

Use of functionalized organocobalt initiators in processes of emulsion polymerization

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Received: 7 December 2005 / Revised version: 2 March 2006 / Accepted: 5 March 2006

Published online: 30 March 2006 – © Springer-Verlag 2006

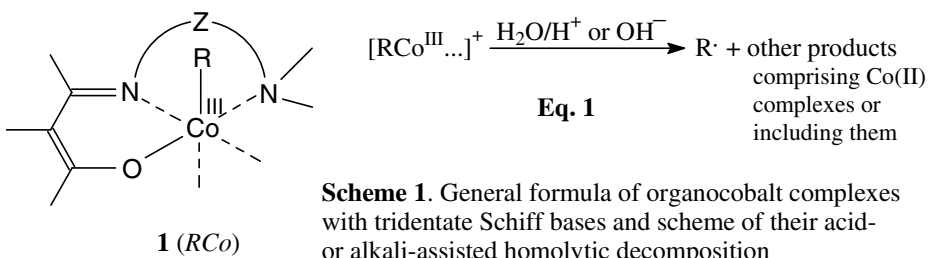
Summary

Characteristics of novel organocobalt–tridentate Schiff base chelates bearing a heteroatomic group capable of donating an electron couple, namely amino or hydroxyl function, or the carboxylate anion, at the terminal position of an alkyl ligand, are reported in respect to their presumable application as initiators of radical polymerization. These processes were studied in water emulsions using styrene as a model monomer at various pH and temperatures. Polymerization rates proved relatively low if both the length of carbon chain of the alkyl ligand and pH range favored extra chelation in the given initiator due to coordination of the functional group. With this reservation, the complexes in question act as highly effective pH-dependent initiators of emulsion polymerization, by general analogy with the corresponding non-functionalized initiators. Characteristics of the polymer products, including latexes, are presented and discussed.

Introduction

The search for novel advanced polyfunctional initiators and their use to produce specific high-molecular species for various applications in fine chemical technology and, especially, in medicine and biotechnology is an important modern trend in studies of radical polymerization [1-3]. In our opinion, organocobalt–tridentate Schiff base chelates well may fit as basic structures for this purpose. The complexes in question, namely those with a *plain, i. e.* non-functionalized alkyl group as the *organyl* ligand, were first prepared in 1980-ies and have been under permanent investigation ever since. These studies were twice self-reviewed by their principal authors [4, 5].

The compounds referred to are octahedral cobalt(III) complexes including, above a σ -bonded alkyl group and a chelating tridentate [N2O] Schiff-base anionic ligand, either a bidentate chelating Lewis base or two monodentate ones (Scheme 1: **1**, *RCo*).



Their main feature consists in the capability of homolytic splitting at the Co-C bond under the action of both acid [6, 7] and, though far slower, alkali [8], yielding the corresponding carbon-centered free radicals $R\cdot$ (Scheme 1: Eq. 1). Practically, the proton-assisted decomposition proceeds under very mild conditions, down to at least -40°C .

As initiators of radical polymerization, RCo's substantially differ from conventional ones such as peroxides, being advantageous over them in certain respects, particularly in emulsion systems. The last point was proved using a number of vinylic monomers as well as surfactants of various types [9-14].

First, in neutral to moderately acidic media, the polymerization rates rise with decreasing pH, that is in qualitative accordance with growing rate of homolytic decomposition of RCo's. Therefore they allow convenient control of the polymerization process by means of pH. Simultaneously, a strict and wider regulation of molecular mass of polymer products and size of latex particles is achieved. Also, polymer products proved more uniform, that is distributions of molecular mass in the polymers and size of latex particles are much narrower than in the case of conventional initiators. Further, since these complexes allow polymerizations to be carried out at notably mild conditions, they can be used to reduce branching of the polymer chain usually observed with conventional initiators in the case of highly reactive monomers. This point was proved by the example of vinyl acetate [13].

Second, due to apparently total irreversibility of the homolytic decomposition of RCo's [4], no cage effect is displayed in processes initiated by these complexes. Mainly for that reason, they are much more efficient than conventional initiators and, in particular, can be used at far lower concentrations. Namely, they were proved properly operable at as small quantities with respect to common vinylic and diene monomers as 10^{-4} by moles [9].

Thus, alkylcobalt chelates with tridentate Schiff base ligands can be treated as advanced pH-dependent initiators of radical polymerization. One could expect that the corresponding bifunctional initiators, *i. e.* related complexes with an appropriate functional group at the alkyl ligand, would keep the above advantages.

Here we have tried to verify this suggestion by the example of RCo's bearing a functional group, which appeared particularly fit for biomedical applications, at the terminal position of an alkyl ligand. Such bifunctional organocobalt initiators have not been properly reported yet in any regular scientific edition while recently patented [15] and dealt with in a poster at the European Polymer Congress-2005 [16].

Experimental

Materials

Organocobalt complexes **2a-c** and **3a-c** (Figure 1–
 (ω -functionalized *n*-alkyl)[2-[(2-aminoethyl)imino]pent-3-ene-4-olato]- and
 -[2-[1-[(2-aminoethyl)imino]ethyl]phenolato](1,2-ethanediamine)cobalt(III) bromides,

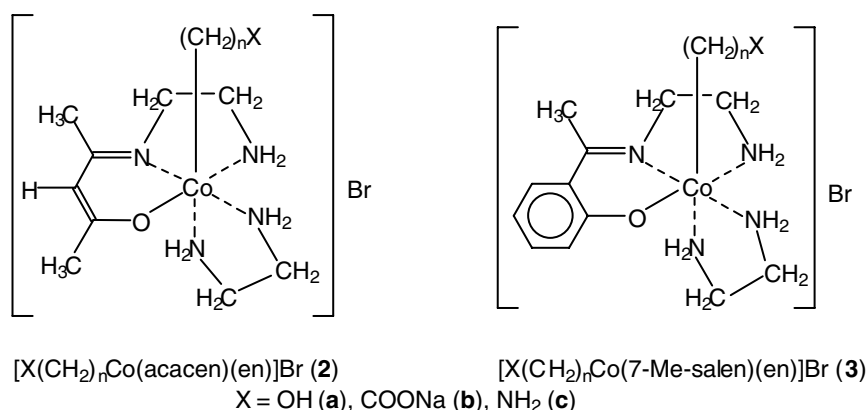


Figure 1. Structures of functionalized organocobalt initiators used

respectively) with $n = 3-11$ if $X = OH$ or NH_2 , or $2-11$ if $X = COONa$, were prepared and characterized according to the above-mentioned patent [15]. Commercial styrene (Russia) stabilized with hydroquinone was liberated from the latter by washing with a 10% aqueous solution of NaOH. Then it was washed with water until its reaction turned neutral, dried with anhydrous calcium chloride, twice recondensed under vacuum and characterized as follows: b. p. 145°C, d_4^{20} 0.909 g/cm, n_D^{20} 1.5462. Other reagents, namely sodium alkylsulfonate *n*-C₁₅H₃₁SO₃Na (*E-30*) of *pure* grade, and potassium dihydrophosphate and sodium hydrophosphate dihydrate, both of *pure for analysis* grade (Russia, *Reanal*), were used as received.

Techniques

Progress of the polymerization process was followed by means of dilatometry. Mean molecular masses of polymers were determined *via* measurements of intrinsic viscosities of solutions in toluene at 25°C. The diameter of particles in polymer suspensions and their size distribution, and values of the Z-potential were measured by laser spectroscopy using a *Z-sizer* instrument (*Malvern Instruments Ltd.*, U.K.).

Polymerization

This process was performed under anaerobic conditions, temperature control and permanent stirring. A typical experiment was carried out as follows. A calibrated dilatometric vessel provided with a magnetic stirrer was first charged with an initiator, e. g. **3c** (4.5 mg, 12 μ mol), and then connected to a vacuum apparatus including reservoir flasks for a monomer and an aqueous phase. They had been pre-charged with styrene (4.53 g, 44 mmol), and a water solution (10 mL) of a standard phosphate

buffer, *e. g.* 45 mg of KH_2PO_4 and 59 mg of $\text{Na}_2\text{HPO}_4 \times 2\text{H}_2\text{O}$ to get pH 7.0, as well as the E-30 surfactant (0.40 g). Both the monomer and the water solution were degassed by two freeze/pump cycles and allowed to pour out into the dilatometric (reaction) vessel. Then the vessel was disconnected from the vacuum apparatus and closed under argon flow, and thermostated within 0.1°C . Polymerization was launched by turning on the stirrer.

In other experiments, the initiator, temperature and/or pH (practically, a ratio of the components in a buffer mixture) were varied.

The polymerization process was brought up to a plateau region of the kinetic curve.

Working up reaction mixtures

While a portion of the resulting latex was left alone for examination, most of it was treated with methanol. The precipitated polymer was twice washed with distilled water and finally dried at 20°C under vacuum.

Results and discussion

Initiators

Structures of organocobalt initiators tested in this work are described by Formulas **2** and **3** (Figure 1), where X was OH, COONa or NH_2 , and n varied from 2 if X = COONa, or 3 if X = OH or NH_2 , to 11.

As one could expect, solubilities of the functionalized RCo's in water and styrene proved higher and at least not lower, respectively, than those of the related plain alkylcobalt complexes. Some illustrative data on solubility of the non-functionalized complexes are presented in Table 1. In combination with the just applied consideration, they allow conclusion that the functionalized initiators in question are readily dissolved under conditions of our experiments on emulsion polymerization.

Table 1 includes also experimental values of distribution coefficient of the complexes between water and styrene; they may be useful in assessment of topochemistry of the polymerization processes.

Table 1. Solubility and phase distribution characteristics of non-functionalized alkylcobalt complexes of the $[\text{RCo}(\text{acacen})(\text{en})]\text{Br}$ series at 20°C

R	Solubility in water (weight %)	Distribution between water and styrene (w/w) [#]
Et	> 5	770
<i>i</i> -Pr	> 5	420
<i>n</i> -Oct	0.2	6.8
<i>n</i> -Cet	0.05	0.35

[#] Measured using spectrophotometric technique.

In most aspects, the functionalized complexes are similar to the related plain alkylcobalt chelates.* The main difference consist in a specific reactivity of the

* Reactivity of RCo's including functionalized ones was investigated in aqueous, mostly buffer solutions in the temperature range of $20\text{-}60^\circ\text{C}$ using spectrophotometric and oxymetric (Clarke electrode) techniques. Results of these studies as well as experimental details will be published in full in an appropriate edition in the field of coordination and organometallic chemistry such as *Inorg. Chim. Acta*.

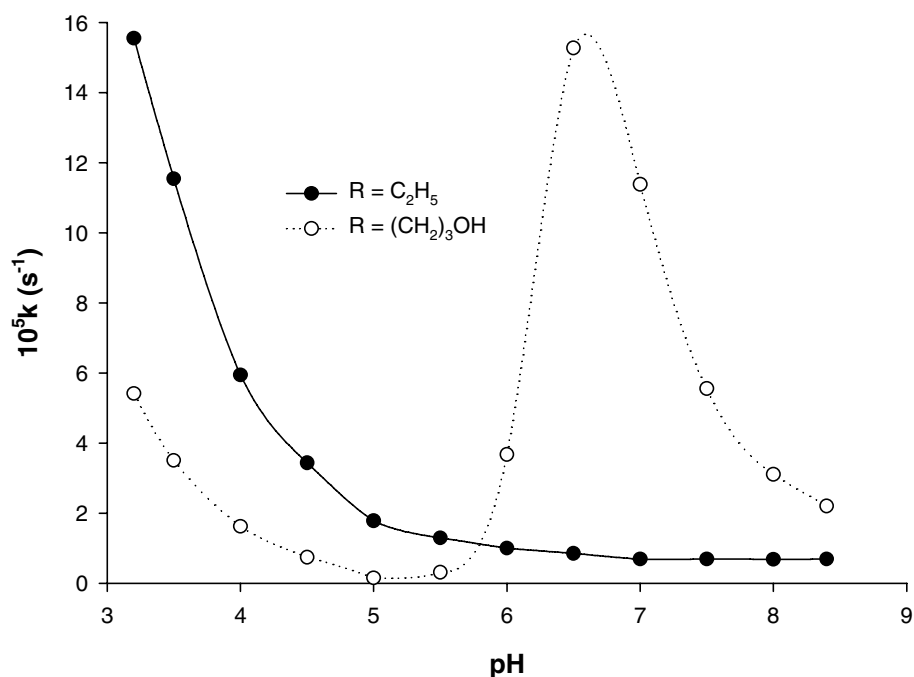
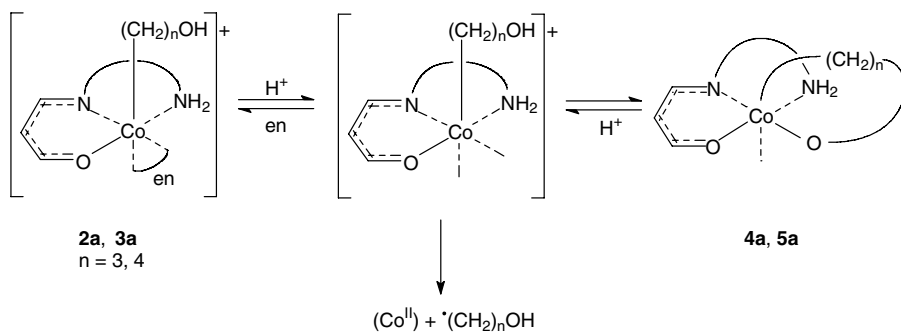


Figure 2. pH profile of pseudo-1st order rate constants of decomposition of two complexes of the $[\text{RCo}(\text{acacen})(\text{en})]^+$ series. Aqueous buffer solutions, 37°C



Scheme 3. Mechanism of homolytic decomposition of γ - and δ -hydroxyalkylcobalt complexes with a tridentate Schiff base and ethylenediamine at intermediate pH values

Polymerization

Kinetics of emulsion polymerization of styrene was studied in the presence of complexes of the **2a-c** and **3a-c** series. Measurements were carried out at temperatures 20 to 60°C and pH 4 to 7, using sodium alkylsulfonate E-30 as surfactant, since just those of the anion-active type proved preferable in the case of the related non-functionalized RCo initiators in the neutral to acidic pH range [12].

Table 2 summarizes results of the polymerization studies while Figure 3 presents examples of kinetic curves. They are S-shaped, which is common to radical polymerizations, with a short induction period and a lasting stationary section. High conversions of the monomer were attained at low concentrations of the initiators, down to 0.05 mass % with respect to the former.

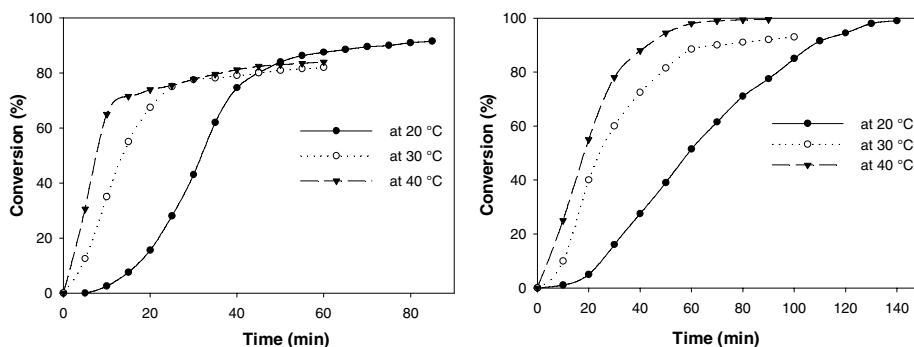


Figure 3. Kinetics of emulsion polymerization of styrene, initiated by $[\text{HO}(\text{CH}_2)_{11}\text{Co}(7\text{-Me-salen})(\text{en})]\text{Br}$ (left) and $[\text{H}_2\text{N}(\text{CH}_2)_5\text{Co}(7\text{-Me-salen})(\text{en})]\text{Br}$ (right) at pH 7.00 and various temperatures; other conditions are given in the title of Table 2

A hydroxyalkylcobalt complex having a short carbon chain ($n = 3$) in the organyl ligand proved a far less active initiator as compared with its middle- and long-chain analogs as well as the related plain alkylcobalt complexes. *E. g.*, in its presence at 20°C and pH 4, the polymerization proceeds slowly ($V = 0.2\%/min$) and with a long (> 120 min) induction period. Therefore further studies with this initiator were carried out at higher, up to 60°C, temperatures.

Its relative low activity agrees well with the ready “extra chelation” of organocobalt–tridentate Schiff-base complexes bearing a donor functional group at the terminal position of a short-chain alkyl ligand in neutral to moderately acidic media, which was discussed above.

On the other hand, activities of functionalized initiators **2a-c**, **3a-c** with a middle or long carbon chain in the alkyl ligand, are generally comparable with those of plain organocobalt complexes **2**, **3** with $X = \text{H}$ (and $n \geq 2$), so that polymerizations proceed fast under mild conditions. *E. g.* in the case of complex **3a** with $n = 11$, the polymerization rate and monomer conversion were as high as 3.4%/min and 96% respectively at 20°C and pH 7.

Finally, two unusual relationships between temperature of polymerization and molecular mass of polymer product should be mentioned.

First, the temperature effect on molecular mass of the polymer here is not clear-cut, which is uncommon for radical polymerizations. Apparently, in these cases both a number of free radicals and that of polymer-monomer particles increase with rising temperature, so that the mean number of radicals per a particle varies not much.

Second, in the case of a functionalized initiator with a long-chain alkyl ligand, namely **3a** with $n = 11$, effect of pH on the polymerization rate in neutral to moderately acidic media is rather weak, so that they are substantially higher at pH 7 and lower at pH 5 than those of the corresponding plain organocobalt initiators.

Table 2. Water emulsion polymerization of styrene in the presence of organocobalt chelates with tridentate Schiff bases and ethylenediamine bearing a functional group at the alkyl ligand. [Initiator] = 0.028 molar % with respect to monomer; surfactant E-30 to monomer ratio (w/w) 0.04; monomer to buffered aqueous solution ratio (v/v) 1:2

Initiator Series	X	n	Conditions and rate of polymerization			Characteristic of the product: $10^{-6}M_n$
			t (°C)	pH	V, %/min *	
2(a)	OH	3	20	4	0.2	3.2
			30		0.3	2.5
			40		0.5	2.6
				5	0.4	1.7
			50	4	1.1	2.5
			5	0.8	1.4	
			60	2.2	2.1	
		6	40	5	3.4	2.3
				7	1.6	2.3
			3(a)	11	20	4
	5				2.9	3.1
	6				3.5	3.7
	7	3.4	7.1			
	30	4.0	4.4			
	40	8.4	3.4			
2(b)	COONa	2	20	7	1.4	4.5
			30		2.1	4.7
			40		3.5	4.5
3(c)	NH ₂	5	20	5	1.9	6.2
				6	1.6	6.7
				7	1.1	7.8
			30	2.2	7.6	
			40	2.8	7.3	
		2**	H	2	20	7
			25		0.8	11.3
			30		1.4	10.2
		8	20	5	4.0	3.4
				7	2.1	8.8

* At stationary portions of the kinetic curves. ** Data on the non-functionalized initiators are taken from [12] and quoted here for the sake of comparison.

Study of latexes thus obtained

Laser autocorrelation spectroscopy was used to measure electrokinetic Z-potentials and sizes of particles of polymer dispersions obtained in the presence of the functionalized organocobalt initiators and the E-30 surfactant. Considerable variations in Z-potential were observed: *e. g.* in the case of complexes **2b**, $n = 2$ and **3a**, $n = 11$, its values were -41.9 and -63.3 mV respectively. Such marked differences suggest participation of functional groups in the formation of adsorption layer.

Latexes thus obtained consisted of rather small particles: *e. g.* in the case of complexes **2b**, $n = 2$, and **3a**, $n = 11$, their mean diameter was 68.9 and 48.2 nm, respectively. Quite narrow distributions of the particle sizes exemplified by Figure 4 were observed: namely, polydispersity of the polymer microspheres was as low as 0.1. Such a high uniformity is apparently characteristic of latexes prepared using RCo initiators in general (*cf.* [12]).

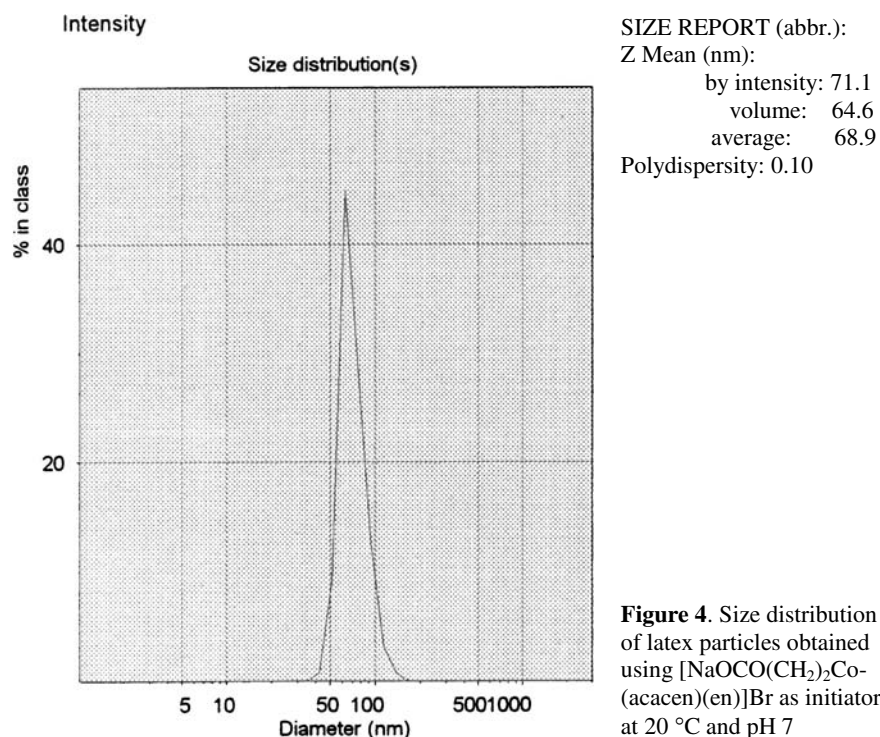


Figure 4. Size distribution of latex particles obtained using $[\text{NaOCO}(\text{CH}_2)_2\text{Co}(\text{acacen})(\text{en})]\text{Br}$ as initiator at 20 °C and pH 7

The latex obtained in the presence of the initiator including carboxylate group has been used in an attempt to prepare diagnostic test systems. Immunoglobulin isolated from a goat antiserum specific with respect to a C-reactive protein was immobilized on surface of the polymer microspheres *via* covalent binding with carboxyl groups pre-activated with carbodiimide. This product is now tried as a probe for causative agents of various inflammatory processes in human blood.

Conclusions

Bifunctional organocobalt initiators of radical polymerization studied in this work, *viz.* alkylcobalt chelates with tridentate Schiff-base ligands of the $[\text{N}_2\text{O}]$ type bearing a heteroatomic group capable of donating an electron couple, display the same advantages over conventional initiators as their non-functionalized analogs do. In particular, they operate at ambient temperatures and low concentrations, can be readily controlled by pH and give latexes that are highly uniform in size of particles. Peculiar reactivity of those complexes in question which have a short carbon chain between the cobalt atom and the functional group allows conditions for application of the bifunctional organocobalt initiators to be further diversified.

Acknowledgement. The research was supported by the Russian Foundation for Basic Research according to Grant No. 04-03-32738.

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