

NOTES

## Magnetic Properties of Polymer Containing Verdazyl in the Side Chain

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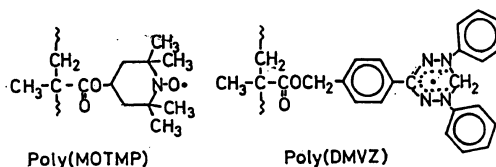
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ESR spectra of polymers containing paramagnetic species in their side chains show that electron exchange interactions take place between paramagnetic side chains.<sup>1-3</sup> These phenomena suggest the possibility that the organic polymers containing paramagnetic species might be a new type of magnetic material owing to the magnetically long-range ordering of unpaired electron through spin-spin interactions. Based on this idea, we compared the temperature dependence of the magnetic susceptibility of a polymer containing the 2,2,6,6-tetramethyl piperidin-1-oxyl group (poly(MOTMP)) with that of the corresponding monomeric compound.<sup>1</sup> A weak antiferromagnetic interaction was observed in the polymer, while there was no recognizable magnetic interaction between the neighboring paramagnetic species in the monomer. The exchange interaction of electron spins between nitroxyls was not so strong in the polymer as expected. This is possibly due to the fact that the distance between the neighboring nitroxyl groups is too far for the unpaired electrons to interact with each other through the side chains, because an unpaired electron of the nitroxyl is

localized on the N—O bond. A paramagnetic side group whose electron is more delocalized is preferable to obtain a magnetically interacting polymer. Since an unpaired electron of the verdazyl is known to be delocalized on the



verdazyl ring,<sup>4</sup> we prepared a polymer containing verdazyl in the side chain.

In this paper, we compare the magnetic susceptibility of the polymer containing the verdazyl radical in the side chain with that of the corresponding monomeric one.

### EXPERIMENTAL

#### Materials

1,5-Diphenyl-3-(*p*-methacryloyloxymethylphenyl)formazane was synthesized according to the literature<sup>5</sup> starting from methacryloyl chloride and 1,5-diphenyl-3-(*p*-hydroxymethyl

Abbreviations: DMVZ, 1,5-diphenyl-3-(*p*-methacryloyloxymethylphenyl)verdazyl.

ylphenyl)formazane which was prepared by terephthalaldehyde and phenylhydrazine.<sup>5</sup> Reddish brown needles of mp 103–105°C were obtained in 81% yield.

1,5-Diphenyl-3-(*p*-methacryloyloxymethylphenyl)verdazyl (DMVZ) was prepared according to the literature,<sup>5</sup> starting from 1,5-diphenyl-3-(*p*-hydroxymethylphenyl)formazane, 37% formaldehyde, and phenylhydrazine. Dark green needles of mp 124–126°C were obtained in 84% yield,  $\lambda_{\max}$ ; 730 nm.<sup>5</sup>

Poly(DMVZ) was prepared by the polymerization of DMVZ with butyllithium in THF at 0°C. The polymer was precipitated with diethyl ether, and reprecipitated twice with benzene-diethyl ether. The molecular weight was determined to be 4500 by vapor pressure osmometry.

#### Measurement

ESR spectra were measured with a Japan Electrom Optics Laboratory Model JEOL FE-1X ESR spectrometer with a 100 KHz modulator.

Gram magnetic susceptibility ( $\chi_g$ ) was determined by the Faraday method using a Cahn balance in a temperature range from 4 to 273 K. The molar magnetic susceptibility ( $\chi_M = \chi_g \times M$ , where  $M$  is the molecular weight of DMVZ or monomer unit of the polymer) was corrected for diamagnetic contributions of atoms with their Pascal constants<sup>6</sup>; the  $\chi_{\text{dia}}$  was  $-350 \times 10^{-6}$  cgsemu.

## RESULTS AND DISCUSSION

The ESR spectra of DMVZ and poly(DMVZ) are shown in Figures 1 and 2. In the case of DMVZ the line shape depends on the concentration of the radical. A nine line spectrum due to four nitrogen nuclei, which was observed at  $10^{-4}$  M, became broader on increasing the concentration of the radical, and then coalesced to a single line at 1.0 M. The ESR spectra of poly(DMVZ) showed a broad line with nine shoulders even at  $10^{-4}$  M of the

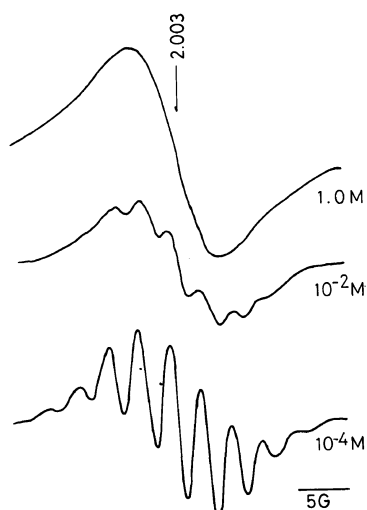


Figure 1. ESR spectra of DMVZ at various concentrations.

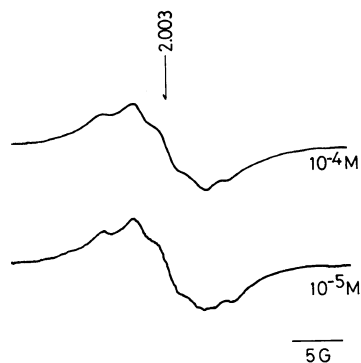


Figure 2. ESR spectra of poly(DMVZ) monomer unit concentration at  $10^{-4}$  M and  $10^{-5}$  M.

radical unit, and the line was independent of concentration. Thus, electron exchange between the paramagnetic side chains of poly(DMVZ) was found to be much easier than the intermolecular exchange of DMVZ.

The temperature dependences of the reciprocal of magnetic susceptibility of poly(DMVZ) and DMVZ are shown in Figure 3. An extrapolation from the high temperature region gave a positive intercept on the ordinate for DMV, indicating that the temperature dependence of  $\chi_M$  follows the Curie–Weiss law with  $\theta = -21.9$  K.

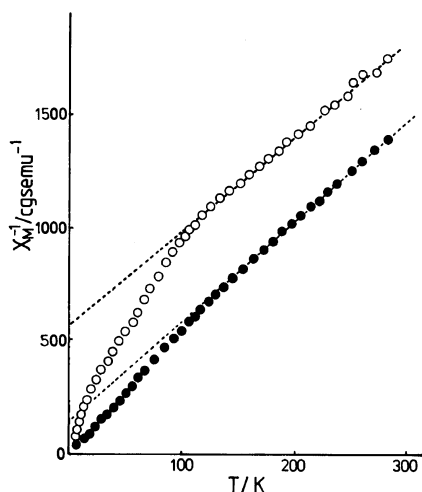


Figure 3. Relation between the reciprocal of magnetic susceptibility and temperature: (○) poly(DMVZ); (●) DMVZ.

For poly(DMVZ), a straight line across a higher value of the positive ordinate was observed when extrapolated, indicating that  $\chi_M$  obey the Curie-Weiss law with  $\theta = -150$  K. The results show that a stronger antiferromagnetic interaction takes place between verdazyl groups in a polymer chain as compared to the corresponding monomeric compound. The lower values of  $\chi_M$  in the polymer as compared to the monomer support the occurrence of antiferromagnetic interactions. The degree of antiferromagnetic interaction of the

verdazyl group in the polymer is larger than that of in the nitroxyl group ( $\theta = -6.6$  K). This difference may be due to differences in the delocalizability of the unpaired electron of verdazyl and nitroxyl.

The antiferromagnetic interaction of poly-(DMVZ) is much weaker than that of the polymer containing porphyrin-Ag(II),<sup>2,3</sup> whose Neel point is about 0°C, but, to our knowledge, it is the strongest in the organic polymers.<sup>1-3</sup> These results may possibly serve in the molecular design of a polymer magnet.

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