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The influence of pivalate metal complexes on the radical polymerization of methyl methacrylate

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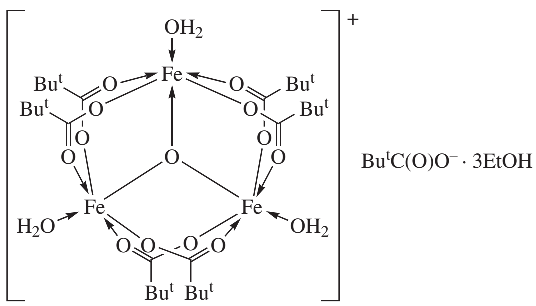
The pivalate complexes of metals used in the radical polymerization of methyl methacrylate increase rate of process initiated by both benzoyl peroxide and azobisisobutyronitrile and decrease the molecular weight of the resulting polymethyl methacrylate.

Two important trends of controlled synthesis as ‘living’ radical polymerization and complex-radical polymerization have been rapidly developed. The use of metal-containing substances in polymerization advances new prospects for obtaining well-defined polymers. Transition-metal complexes influence all of the steps of polymerization such as initiation, propagation and termination.[1–5]

Here, we consider the radical polymerization of methyl methacrylate (MMA) initiated by benzoyl peroxide (BP) or azobisisobutyronitrile (AIBN)[†] in the presence of the following pivalate complexes: $[Fe_3O(Piv)_6(H_2O)_3]^+(Piv)^-\cdot 3EtOH$ **1** (Piv^- is the pivalate anion), $[Mn(Piv)_2(EtOH)]_n$ **2**, $Cu_2(Piv)_4(HPiv)_2$ **3**, $Ni_9(OH)_6(Piv)_{12}(HPiv)_4$ **4** and $[Co(Piv)_2]_n$ **5**.

We found that addition of pivalate complexes **1–5** leads to an increase in the overall rate of MMA polymerization at 60 °C initiated by BP [Figure 1(*a*)]. Note that the solubility of compounds **1–4** in organic solvents is higher than that of compound **5**.



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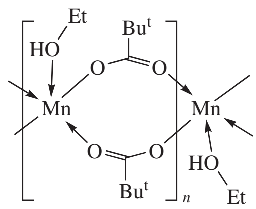

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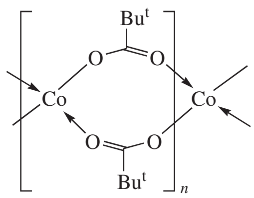

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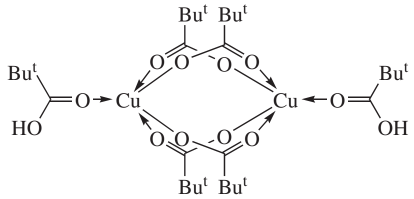

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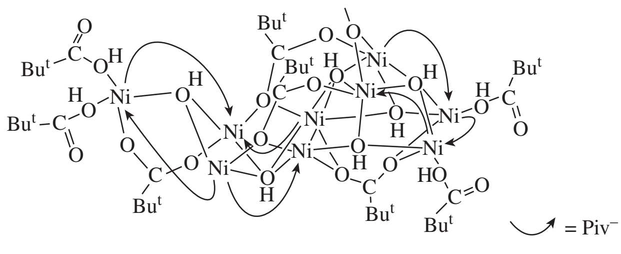

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[†] Methyl methacrylate (Fluka) was twice distilled under reduced pressure (bp 48 °C, 140 Torr). BP and AIBN were recrystallized three times from ethanol and dried at room temperature in a vacuum. Pivalate metal complexes **1–5** were synthesized and purified as described previously.[6–9] The purity of substances was controlled by $^{13}C\{^1H\}$ NMR spectroscopy.

For bulk polymerization, the reaction mixtures were placed in glass ampoules, the solution was degassed by freeze–pump–thaw cycles repeated three times to a residual pressure of 1.3 Pa, and the ampoules were sealed and placed in a thermostat at temperature of (30–70)±0.1 °C and kept until a specified degree of conversion was achieved. After the reaction, the ampoules were cooled and unsealed. The resulting polymer was dissolved in acetone and precipitated with a 10- to 15-fold amount of methanol. Polymers were purified from the remainder of the initiator and metal complex by three reprecipitations. The process kinetics at initial and high degrees of monomer transformation (glycerol was used as the sealing liquid) was studied by dilatometry.[10]

Molecular weight characteristics (weight-average M_w and number-average M_n molecular weights) were determined by gel penetration chromatography on a Waters GPC 2000 System chromatograph (eluent, THF; flow rate, 0.5 ml min^{-1}). Chromatographic columns were calibrated against polystyrene standards ($M_w/M_n \leq 1.2$).

The ^1H NMR spectra were recorded in $CDCl_3$ on a Bruker AM-300 spectrometer at 25 °C. TMS was used as an internal standard. The concentrations of syndio-, hetero- and isotactic fragments were determined using a published procedure.[11]

Dynamic thermogravimetric analysis was performed on a MOM Q-1000 derivatograph (heating rate, 5 K min^{-1}; sample mass, 100 mg) in air.

The physicochemical characteristics of used distilled solvents and glycerol were consistent with literature values.[12]

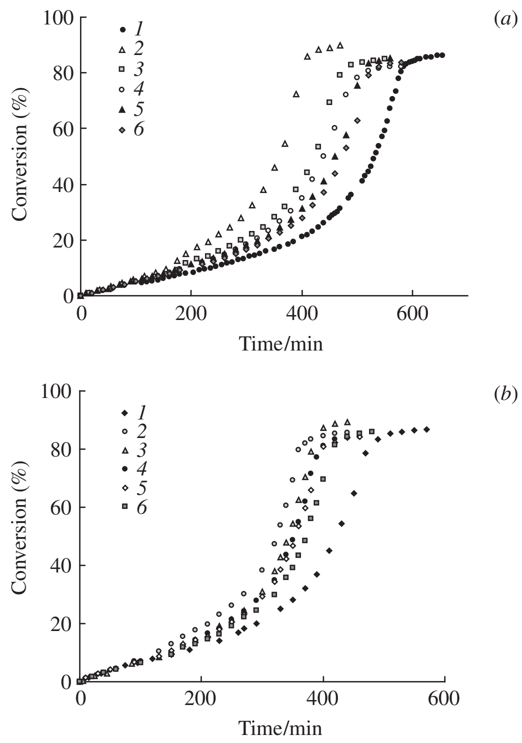

Figure 1 (*a*) Conversion *vs.* MMA polymerization time at 60 °C in the presence of (*1*) BP and (*2*) BP–**1**, (*3*) BP–**2**, (*4*) BP–**3**, (*5*) BP–**4**, (*6*) BP–**5**. [BP] = [**1**] = [**2**] = [**3**] = [**4**] = 1.0 mmol dm^{-3}, [**5**] = 0.1 mmol dm^{-3}. (*b*) Conversion *vs.* MMA polymerization time at 60 °C in the presence of (*1*) AIBN and (*2*) AIBN–**1**, (*3*) AIBN–**2**, (*4*) AIBN–**3**, (*5*) AIBN–**4**, (*6*) AIBN–**5**. [AIBN] = [**1**] = [**2**] = [**3**] = [**4**] = 1.0 mmol dm^{-3}, [**5**] = 0.1 mmol dm^{-3}.

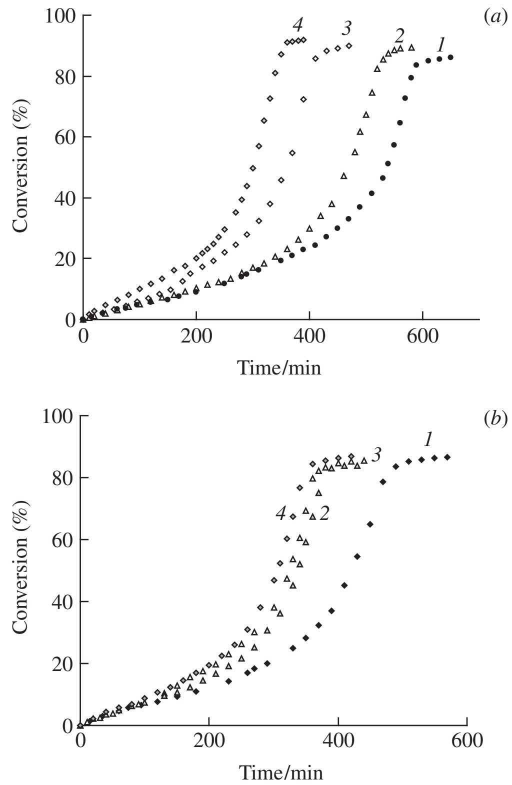

Figure 2 (*a*) Conversion *vs.* MMA polymerization time at 60 °C in the presence of (*1*) BP and BP–**1**. [BP] = 1.0 mmol dm^{-1}, [**1**] = (*2*) 0.1, (*3*) 1.0 and (*4*) 10.0 mmol dm^{-3}. (*b*) Conversion *vs.* MMA polymerization time at 60 °C in the presence of (*1*) AIBN and AIBN–**1**. [AIBN] = 1.0 mmol dm^{-3}, [**1**] = (*2*) 0.5, (*3*) 1.0 and (*4*) 10.0 mmol dm^{-3}.

The highest concentration of complex **5** in MMA at 25 °C is 0.5 mmol dm^{-3}. In this connection, the concentration of a cobalt complex **5** in the polymerization mixture is lower by one order of magnitude in comparison with that of compounds **1–4**.

When the component ratio in the BP–complex **1–4** initiating system is 1:1 (the concentration of each component, 1.0 mmol dm^{-3}), the influence of additives on the polymerization rate can be arranged in the order **1** > **2** > **3** > **4**. The polymerization rate in the presence of complex **5** (concentrations of **5** and BP are 0.1 and 1.0 mmol dm^{-3}, respectively) is approximately equal to the rate of process in the presence of complex **4** (the concentration of **4** is 1.0 mmol dm^{-3}).

Furthermore, the use of complexes **1–5** in the polymerization of MMA initiated by both AIBN and BP promotes a decrease in the maximum conversion time [Figure 1(*a*),(*b*)]. The influence of pivalate metal complexes on the kinetic curves of polymerization depends on the nature of the central ion. The most effective complex in polymerization initiated by both BP and AIBN is iron-containing complex **1**. Other additives are less active; therefore, a further investigation was carried out with the use of complex **1**.

The study of the dependence of the overall MMA polymerization rate on complex **1** concentration showed that an increase in the additive content to 10.0 mmol dm^{-3} in the initiation system leads to an increase in the rate of process initiated by both BP and AIBN (Figure 2). When the peroxide initiator is used, the increase in pivalate complex concentration affects the kinetics of the process to a greater extent than in the case of using the azo initiator.

At the synthesis temperature of 30 °C efficiency of complex **1** is higher than that at 60 °C because at 30 °C in the absence of metal complex additives used initiators (BP and AIBN) decompose very slowly.[12] The addition of compound **1** leads to a dramatic increase in the process rate (Figure 3). In the presence of BP–**1** and AIBN–**1** systems, the time of maximum conversion is 44 h, while in the absence of **1** it is ~98 or 86 h for BP or AIBN, respectively.

In the presence of BP–**1**, the increase in the initial rate of MMA polymerization (W_0) is observed for the temperature range 30–70 °C (Table 1). W_0 grows with the concentration of complex **1** (0.1–5.0 mmol dm^{-3}, the BP concentration is 1.0 mmol dm^{-3}).

The orders of reaction with respect to the initiator (BP) and additive (complex **1**) are 0.5 and 0.2, respectively, at the test temperatures. The effective activation energy (E_a) of MMA polymerization in the presence of complex **1** is 60±4 kJ mol^{-1}, while E_a of polymerization initiated by BP is 80±5 kJ mol^{-1}.

Polymers with different molecular weights can be obtained depending on temperature and metal complex (Table 2). The polydispersity coefficients on high monomer conversion are 3.5.

In the microstructure of PMMA obtained in the presence of complexes **1–5** and BP or AIBN, the content of syndiotactic structures in a polymer chain increased by ~6–9% in comparison

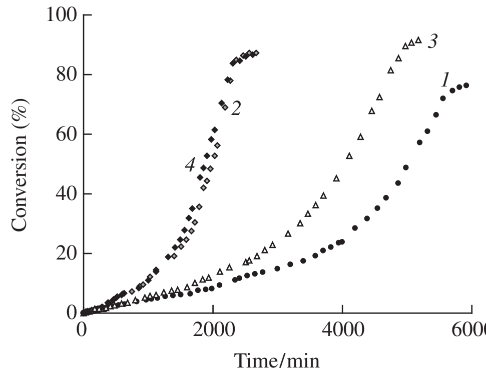

Figure 3 Conversion *vs.* MMA polymerization time at 30 °C in the presence of (*1*) BP, (*2*) BP–**1**, (*3*) AIBN and (*4*) AIBN–**1**. [BP] = [AIBN] = [**1**] = = 1.0 mmol dm^{-3}.

Table 1 Initial rates of MMA polymerization in the presence of BP and **1** at various temperatures (5–7% monomer conversion).

$T_{synthesis}$/°C	[**1**]/mmol dm^{-3}	[BP]/mmol dm^{-3}	W_0/mmol dm^{-3} min^{-1}
30	0.0	1.0	0.3
	0.1	1.0	0.6
	1.0	1.0	1.0
	5.0	1.0	1.4
50	0.0	1.0	2.5
	0.1	1.0	2.6
	1.0	1.0	4.3
	5.0	1.0	4.8
	1.0	0.5	3.3
	1.0	2.0	6.1
70	0.0	1.0	9.6
	0.1	1.0	10.1
	1.0	1.0	15.7
	5.0	1.0	19.0

Table 2 Dependence of the molecular weight of PMMA obtained in the presence of BP or AIBN and **1**–**5** on monomer conversion. [BP] = [AIBN] = [**1**] = [**2**] = [**3**] = [**4**] = 1.0 mmol dm^{-3}, [**5**] = 0.1 mmol dm^{-3}.

Complex	Initiator	Conversion (%)	M_w×10^{-3}	M_n×10^{-3}	M_w/M_n
		$T_{synthesis}$ = 60 °C			
–	BP	10	2340	1190	2.0
1		10	2280	950	2.4
		20	2530	980	2.6
		40	4600	1320	3.5
		60	5290	1560	3.4
		80	5450	1690	3.2
2		10	2190	950	2.3
3		10	2230	760	2.9
4		10	1960	830	2.4
5		10	2870	970	2.9
		$T_{synthesis}$ = 30 °C			
–	BP	10	6340	2380	2.7
1		10	4120	1990	2.1
1	AIBN	10	4340	2270	1.9

with a reference template of PMMA (Figure 4) and it does not depend on the structures of additives. The change of the stereochemical composition of macrochain evidences the influence of complexes **1–5** on the propagation stage.

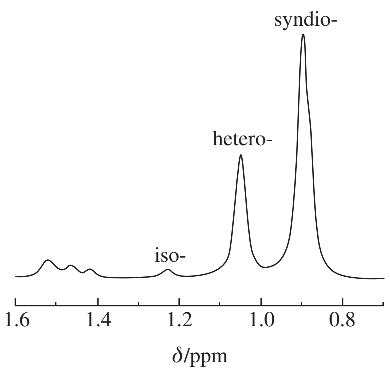

Figure 4 ^{1}H NMR spectra of PMMA obtained in the presence of BP. [BP] = 1.0 mmol dm^{-3}; synthesis temperature, 60 °C; the measurements were performed in $CDCl_3$ at 25 °C.

According to the results of dynamic thermogravimetric analysis, the onset temperature of degradation for PMMA synthesized in the presence of BP–**1** and AIBN–**1** rises by 20–35 °C in comparison with those for a reference template of PMMA obtained with a peroxide or azo initiator (224 and 232 °C, respectively).

Thus, the use of pivalate metal complexes in the radical polymerization of MMA accelerates the processes initiated by both BP and AIBN. The most effective pivalate complex is **1** with the central atom of iron, which influences the characteristics of PMMA (molecular weight, stereoregularity and thermal stability). When the polymerization of MMA is initiated by AIBN the additive has an influence not only upon the initiation stage (as in the case of BP) but also propagation due to the coordination of metal complexes with monomer and macroradical. It is most likely that MMA polymerization in the presence of pivalate complexes proceeds by a complex–radical mechanism.[13]

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