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Comments on and Updating of the Paper "Controlled Radical Polymerization of Methyl Methacrylate Mediated by 4-Methoxypyridine-*N*-oxide"[1]

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Introduction. In previous paper,[1] oral presentations, and patent,[2] 4-methoxypyridine-*N*-oxide (4-MPNO) was shown to promote the controlled radical polymerization of alkyl methacrylates initiated by the cumyl hydroperoxide (CH)/$FeSO_4$ or $K_2S_2O_8$/$FeSO_4$ systems in aqueous media and thus the formation of polymers of a predictable molecular weight and a low polydispersity which however increased with the monomer conversion. This polymerization was conducted under mild experimental conditions, including the use of water as (co)solvent and low temperature ($20\ °C \le T \le 80\ °C$). 4-MPNO and $FeSO_4$ had to be used simultaneously to impart control to the polymerization, although only a low amount of $FeSO_4$ was necessary. According to the scientific literature,[3] these two compounds are known for strong coordination, such that the parent complexes were thought to be key actors in the control of the radical polymerization.

Experimental Section. a. Materials. 4-Methoxypyridine-*N*-oxide (4-MPNO) was purchased from company X and Aldrich. Methyl methacrylate (MMA) from Aldrich was distilled just before use in order to remove the stabilizer. Bidistilled water was degassed prior to use. Cumyl hydroperoxide (CH, Aldrich) and $FeSO_4 \cdot 7H_2O$ (Aldrich) were used as received. Liquids were transferred under nitrogen by syringes or through stainless steel capillaries.

b. Polymerization. 0.022 g of $FeSO_4$ (0.08 mmol) and 0.0119 g of 4-MPNO (0.08 mmol) were added to a 50 mL one-necked, round-bottom flask fitted with a three-way stopcock connected to either a nitrogen line or a vacuum pump. Oxygen was removed from the reaction flask by repeated vacuum−nitrogen cycles. Once filled with nitrogen, 10 mL of water was added to the flask. After stirring for 5 min at 50 °C, 8 mL of MMA followed by a degassed solution of 0.011 mL of cumyl hydroperoxide (CH, 0.06 mmol) in 10 mL of acetonitrile was transferred to the flask. Polymerization was conducted at 50 °C under magnetic stirring. Samples were withdrawn all along the polymerization. After evaporation of the residual monomer and solvent, the polymer was dissolved in THF and filtered in order to remove $FeSO_4$ and 4-MPNO. After solvent evaporation and polymer drying under vacuum at 80 °C, the monomer conversion was determined gravimetrically.

c. Characterization. Size exclusion chromatography (SEC) was carried out in THF at 40 °C using a Hewlett-Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 1037A refractive index detector. Columns HP PL gel 5μ (10^5, 10^4, 10^3, and 100 Å) were calibrated with PMMA standards. ^1H NMR spectra were recorded in $CDCl_3$ with a Bruker AM 250 MHz apparatus at 25 °C.

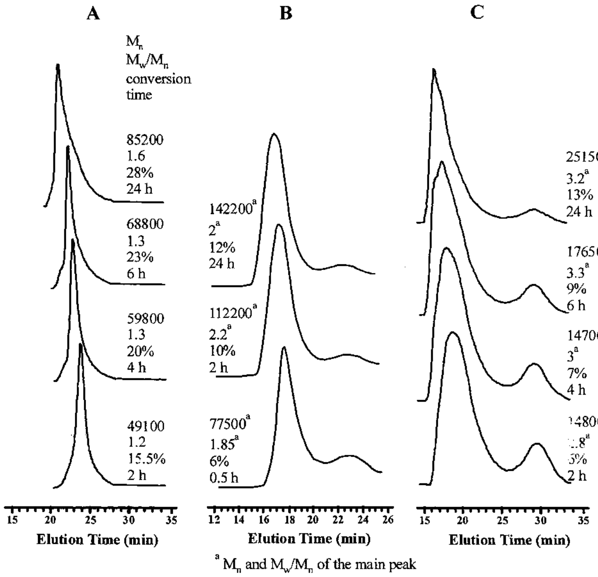

Figure 1. SEC chromatograms of PMMA formed in a 1/1 (v/v) water/acetonitrile mixture at 50 °C in the presence of 4-MPNO from company X (A), of 4-MPNO from Aldrich (B), and in absence of any 4-MPNO (C) [1.5 equiv of 4-MPNO when used, 1.3 equiv of $FeSO_4$, 1 equiv of CH, 1260 equiv of MMA, $H_2O/MMA = 1.25$ (v/v)].

Results and Discussion. From the very beginning of this research program, 4-MPNO of the same origin (company X) was used, which was reported as 99% pure. When the polymerization of MMA was initiated by the CH/$FeSO_4$ system in the presence of this 4-MPNO, M_n increased linearly with the monomer conversion, and the polydispersity remained narrow at least until 25% monomer conversion ($M_w/M_n = 1.2-1.3$ compared to $M_w/M_n \ge 1.5$ for classical free radical polymerization).[1] At higher monomer conversion, the molecular weight distribution became broader, which indicated the occurrence of termination and/or transfer reactions.

Because of stock shortage of 4-MPNO by the usual supplier X, this compound was purchased from another company (Aldrich). Very surprisingly, although repeated under the same conditions as before, the polymerization of MMA was completely out of control. Figure 1 compares the SEC chromatograms for the MMA polymerization initiated by the CH/$FeSO_4$ redox system, in the presence of 4-MPNO supplied by company X (Figure 1A) and by Aldrich (Figure 1B) and in the absence of 4-MPNO (Figure 1C) in a 1/1 (v/v) water/acetonitrile mixture at 50 °C. Whenever the 4-MPNO supplied by Aldrich was used, a typical bimodal molecular weight distribution was observed, the molecular weight of the major population was rapidly much higher than the molecular weight observed whenever 4-MPNO was supplied by company X, and the polymerization stopped early, thus at 10−15% monomer conversion. This behavior is typical of the conventional MMA radical polymerization carried out under the same experimental conditions (Figure 1C) and completely different from the polymerization conducted in the presence of the 4-MPNO supplied by company X.

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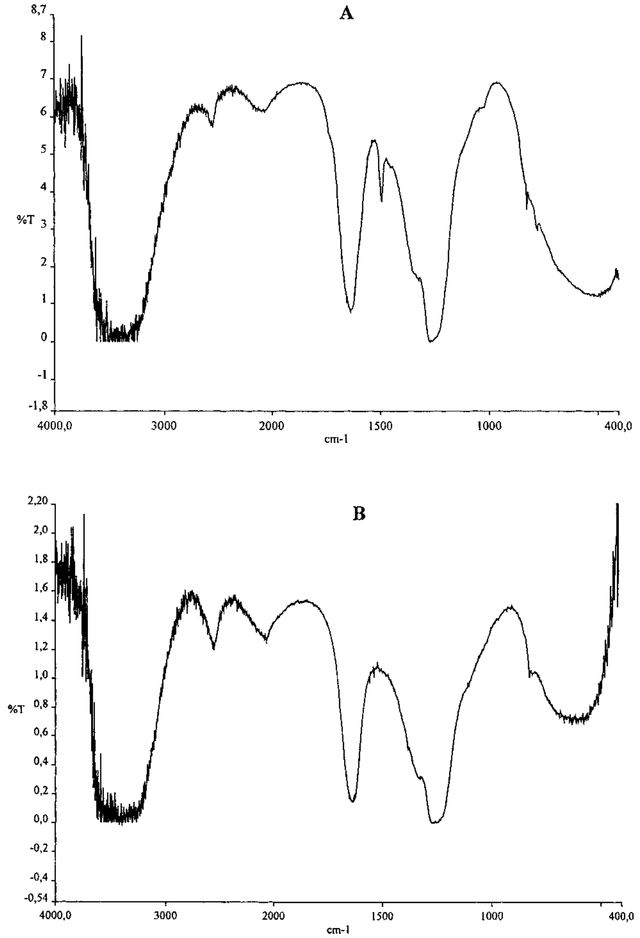
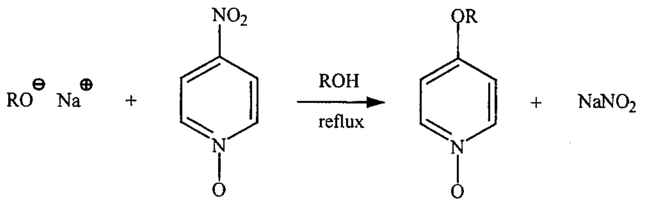


Figure 2. IR spectra for the impurity isolated from the company X 4-MPNO (A) and pure sodium nitrite (B).

Table 1. Elemental Analysis of Monohydrated 4-MPNO of Different Origins

	company X 4-MPNO	Aldrich 4-MPNO	theoretical data
% N	10.88	9.9	9.79
	11.13	9.95	
% C	43.22	50.35	50.33
	44.84	50.37	
% H	5.62	6.74	6.35
	5.96	6.88	
% O			33.53

Because 4-MPNO supplied by Aldrich (97% pure) gave negative results compared to 4-MPNO supplied by X, we decided to purify it further by recrystallization in an acetone/ether mixture. Despite the higher purity checked by GC, ^{1}H NMR, and elemental analysis, no improvement was observed in the polymerization control. Therefore, we suspected that the 4-MPNO supplied by X was contaminated by an impurity that might interfer with the radical polymerization. This 4-MPNO was dissolved in $CDCl_3$ with the purpose to analyze it by ^{1}H NMR, ^{13}C NMR, and GC. Although the soluble product showed no impurity, an insoluble fraction was left in the organic solution prepared for analysis. The elemental analysis of the 4-MPNO (from X) concluded to a purity of 87.5% instead of 99% (Table 1). To trace the impurity, attention was paid to the possible synthetic routes for 4-MPNO. The 4-nitropyridine-*N*-oxide is the reagent usually used for the synthesis of 4-alkoxypyridine-*N*-oxide. It is prepared by reaction of the desired alkoxide with 4-nitropyridine-*N*-oxide according to the following equation.[4]



The sodium nitrite formed as a byproduct is easily removed by filtration and purification on silica. However, in the case of 4-MPNO supplied by X, this inorganic salt was still contaminating the organic product, which was not the case for the 4-MPNO supplied by Aldrich. When this salt was eliminated from the 4-MPNO (from X), any control of the MMA polymerization was lost, in complete agreement with the observations reported for the Aldrich 4-MPNO.

To prove that the impurity found in the 4-MPNO supplied by X was sodium nitrite, the elemental composition was calculated on the assumption that 4-MPNO was contaminated by 12.5% of sodium nitrite. This composition, i.e., 44.04% C, 11.1% N, and 5.55% H, is in good agreement with the elemental analysis of 4-MPNO supplied by X (Table 1). An additional confirmation of the contamination by sodium nitrite was found in the IR spectrum of the insoluble fraction, which is the same as that one of the commercially available sodium nitrite (Backer) (Figure 2). The small peak at 1495 cm^{-1} in the spectrum of the insoluble fraction originates from residual 4-MPNO.

Conclusions. It is now clear that only sodium nitrite and not 4-MPNO can impart a control to the radical polymerization of alkyl methacrylates, as will be illustrated in forthcoming papers.

The moral of this story (dramatic for the Ph.D. student who worked with the 4-MPNO from X for ca. 3 years) is that even though it takes time to check whether the actual purity of any chemicals supplied fits the announced data, it may however prevent from taking a wrong way and wasting a lot of effort.

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