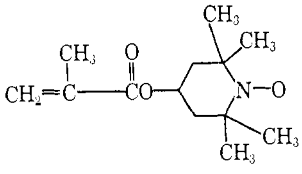
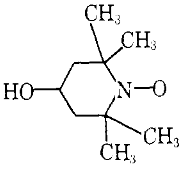
Preparation and Magnetic Resonance of Nitroxide Polymers

Sir:

All known organic polymers have at least one property in common: they are diamagnetic. It is not difficult to envision other classes of polymers that have markedly different magnetic properties. Such polymers, for example, might be prepared as linear chains of organic free radicals. Inherent instability of free radicals has made this approach to new polymers unattractive in the past. Recently, however, nitroxide free radicals have been reported[1] which are stable over a wide variety of conditions. We wish to report here the preparation and preliminary study of the first nitroxide polymers.

Examples of nitroxide polymers were obtained by two quite different general approaches: (a) the preparation and subsequent polymerization of a nitroxide monomer and (b) the attachment of nitroxide units to a previously prepared conventional polymer. In the first approach the orange nitroxide monomer I, mp 81.5–82.5° (hexane) (*Anal.* Found: C, 65.05; H, 9.10; N, 5.77), was prepared by adding freshly distilled methacryl chloride to 1 equiv of 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl (II)[2] in pyridine at 25°. The methacrylate ester I was polymerized by the method of Goode.[3] To 9.5 ml of toluene at 0° under nitrogen was added 0.60 ml of diethyl ether 1.73 *M* in phenylmagnesium bromide. Then a solution of 2.0 g of nitroxide I in 10.5 ml of toluene was added dropwise over 20 min with stirring. The reaction mixture was stirred at 25° for 1 hr and then poured into 200 ml of chilled pentane. The resulting orange granular precipitate was washed twice with pentane, ten times with aqueous methanolic hydrogen chloride, and twice with water and then dried, affording 1.3 g (65% yield) of the polymer III (not shown). The intense bands at 6.12 and 12.32 μ present in the infrared spectrum of monomer I were clearly absent in the spectrum of the polymer. The average molecular weight of III was found by osmometry[4] to be 1050. Similar polymers were obtained using chloroform as the solvent. In this case the nitroxide polymer appeared to have a somewhat larger molecular weight (~1950).


I


II

In the second approach a nitroxide polymer was prepared by heating a xylene solution of 0.60 g of maleic anhydride–methyl vinyl ether (1:1) copolymer (Borden Co., mol wt ~500,000) and 1.15 g of nitroxide alcohol II in the presence of 60 mg of *p*-toluenesulfonic acid and 90 mg of hydroquinone at 100° for 5 min.[5] A nitrogen analysis of the resulting brown powder IV (not shown) (0.14 g) revealed that approximately one-half of the anhydride groups in the original copolymer had reacted with the nitroxide alcohol II to give the corresponding half-ester.

The room-temperature electron spin resonance (esr) spectra of solid polymers III and IV each consist of a single exchange-narrowed line. The line widths and *g* values are given in Table I. The room-temperature spectra are typical of organic paramagnetic solids and resemble, for example, the spectrum of the alcohol nitroxide II (Table I). At lower temperatures the spectra of the two polymers differ markedly. As expected, the line width of polymer IV is essentially constant over the temperature range of +23 to −185°. The esr line width of polymer III, however, increases twofold as the temperature is lowered from +23 to −80°. This effect is *apparently* due to temperature-dependent exchange and dipolar interactions which can, for example, be caused by molecular motion or reorientation of the polymer. Thus, although the nitroxide polymers reported here are probably not ideal (from the point of view of chain length and stereoregularity), they do suggest that the polymerization of nitroxide monomers may be useful in studying exchange effects and polymer dynamics. Furthermore, if stereoregular linear chain nitroxide polymers can be prepared, one may well observe cooperative effects leading to a wide range of interesting magnetic properties[6] (*e.g.*, antiferromagnetic states, triplet excitons, phase transitions,[7] etc.).

Table I. Electron Spin Resonance Data[a]

Nitroxide	*g* value, ±0.0003	Line width,[b] ±0.3 gauss
II (alcohol)	2.0057	8.9
III (methacrylate polymer[c])	2.0067	11.2
IV (copolymer)	2.0058	10.6

[a] X-band esr spectra of the solid compounds were measured at room temperature. [b] These values represent the full peak-to-peak widths measured from the first derivative esr spectra. [c] The *g* value and line width reported are those of the polymer prepared in toluene.

Acknowledgments. It is a pleasure to thank Drs. T. Buckman, T. G. Fox Jr., and T. W. Koenig for valuable discussions. This work was supported by the National Science Foundation (GP-5509) and by the Office of Scientific and Scholarly Research of the Graduate School of the University of Oregon.

O. H. Griffith, J. F. W. Keana
S. Rottschaefer, T. A. Warlick
Department of Chemistry, University of Oregon
Eugene, Oregon 97403

Received July 17, 1967

---

(1) A. B. Sullivan, *J. Org. Chem.*, 31, 2811 (1966), and references cited therein.

(2) R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. France*, 3273 (1965).

(3) W. E. Goode, F. H. Owens, R. P. Fellmann, W. H. Snyder, and J. E. Moore, *J. Polymer Sci.*, 46, 317 (1960); W. E. Goode, F. H. Owens, and W. L. Myers, *ibid.*, 47, 75 (1960).

(4) Determined in dimethylformamide solution by Galbraith Laboratories, Knoxville, Tenn.

(5) Johnson and Johnson Co., British Patent 798,806 (1959); *Chem. Abstr.*, 53, 3784*g* (1959).

(6) See, for example, A. S. Edelstein and M. Mandel. *J. Chem. Phys.*, 35, 1130 (1961); P. L. Nordio, Z. G. Soos, and H. M. McConnell, *Ann. Rev. Phys. Chem.*, 17, 237 (1966).

(7) The line broadening made intensity measurements inaccurate but it is clear there are no abrupt or unusual intensity variations over the temperature range studied and thus no phase transitions were detected in polymers III and IV.