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Synthesis and Magnetic Properties of a Rigid High Spin Density Polymer with Piperidine-*N*-oxyl Pending Groups

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ABSTRACT: A rigid polymer with pending piperidine-*N*-oxyl groups has been synthesized by polymerization of the appropriately substituted isocyanide catalyzed by nickel(II) salts. The rigid high-spin polymer has been characterized by ESR spectroscopy and magnetic susceptibility (χ_m) measurements. The $1/\chi_m$ versus T plot obeys the Curie law, passing through the origin. Despite the touching of the pending groups and the expectation of a cooperative effect, this high-spin polymer is paramagnetic with an estimated spin density of $1.3\text{--}2.4 \times 10^{21}$ spins/g.

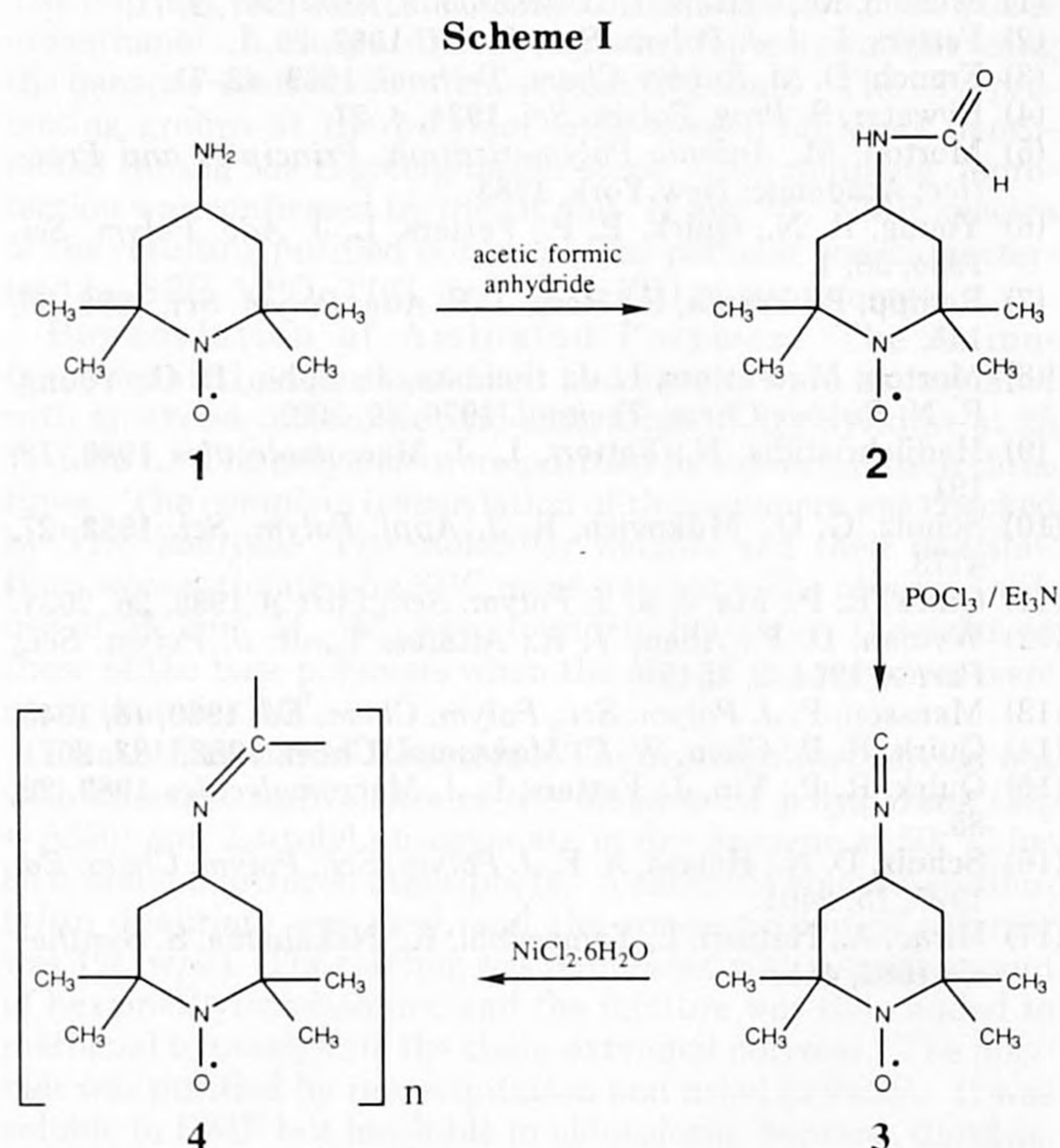
Introduction

The current interest in high-spin polymers is inspired by the search for possible ferromagnetic materials made from organic elements only.¹⁻⁴ A variety of polymers with stable radical substituents has been presented and ferromagnetism has been claimed in some cases.^{1,2} In order to obtain macroscopic ferromagnetism, it seems a prerequisite to have a high level of ordering of the stable radicals in the polymer.^{1,3} Paramagnetism is observed in amorphous polyacrylates, polymethacrylates, and polyacetylenes with dangling radicals.⁴

Polyisocyanides, $[\text{RN}=\text{C}]_n$, more systematically called poly(iminomethylenes) or poly(carbonimidoyls), are polymers made from isocyanides, $\text{RN}=\text{C}$. Their molecules are rigid rods with a helical configuration, as was found by Millich.⁵ In our laboratory we discovered that the polymerization of isocyanides is catalyzed by nickel(II) salts.⁶ In this way we prepared a large variety of polymers, supporting the proposed helicity and rigid-rod character, in particular for polymers from α -branched isocyanides.⁷ From circular dichroism spectra we concluded that the rigid-rod polymers have approximately four repeating units $\text{RN}=\text{C}$ per helical turn⁸ (Figure 1), as suggested earlier by Millich.⁵ Hence, each rodlike molecule has four stacks of side groups. The periodicity of the helix and the intracolumnar distance in a stack amount to approximately 0.4 nm. Therefore, in each stack successive side groups are touching and cooperative effects might be observed in their properties. The aim of the present study was to synthesize a polyisocyanide from 4-isocyano-2,2,6,6-tetramethylpiperidine-*N*-oxyl free radical and to determine its magnetic properties.

Results and Discussion

The monomeric free-radical 4-isocyano-2,2,6,6-tetramethylpiperidine-*N*-oxyl (**3**)⁹ was prepared from the corresponding amine, **1**, through the formamide, **2**, which was dehydrated with phosphorus oxychloride and triethylamine¹⁰ (Scheme I). Monomer **3** was polymerized with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in methanol/chloroform, according to



the polymerization procedure for isocyanides.⁷ The reaction was followed by infrared spectroscopy. After the disappearance of the isocyanide signal at 2140 cm^{-1} , the precipitate that had formed was isolated by centrifugation and washed with MeOH. An amount of 80 mg (32%) of polymer **4** was obtained. The sample is insoluble in common organic solvents.

Powder ESR spectra of a sample of compound **4** show a single isotropic Gaussian signal without hyperfine splitting (Figure 2). A g factor of 2.0050 and a peak-to-peak line width of 24 G were found. The spin density was estimated to be 1.3×10^{21} spins/g. Theoretically, a spin density of 3.3×10^{21} spins/g was expected.

Magnetic susceptibility (χ_m) measurements were performed at the temperature range of 77–300 K. The temperature dependence of χ_m of **4** is shown in Figure 3. A good linear relation between $1/\chi_m$ and temperature was observed, passing through the origin. The observed χ_m obeys the Curie law ($\chi_m = c/T$) and is illustrative of a paramagnet without a transition to a more ordered spin

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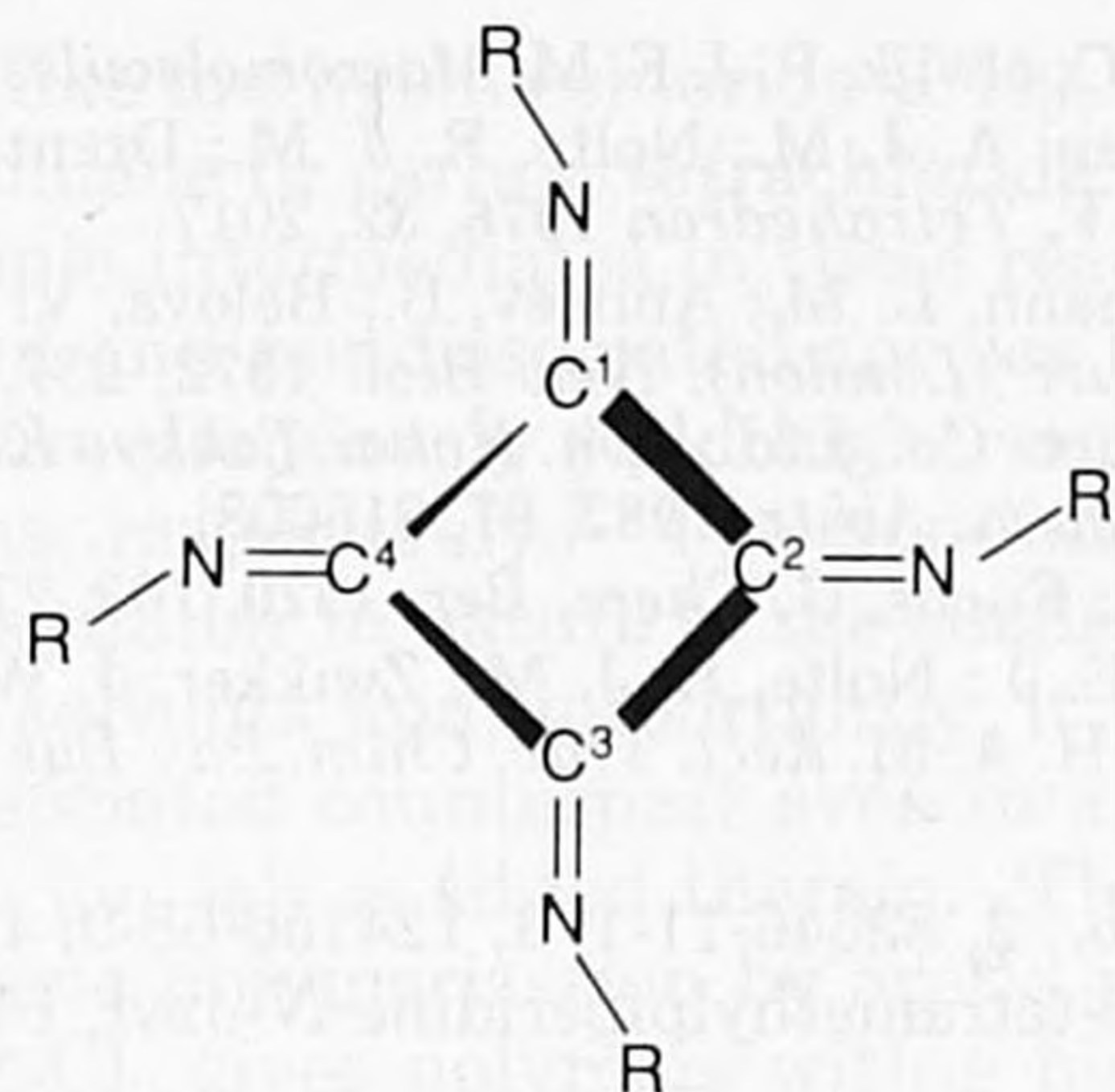


Figure 1. Top view of right-handed helix. Unit 5 behind unit 1, etc.

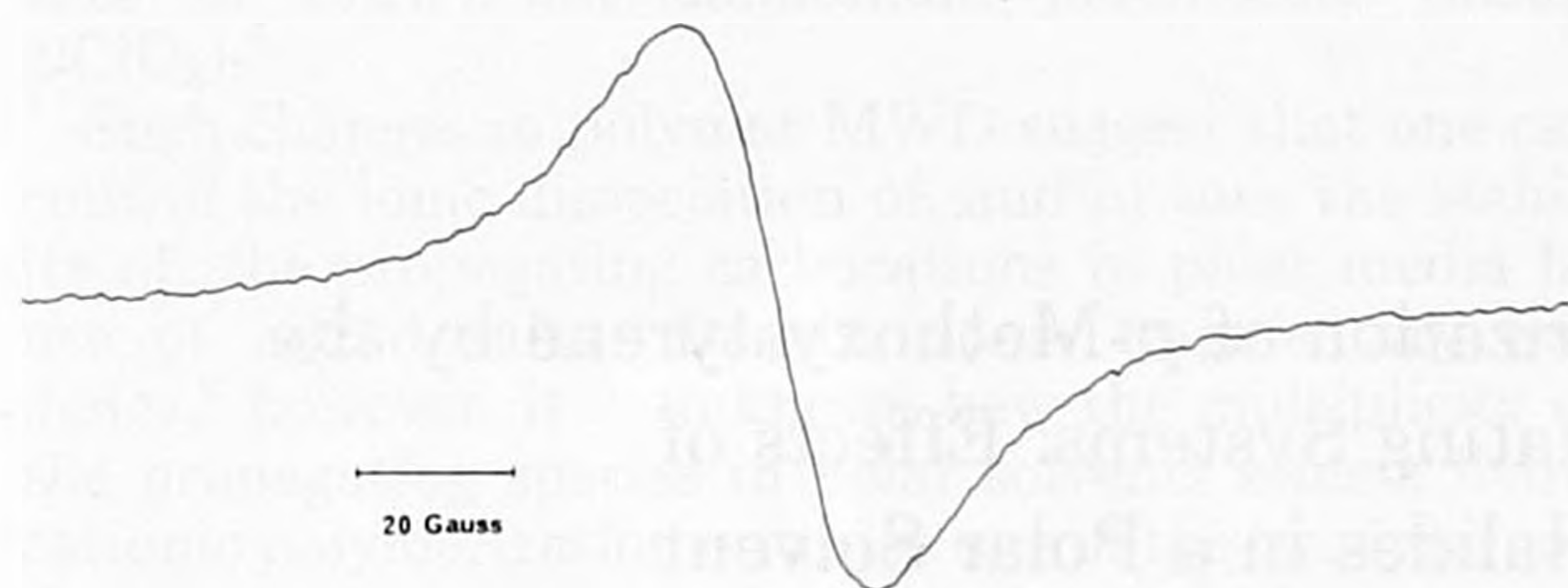


Figure 2. Powder ESR spectrum of polymer 4.

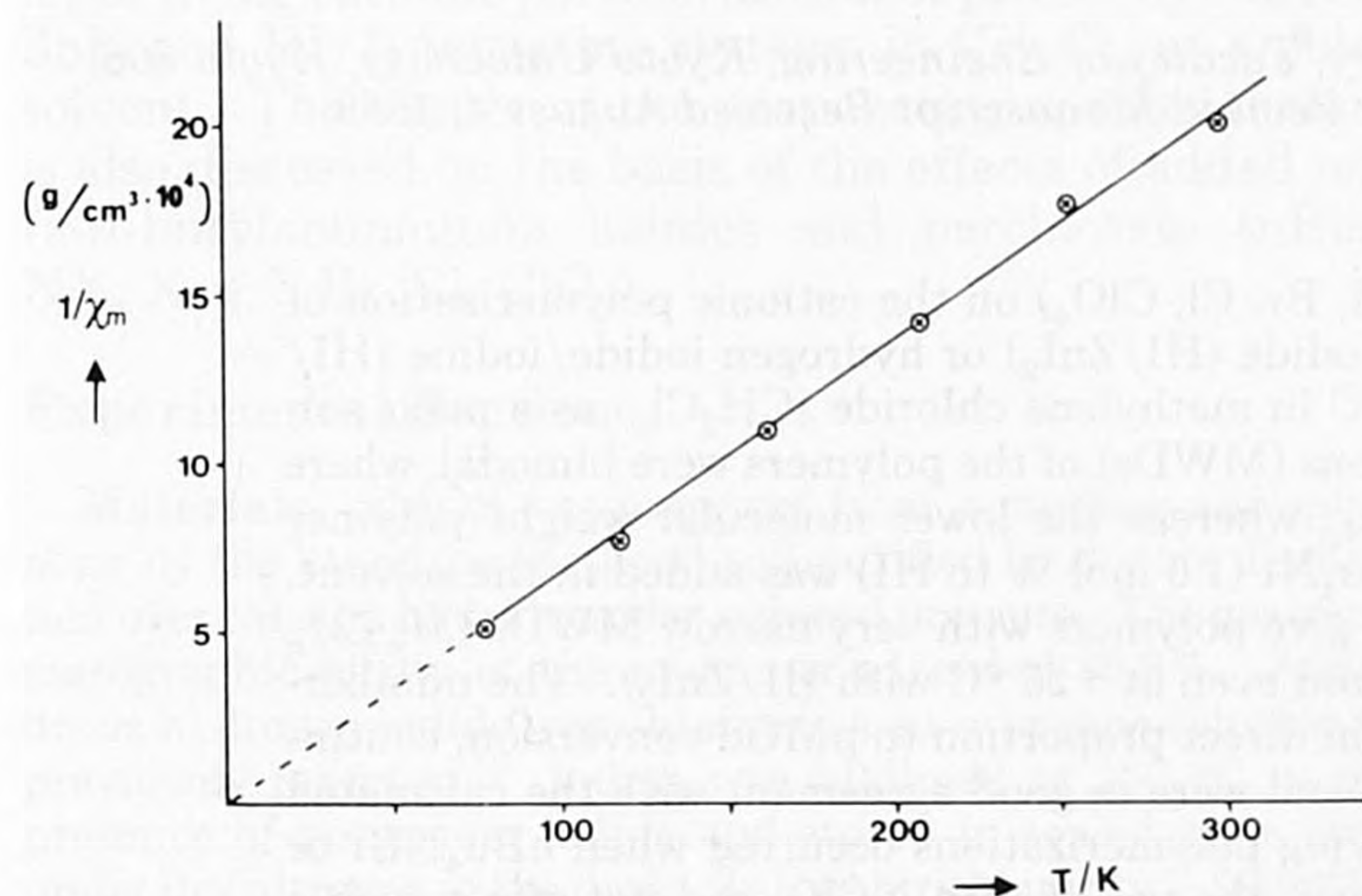


Figure 3. Magnetic susceptibility ($1/\chi_m$) versus temperature of polymer 4.

state within the temperature range studied. The estimated spin density is 2.4×10^{21} spins/g (using a density of 1 g/cm^3), corresponding to approximately 0.73 spins/monomeric unit.

The data presented show that high-spin polymer 4 can be made from the corresponding isocyanide without appreciable amounts of degradation of the nitroxyl radical. The rigid-rod polyisocyanide enhances the rigidity and ordering of the nitroxyl free radicals. Despite the expected close packing of these free radicals, no magnetic order is found in the temperature range from 77 to 300 K. Further research to evaluate the magnetic properties of polyisocyanide high-spin polymers will be conducted.

Experimental Section

Analytical Techniques. Infrared spectra were recorded on a Perkin Elmer 283 spectrophotometer. The melting points were determined on a Mettler FP5/FP51 photoelectric melting point apparatus. ESR spectra were recorded on a Bruker ER 220D SR spectrometer using a fresh sample of 2,2-diphenyl-1-picrylhydrazyl (Fluka Chemie) as a standard. Calibrations were performed in the usual manner. Magnetic susceptibility measurements were performed on a home-built Faraday balance. The susceptibilities at $H = 0$ of a sample of 4.9 mg were extrapo-

lated from seven measurements at magnetic fields between 15 000 and 9000 Oe.

4-(Formylamino)-2,2,6,6-tetramethylpiperidine-*N*-oxyl (2). An amount of 0.6 g (3.5 mmol) of 4-amino-2,2,6,6-tetramethylpiperidine-*N*-oxyl (purchased from Janssen Chimica, Beerse, Belgium) was treated at room temperature with an excess of acetic formic anhydride.¹¹ As soon as a ninhydrin TLC spot test showed complete disappearance of amine (approximately 3 h), the reaction mixture was concentrated at 14 mmHg. The oily residue was codistilled with toluene at the same low pressure several times in order to remove acetic acid. Removal of the last traces of volatile compounds at 0.01 mmHg resulted in a pure, colorless, viscous oil, which slowly crystallized on standing: mp 142–143 °C; yield 0.7 g (100%).

4-Isocyno-2,2,6,6-tetramethylpiperidine-*N*-oxyl (3). An amount of 500 mg (2.51 mmol) of formamide 2 was converted into the isocyanide 3 according to a literature method.¹⁰ Removal of volatile traces in vacuo (0.01 mmHg) resulted in a slightly colored product 3: yield 432 mg (95%). Purification using column chromatography (SiO_2 60, eluents CHCl_3 /acetone, 25:1) resulted in a pure, colorless, crystalline solid with a sharp melting point of 147–148 °C (lit.⁹ mp 133–134 °C). The IR signal of the isocyanide appeared at 2140 cm^{-1} .

Polymer of 4-Isocyno-2,2,6,6-tetramethylpiperidine-*N*-oxyl (4). A total of 250 mg (1.38 mmol) of the isocyanide 3 was dissolved in a mixture of 5 cm^3 of MeOH and 1 cm^3 of CHCl_3 . The solution was treated with 0.5 mol % $\text{NiCl}_2 \cdot 6 \text{ H}_2\text{O}$ at 40 °C for several days. The reaction was followed by infrared spectroscopy. After the disappearance of the isocyanide signal at 2140 cm^{-1} , the precipitate that had formed was isolated by centrifugation. Washing with MeOH resulted in 80 mg (32%) of polymer 4.

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Registry No. 2, 83646-11-1; 3, 124156-68-9; 4, 124156-69-0; 4-amino-2,2,6,6-tetramethylpiperidine-*N*-oxyl, 14691-88-4.

Living Cationic Polymerization of *p*-Methoxystyrene by the HI/ZnI₂ and HI/I₂ Initiating Systems: Effects of Tetrabutylammonium Halides in a Polar Solvent

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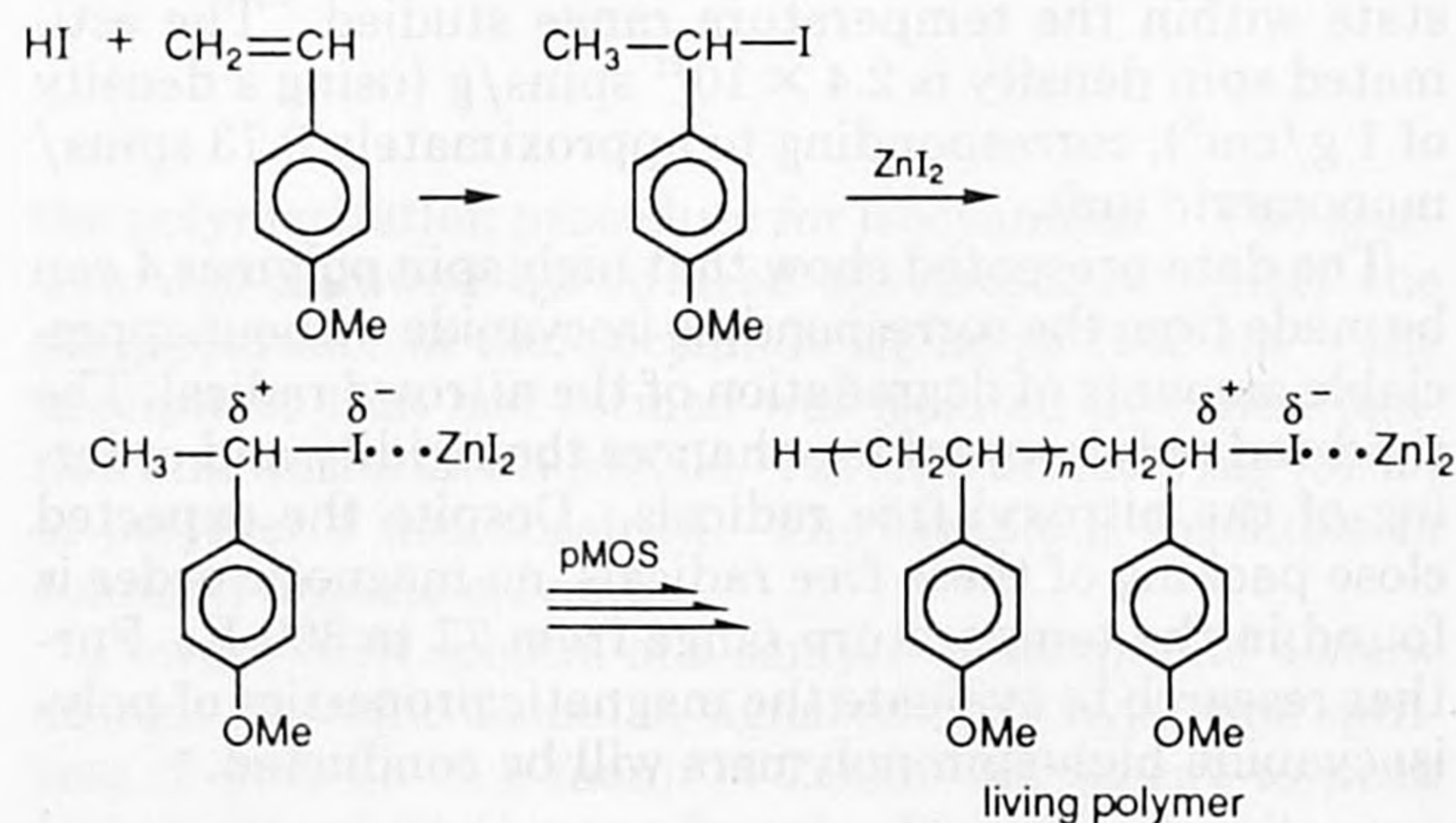
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ABSTRACT: The effects of added salts (nBu₄NX; X = I, Br, Cl, ClO₄) on the cationic polymerization of *p*-methoxystyrene (pMOS) by the hydrogen iodide/zinc iodide (HI/ZnI₂) or hydrogen iodide/iodine (HI/I₂) initiating systems were investigated at -15 and +25 °C in methylene chloride (CH₂Cl₂) as a polar solvent. In salt-free CH₂Cl₂, the molecular weight distributions (MWDs) of the polymers were bimodal, where the higher molecular weight polymer peak was nonliving, whereas the lower molecular weight polymer fraction had a long lifetime. When a small amount of nBu₄NI (1.0 mol % to HI) was added in the solvent, the higher polymer fraction was completely eliminated to give polymers with very narrow MWDs ($\bar{M}_w/\bar{M}_n \leq 1.1$) that turned out to be living (at -15 °C with HI/I₂ and even at +25 °C with HI/ZnI₂). The number-average molecular weight (\bar{M}_n) of the polymers increased in direct proportion to pMOS conversion, continued to increase upon sequential addition of pMOS feeds, and were in good agreement with the calculated values assuming one living chain per HI. Very similar living polymerizations occurred when nBu₄NBr or nBu₄NCl was employed in place of the iodide salt; however, the use of nBu₄NClO₄ did not effect such a living process at all. It is concluded that through their high nucleophilicity, the added halide anions efficiently eliminate a dissociated nonliving growing species (1), thereby selectively permitting living propagation via the nondissociated living counterpart (2) (Scheme I).

Introduction

Recently, we have found living cationic polymerization of *p*-methoxystyrene (pMOS) to proceed with the hydrogen iodide/zinc iodide (HI/ZnI₂) initiating system in toluene solvent.¹ This finding permitted the first synthesis of nearly monodisperse styrenic polymers of controlled molecular weights under cationic conditions even at room temperature. A similar but less controlled polymerization of pMOS has been achieved by us using iodine as an initiator in carbon tetrachloride, in which process the growing species also exhibits the living character.^{2,3} These living pMOS polymerizations specifically employ nonpolar solvents.

In general, solvent polarity remarkably affects the rate of cationic polymerization and the molecular weight distribution (MWD) of the polymers. For example, the use of a polar solvent usually increases the polymerization rate but renders the propagating carbocations more ionically dissociated and hence less stable than in nonpolar media. It is therefore expected that living cationic polymerization would be more difficult to occur in polar solvents.



Another complexity associated with polar solvents is the involvement of multiple growing species with different ionic dissociation states, the existence of which is shown by bimodal MWDs of product polymers.⁴ The typical examples of the double-peaked distribution have been found for the polymerizations of styrene,^{5,6} *p*-methylstyrene,^{7,8} and pMOS^{2,7} initiated by perchloric acid, acetyl perchlorate, or iodine, all being carried out in relatively