylenediamine which contain N atoms. At first, dependence of the spin concentrations of the pyrolyzed materials on the pyrolyzing temperature is examined by ESR measurements. Next, the magnetic properties of magnetically active part in this material are examined by the measurements of the ESR signals and the magnetization curves. An isomer effect of the phenylenediamine on the magnetic properties is discussed. In the last section, we refer to the trials to obtain some ferromagnetic or ferromagnetic materials from the other organic compounds containing nitrogen atoms, such as melamine and benzoguanamine.

2. Experimental Procedures

The mixture of 2, 4, 6-triphenoxy-1, 3, 5-triazine (TPTA) and phenylenediamine (PDA) (molar ratio 1:1) of 2.5 g was pyrolyzed at a temperature of 500-1100°C in a quartz glass tube (25 mm ϕ x 500 mm) under Ar gas flow. To investigate an isomer effect of PDA, ortho (o)-PDA, meta (m)-PDA and para (p)-PDA were utilized. Materials prepared from the mixture of molar ratio 1/1 of TPTA/benzoguanamine (BG), TPTA/melamine (M), BG/m-PDA and M/m-PDA by the pyrolysis at 600°C were also used for the magnetic study. All of the pyrolyzed materials were black in color. The molecular structures of those raw materials are shown in Fig. 1.

For ESR measurement, the sample was ground into fine powder and put into a quartz tube having the diameter of 2 mm, which was then sealed after heating at 300°C in a high vacuum. ESR measurements were performed with a Bruker ESP 300 spectrometer at the x-band (9.4 GHz) keeping the sample at a temperature between 100 and 300 K with a liquid nitrogen flow cryostat.

A 1,1-diphenyl-2-picrylhydrazyl (DPPH) film diluted in polystyrene was used as a reference sample for the determination of the spin concentration and the g value.

Some part of the pyrolyzed material was found to be attracted by a small magnet. This active part was 10^{-2} –1% of the batch prepared at a pyrolyzing temperature, and separated by a small magnet.

The magnetization (M-H) curve tracing was performed by an alternating force magnetometer PM-2900 at room temperature.

Electrical conductivity was measured by the Van der Pau technique.

It should be mentioned that any magnetic impurity such as a transition metal element was not detected by the atomic absorption spectrochemical analysis down to the lowest limit of the detection (0.5 ppm).

Fig. 1. The molecular structures of 2, 4, 6-triphenoxy-1, 3, 5-triazine (TPTA), phenylenediamine (PDA), benzoguanamine (BG) and melamine (M).

X-ray diffraction of the powdered sample was examined by a Rigaku RINT-1100 Diffractometer.

3. Results and Discussion

First, it should be mentioned that some parts of the powdered sample prepared by the pyrolysis of TPTA/PDA at a temperature of 500-1000°C were attracted by a magnet. We also confirmed that the content of magnetically active part was larger in the sample pyrolyzed at around 600°C than in those pyrolyzed at higher and lower temperatures. TPTA/m-PDA gave a larger content of magnetically active part by pyrolysis than TPTA/p-PDA or TPTA/o-PDA.

Figure 2 shows the pyrolyzing temperature dependence of the molar ratio determined by the elemental analysis for the pristine sample prepared by the pyrolysis of TPTA/p-PDA (molar ratio 1/1). In this figure, electrical conductivity of some selected samples are also indicated. The fractional elimination of hydrogen and oxygen was observed throughout the temperature range examined, while the fractional elimination of nitrogen started at a temperature between 700 and 800°C.

Figure 3 shows the pyrolyzing temperature dependence of spin concentration (N_s) in the samples prepared by the pyrolysis of TPTA/p-PDA (molar ratio 1/1). In those measurements, the pristine nonseparated powdered samples were utilized. The value of N_s ranges over three decades (10^{17} - 10^{19} spins/g) depending on pyrolyzing temperature. The maximum N_s was obtained in the sample pyrolyzed at 600°C. In the sample pyrolyzed around 600°C, the molar fraction of hydrogen atom decreased but that of nitrogen atom did not decrease. However, in the sample pyrolyzed at a temperature higher than 1000°C, the nitrogen content also decreased, resulting in the carbonaceous material.

Figure 4 shows a X-ray diffraction profile in the sample pyrolyzed at 600°C. The peaks C (002), C (101) and C (004) in this profile are similar to those of the graphite powder. The origin of the peaks P_1 and P_2 is unknown.

The layer spacing estimated from the diffraction angle of those peaks is shown in Fig. 5 (a) as a function of the pyrolyzing temperature. Fig. 5 (b) is the variation of the layer spacing of the largest peak C (002) with the pyrolyzing temperature redrawn with an enlarged vertical scale. A minimum of the layer spacing appears around 600°C. The value 3.416 Å of this minimum spacing is 0.062 Å larger than that of graphite single crystal (HOPG).

Figure 6 shows the pyrolyzing temperature dependence of both the apparent crystalline thickness L_c (002) and diameter L_a (101) determined from the half width of those diffraction spectra. The maximum

Fig. 2. The change of molar ratio in the sample prepared by the pyrolysis of the mixture of TPTA and p-PDA (molar ratio 1:1), as a function of the pyrolyzing temperature. Electrical conductivity for the some selected samples is also shown.

Fig. 3. The pyrolyzing temperature dependence of the spin concentration N_s in the sample prepared by the pyrolysis of the mixture of TPTA and p-PDA (molar ratio 1:1).

Fig. 4. The X-ray diffraction profile of the sample prepared by the pyrolysis of the mixture of TPTA and p-PDA (molar ratio 1:1) at 600°C.

Fig. 5. (a) The layer spacing of the sample prepared by the pyrolysis of the mixture of TPTA and m-PDA at various pyrolyzing temperatures.

Fig. 5. (b) The pyrolyzing temperature dependence of the layer spacing d_{002} .

of the crystalline size presents around 600°C.

Above phenomena suggest that the molecular structure of the organic compound obtained by the pyrolysis around 600°C is more suitable for giving ferromagnetic behavior.

It should be mentioned that the effects of the molar ratio of TPTA and PDA on the magnetic properties were recognized. The sample obtained with the molar ratio 1.5-1.8/1.0 was more strongly attracted by a magnet.

Table 1 shows the molar ratio determined by the elemental analysis in the pristine samples pyrolyzed from TPTA/p-PDA (molar ratio 1.8/1.0) at 600°C and that in the starting material. The fractional elimination of hydrogen and oxygen occurs, while the elimination of carbon and nitrogen is not observed. The difference in the molar ratio between the samples obtained by the pyrolysis of different isomers is small.

Fig. 6. The apparent crystalline thickness L_c and diameter L_a of the sample prepared by the pyrolysis of the mixture of TPTA and p-PDA at various pyrolyzing temperatures.

Table 1. The molar ratio in the sample prepared by the pyrolysis of the mixture of TPTA and p-PDA (molar ratio 1.8:1.0) at 600°C. The second line indicates the molar ratio in the starting material (S.M.).

Sample	H	C	N	O
TPTA/p-PDA	0.210	0.555	0.193	0.042
S. M.	0.418	0.436	0.091	0.055

Table 2. Some selected ESR data of the magnetically active parts of the products obtained by the pyrolysis of the mixture of TPTA and o, m, p-PDA (molar ratio 1.8:1.0) at 600°C.

Sample	T (K)	N_s (spins/g)	ΔH_{pp} (G)	$\Delta H_{1/2}/\Delta H_{pp}$	g
TPTA/o-PDA	290	6.69×10^{17}	3.32	1.98	2.0027
	102		3.32	1.88	1.9997
TPTA/m-PDA	290	1.18×10^{19}	2.91	2.00	2.0026
	104		2.25	2.41	2.0005
TPTA/p-PDA	290	1.19×10^{18}	2.92	2.06	2.0024
	100		2.67	2.61	1.9999

The spin concentration N_s obtained by the ESR measurements for the magnetically active part in the sample prepared by the pyrolysis of TPTA/o, m, p-PDA (molar ratio 1.8/1.0) at 600°C is shown in the third column of Table 2. The product obtained by the pyrolytic reaction of TPTA and m-PDA exhibited higher spin concentration than those by the reaction TPTA and o, p-PDA.

Figure 7 shows the ambient temperature dependence of the gram magnetic susceptibility χ , which is estimated from the ESR intensity for the samples mentioned above. The value of χ is proportional to the ESR intensity and estimated using the magnetic moment μ ($=1.66-1.73 \mu_B$, μ_B is a Bohr magneton) in the standard ESR sample DPPH, which is a Curie-type paramagnetic compound. The χ of those samples increased with decreasing temperature. In Fig. 8, the inverse gram susceptibility is plotted as a function of temperature. There is nearly a linear relationship between χ^{-1} and $T-\Theta$, with a Weiss temperature Θ lower than 100 K. Departure from linear characteristics in the range above the Weiss temperature suggests the existence of spin-rich islands composed of spins ferromagnetically correlating in the parallel direction at a close distance.

Fig. 7. The temperature dependence of the gram magnetic susceptibility in the magnetically active parts of the products obtained by the pyrolysis of the mixture of TPTA and o, m, p-PDA (molar ratio 1.8:1.0) at 600°C.

Fig. 8. The temperature dependence of the inverse gram magnetic susceptibility χ^{-1} .

Figure 9 shows the temperature dependence of the peak-to-peak linewidth (ΔH_{pp}) for the magnetically active samples. The ΔH_{pp} of the sample obtained from TPTA/m-PDA was narrower than that from TPTA/o-PDA, and drastically decreased with decreasing temperature. This behavior is expected in the ferromagnetic temperature range and provides a strong evidence of stronger interaction between parallel spins in the sample from TPTA/m-PDA than in another samples.

Figure 10 shows the ESR lines of the samples prepared from TPTA/o-PDA and TPTA/m-PDA measured at 100 K. The type of line shape is determined from the ratio $\Delta H_{1/2}/\Delta H_{pp}$. Where, the $\Delta H_{1/2}$

designates the half width of the ESR absorption line. The shapes of the former and the latter lines were nearly of the Gaussian and the Lorentzian type, respectively. This result suggests the strong exchange

Fig. 9. The temperature dependence of ΔH_{pp} of the magnetically active parts of the products obtained by the pyrolysis of the mixture of TPTA and o, m, p-PDA (1.8:1.0) at 600°C.

interaction between spins correlating at a close distance in the sample prepared from TPTA/m-PDA.

g value of this sample agreed nearly with that of free electron at room temperature and slightly decreased at low temperature without exhibiting an isomer effect. The results of the ESR measurements are given in Table 2.

Figure 11 shows the magnetization curves at room temperature of the samples prepared from TPTA/m-PDA and TPTA/o-PDA. The hysteresis loops were clearly observed. Similar loop was also observed in the magnetization curve of the sample prepared from TPTA/p-PDA. The data from the magnetization curves are listed in Table 3. The saturation magnetization (M_s) of the sample prepared from TPTA/m-PDA are larger than those of the samples prepared from TPTA/p-PDA and TPTA/o-PDA. These results are consistent with the result of ESR measurements in the three kinds of samples obtained from the PDA

Fig. 10. The ESR line shapes of the magnetically active parts of the products obtained by the pyrolysis of the mixture of TPTA and o, m-PDA (molar ratio 1.8:1.0) at 600°C, measured at 100 K.

Fig. 11. The magnetization curve of the magnetically active parts of the products obtained by the pyrolysis of the mixture of TPTA and o, m-PDA (molar ratio 1.8:1.0) at 600°C, measured at room temperature.

Table 3. The values of the saturation magnetization M_s and the coercive force H_c in the magnetically active parts of the products obtained by the pyrolysis of the mixture of TPTA and o, m, p-PDA (molar ratio 1.8:1.0) at 600°C.

Sample	M_s (emu · G/g)	H_c (Oe)
TPTA/o-PDA	2.71×10^{-2}	121
TPTA/m-PDA	6.24×10^{-1}	125
TPTA/p-PDA	5.20×10^{-1}	98

isomers. This isomer effect suggests that the spins at nitrogen radicals originated from the pyrolyzed m-PDA play an important role, while the isomer effect on the coercive force (H_c) is small.

It should also be mentioned that the mixture ratio of TPTA and PDA had a great influence upon the magnetization curve, since N_s of the sample prepared from the TPTA/p-PDA of molar ratio 1/1 was ca. 1/5 of that from the TPTA/p-PDA of molar ratio 1.8/1.0.

The number of spatially correlated spins per one atom in the pyrolyzed material can be estimated from the data of M_s and the molar ratio of elements (Table 1) in the pyrolyzed material. Table 4 shows the value estimated for the nitrogen atom in the pyrolyzed material. For instance, the sample obtained from TPTA/m-PDA has the spatially correlated six spins per 1000 nitrogen atoms at room temperature. Some of possible spin sites are expected to be formed by the elimination of hydrogen from the product of the pyrolytic reaction of TPTA and o, m, p-PDA. The positions of radical substituents have been found to be important for the appearance of spins oriented in parallel in organic compounds from the theoretical consideration of the spin polarization and spin delocalization.¹⁰⁾ In the case of the disubstituted benzene system, meta isomer is considered to be most promissive. The importance of nitrogen radicals have also been pointed out.³⁾

Table 4. The number of spatially correlated spins per one nitrogen atom in the materials obtained by the pyrolysis of the mixture of TPTA and PDA (molar ratio 1.8:1.0) at 600°C. These values were estimated from the data of the saturation magnetization and the elemental analysis of those materials.

Sample	Spins/N atom
TPTA/o-PDA	2.29×10^{-4}
TPTA/m-PDA	6.17×10^{-3}
TPTA/p-PDA	4.96×10^{-3}

It should be noted that the molecular structures of the polymeric compound obtained by the pyrolysis are generally complicated and the results can not be simply interpreted. However, the present experimental results are consistent with above concepts on the formation of parallel spins. We tentatively interpreted the results as follows. That is, in the present conjugated system of alternant hydrocarbon, the parallel spin orientation is more likely to be formed in the product of the pyrolytic reaction of TPTA and m-PDA, than in those of TPTA and o, p-PDA due to the spin polarization effect of the phenylenediamine. These spatially correlated spins are considered to distribute as spin-island in the pyrolyzed molecules. The value of M_s in the sample obtained from TPTA/p-PDA is smaller but comparable to that

from TPTA/m-PDA. This result can not be simply explained only by an isomer effect of PDA and suggests also the existence of another molecular structure effect yielding the ferromagnetic behaviors. In the pyrolytic reaction of TPTA and PDA, if the plural numbers of phenoxys in TPTA are replaced by PDA and nitrogen radicals are formed by the elimination of hydrogen, the parallel spin orientation among those nitrogen radicals is also expected by a spin polarization effect of triazine.

Figure 12 (a), 12 (b), and 12 (c) indicate some of the possible spin sites which can be expected to be formed by the elimination of hydrogen from the product of the pyrolytic reaction of TPTA and o, m, p-PDA. The replacement of two phenoxys in TPTA by PDA can give parallel spin sites as shown in Fig.12 (a), while the replacement of three phenoxys by PDA can give those as shown in Fig.12 (b) or (c). It is indicated clearly in these figures that parallel spin orientation is more likely to be formed in the product of the pyrolytic reaction of TPTA and m-PDA, than in that of TPTA and o, p-PDA, which is consistent with the present observation.

Fig. 12. Possible spin sites (a), (b) and (c) in the products of the pyrolytic reaction of TPTA and o-PDA, m-PDA or p-PDA.

It should be mentioned that we have also obtained the magnetically active compounds by the pyrolysis at 600°C of TPTA/BG, TPTA/M, M/m-PDA and BG/m-PDA which contain nitrogen atoms in their molecular structures, as shown in Fig.1, and observed magnetic hysteresis loop in magnetization of those samples at room temperature.

The spin concentration obtained by the ESR measurements for the magnetically active part in those samples is shown in the third column of Table 5. The pyrolyzed TPTA/BG, TPTA/M and BG/m-PDA exhibited higher spin concentration than those of the pyrolyzed TPTA/o, m, p-PDA.

Figure 13 and 14 show the temperature dependence of χ and χ^{-1} for those samples, respectively. The χ^{-1} is nearly proportional to $T - \Theta_a$, in which the characteristic temperature Θ_a takes zero or a negative value. The magnetically active behavior of those samples indicates that the behavior can be ferromagnetic or ferrimagnetic. However, above result of χ^{-1} suggests that the products obtained by the pyrolysis of

Table 5. Some selected ESR data of the magnetically active parts of the products obtained by the pyrolysis of TPTA/BG (molar ratio 1/1), TPTA/M (1/1), BG/m-PDA (1/1) and M/m-PDA (1/1) at 600°C.

Sample	T (K)	N_s (spins/g)	ΔH_{pp} (G)	$\Delta H_{1/2}/\Delta H_{pp}$	g
TPTA/BG	290	5.23×10^{19}	3.75	1.77	2.0045
	103		3.95	1.79	2.0018
TPTA/M	290	5.63×10^{19}	4.38	1.89	2.0031
	103		4.86	1.91	2.0038
BG/m-PDA	290	5.35×10^{19}	0.96	3.33	2.0037
	103		1.40	2.64	2.0037
M/m-PDA	290	7.44×10^{18}	0.71	1.51	2.0031
	103		0.93	1.85	2.0052

Fig. 13. The temperature dependence of the gram magnetic susceptibility in the magnetically active parts of the products obtained by the pyrolysis of TPTA/BG (molar ratio 1/1), TPTA/M (1/1), M/m-PDA (1/1) and BG/m-PDA (1/1) at 600°C.

Fig. 14. The temperature dependence of the inverse gram magnetic susceptibility χ^{-1} .

Fig. 15. The temperature dependence of ΔH_{pp} of the magnetically active parts of the products obtained by the pyrolysis of TPTA/BG (molar ratio 1/1), TPTA/M (1/1), M/m-PDA (1/1) and BG/m-PDA (1/1) at 600°C.

Fig. 16. The ESR line shapes of the magnetically active parts of the products obtained by the pyrolysis of TPTA/BG (molar ratio 1/1), TPTA/M (1/1) and BG/m-PDA (1/1) at 600°C, measured at 103 K.

TPTA/M, BG/m-PDA and M/m-PDA have the feature of ferrimagnetism rather than that of ferromagnetism.

Figure 15 shows the temperature dependence of ΔH_{pp} in those four samples. The value of ΔH_{pp} at room temperature exhibited a large difference (0.7–4.4 G) among those samples. Temperature dependence of the ΔH_{pp} was not intensive, although a slight increase in the ΔH_{pp} with decreasing temperature was observed in some of the samples.

Figure 16 shows the ESR lines for the four samples measured at 103 K. The line shape of the sample obtained from BG/m-PDA was nearly of the Lorentzian type and that from TPTA/M was the Gaussian type. ΔH_{pp} of the former was 1/3.5 of that of the latter, while the value of spin concentration and the temperature dependence of magnetic susceptibility in the former sample were identical with those in the latter sample.

The g value of those four samples at room temperature is slightly larger than that in TPTA/PDA, and shows only a little change with temperature. The results of the ESR measurements for those samples are given in Table 5.

Above results suggest that parallel or antiparallel spin orientation among the nitrogen radicals is extremely effective for realization of organic ferromagnets or ferrimagnets.

4. Conclusions

The magnetic properties of the material obtained by the pyrolysis of TPTA/PDA, TPTA/BG, TPTA/M, BG/m-PDA and M/m-PDA have been examined by the ESR measurements and the magnetization curve tracing. The experimental results are summarized as follows :

- 1) The products obtained from TPTA/PDA by the pyrolysis at 500-1000°C exhibited a novel ferromagnetic behavior.
- 2) The product obtained from TPTA/PDA by the pyrolysis at 600°C gave a maximum spin concentration, giving 4.4×10^{19} spins/g. The spin concentration ranged over three decades (10^{17} – 10^{19} spins/g) depending on the pyrolyzing temperature.
- 3) There existed an isomer effect of PDA on the spin concentration of the pyrolyzed materials. The magnetically active part of the products obtained from TPTA/m-PDA gave the largest spin concentration, giving 1.18×10^{19} spins/g.
- 4) The magnetization curve for the magnetically active part of the products obtained from TPTA/PDA by the pyrolysis at 600°C exhibited the hysteresis loop. There existed an isomer effect of PDA on the saturation magnetization (M_s). The product obtained from TPTA/m-PDA gave larger M_s values of 6.2×10^{-1} emu • G/g. However, the coercive force (H_c) exhibited a small difference among those samples, giving the values of 100-120 Oe.
- 5) The difference between the values of M_s in the samples prepared from TPTA/m-PDA and TPTA/p-PDA was too small to be interpreted only by an isomer effect of PDA, and another molecular structure effect such as a spin polarization in triazine should also be considered.
- 6) The mixture ratio of TPTA and PDA also had a large influence upon the magnetization curve.
- 7) The spin concentration of the magnetically active part of the pyrolyzed TPTA/BG, TPTA/M and BG/m-PDA was larger than that of the pyrolyzed TPTA/m-PDA.
- 8) The magnetic susceptibility of the magnetically active part of the products obtained from TPTA/M, BG/m-PDA and M/m-PDA by the pyrolysis at 600°C exhibited the ferrimagneticlike behavior.

REFERENCES

1. J. B. Torrance, S. Oostra and A. Nazzari, *Synth. Met.* 19, 709 (1987).
2. Yu. V. Korshak, T. V. Medvedeva, A. A. Ovchinnikov and V. N. Spector, *Nature*, 326, 370 (1987).
3. A. A. Ovchinnikov and V. N. Spector, *Synth. Met.* 27, B615 (1988).
4. Y. Cao, P. Wang, Z. Hu, S. Li and L. Zhang, *Solid State Commun.* 68, 817 (1988).
5. M. Ota, S. Otani, K. Kobayashi and M. Igarashi, *Mol. Cryst. Liq. Cryst.* 176, 99 (1989); M. Ota and S. Otani, *Chem. Lett.* 1179 (1989); M. Ota, S. Otani and M. Igarashi, *ibid.* 1183 (1989).
6. J. S. Miller, A. J. Epstein and W. M. Reiff, *Acc. Chem. Res.* 21, 114 (1988).
7. K. Kawabata, M. Mizutani, M. Fukuda and S. Mizogami, *Synth. Met.* 33, 399 (1989).
8. K. Murata, T. Masuda and H. Ueda, *Chem. Express*, 5, 597 (1990); K. Murata, T. Masuda and H. Ueda, *ibid.* 5, 605 (1990); K. Murata, T. Masuda and H. Ueda, *ibid.* 5, 605 (1990).
9. D. A. Dixon and J. S. Miller, *Mol. Cryst. Liq. Cryst.* 176, 211 (1989).
10. K. Yamaguchi, Y. Toyoda and T. Fueno, *Synth. Met.* 19, 81 (1987).