Brief Communications

Dicyclopentadienyl complexes of titanium, niobium, and tungsten in the controlled synthesis of poly(methyl methacrylate)

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Organometallic compounds Cp_2TiCl_2, $(EtC_5H_4)_2NbCl_2$, and $(Pr^iC_5H_4)_2WCl_2$ were assessed as additives that control polymer chain growth in the polymerization of methyl methacrylate. In the presence of compounds mentioned in amounts comparable with that of the initiator, a uniform process with no gel-effect occured and respective linear increase in the molecular weight of the polymer up to high degrees of the monomer conversion was observed.

Key words: controlled polymerization, methyl methacrylate, dicyclopentadienyl complexes of metals, mechanism of reversible inhibition (Stable Free Radical Polymerization (SFRP)), mechanism of change of metal valence (Atom Transfer Radical Polymerization (ATRP)).

Over the last years, organic compounds of transition metals attract the attention as effective regulators of polymer chain growth in the radical polymerization of a wide range of monomers.[1—4] The reason is that the use of organometallic compounds (OMC) allows regulation of the polymer chain growth not only through the mechanism of reversible inhibition (Stable Free Radical Polymerization (SFRP)) but through the mechanism of change of metal valence (Atom Transfer Radical Polymerization (ATRP)) as well,[1—4] in contrast to the known organic regulators of polymer chain growth, for example, nitroxyl radicals like 2,2,6,6-tetramethyl-1-piperidinyloxy[2,3] and their precursors.[1,5,6]

In the present work, it is proposed for the first time to use titanium, niobium, and tungsten cyclopentadienyl derivatives, in particular dicyclopentadienyltitanium dichloride Cp_2TiCl_2 (**1**), bis(ethylcyclopentadienyl)niobium dichloride $(EtC_5H_4)_2NbCl_2$ (**2**), and bis(isopropylcyclo-

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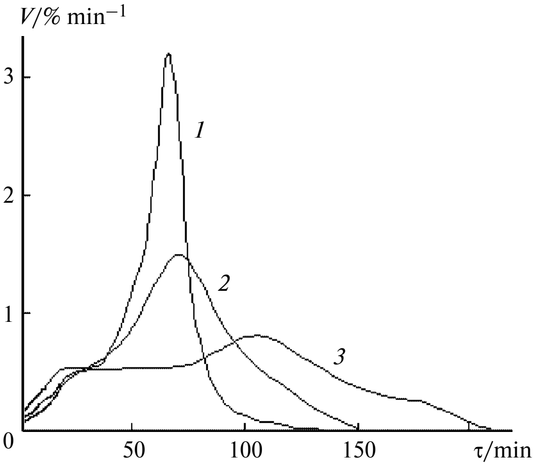


Fig. 1. Differential kinetic curves for the polymerization of methyl methacrylate in the absence of chain growth regulator (*1*) and in the presence of 0.05 (*2*) and 0.10 mol.% (*3*) of $(EtC_5H_4)_2NbCl_2$. The initiator is AIBN (0.1 mol.%), $T = 70$ °C.

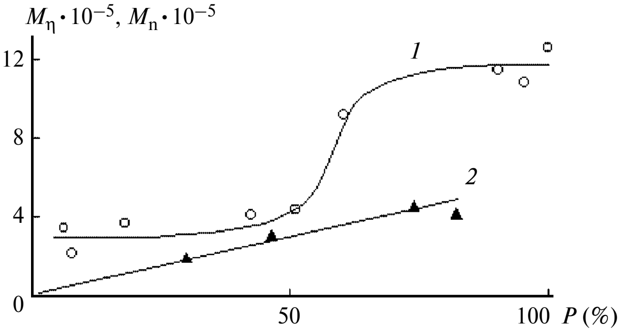


Fig. 2. Dependence of the viscosity-average (*1*) and number-average (*2*) molecular weight of poly(methyl methacrylate) on the degree of conversion in the polymerization with no chain growth regulator (*1*) and in the presence of 0.05 mol.% of $(EtC_5H_4)_2NbCl_2$ (*2*). The initiator is AIBN (0.1 mol.%), $T = 70$ °C.

pentadienyl)tungsten dichloride $(Pr^iC_5H_4)_2WCl_2$ (**3**) as chain growth regulators in the polymerization of methyl methacrylate (MMA).

Data on kinetics of the polymerization of MMA at 70 °C in the presence of compounds **1**—**3** suggest the suppression of the gel-effect for the equimolar OMC concentration with respect to the initiator concentration (AIBN, 0.1 mol.%). In Figure 1, typical differential kinetic curves are given for the polymerization of MMA using compound **2** as the chain growth regulator.

Table 1 lists the molecular-weight characteristics of poly(methyl methacrylate) synthesized in the presence of compounds **1**—**3**. As follows from the data given in Table 1 and Figure 2, the values of both M_η and M_n of the specimens obtained with the use of OMC linearly increase with the increase in the degree of MMA conversion. The molecular-weight distribution (MWD) curves of poly(methyl methacrylate) specimens have characteristic shifts to the higher mass region, though for greater extent of MMA conversion (60 % and more) an increase in the higher mass shoulder of the curve and respective increase in values of the polydispersity coefficient M_w/M_n takes place (see Table 1). Obviously, this is connected with occurrence of both the controlled synthesis and the usual radical polymerization with bimolecular chain termination in the system.[1,2]

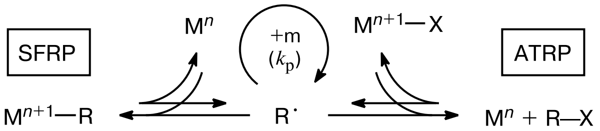
Table 1. Molecular-weight characteristics* of poly(methyl methacrylate) formed in the presence of AIBN and OMC

OMC	Conversion (%)	$M_\eta \cdot 10^{-3}$	$M_n \cdot 10^{-3}$	M_w/M_n
Cp_2TiCl_2	17.0	223	161	1.9
	89.0	554	370	2.9
$(EtC_5H_4)_2NbCl_2$	6.0	258	—	—
	25.0	303	—	—
	30.0	288	196	2.0
	47.0	519	309	2.7
	74.0	997	460	2.8
	82.5	915	418	2.7
$(Pr^iC_5H_4)_2WCl_2$	12.5	276	191	1.8
	34.3	386	277	2.1
	43.8	517	264	2.5
	85.2	1014	466	2.9

M_η — viscosity-average molecular weight, M_n — number-average molecular weight, * M_w — weight-average molecular weight.

By analogy with the literature data on the polymerization of vinyl monomers in the presence of OMC, it can be suggested that in the cases of compounds **1** and **3** the control of polymer chain growth follows the ATRP mechanism. Similar conversions for titanium compounds in radical reactions in nonmonomeric media are well studied and documented.[7,8] For molybdenum compounds, which are bis(isopropylcyclopentadienyl)tungsten dichloride analogs, the ATRP mechanism was convincingly proved in the polymerization of styrene.[4] In the cases of dicyclopentadienylniobium derivatives, with an unpaired electron on the metal atom,[9] the polymer chain growth follows more probably the SFRP mechanism. It is known[1—4] that a similar mechanism operates in the case of stable radicals, for example triphenylmethyl, nitroxyl and other radicals. The polymer chain growth in the presence of the OMC investigated, which follows SFRP or ATRP mechanisms, is depicted in Scheme 1.

Scheme 1



Thus, it was shown that dicyclopentadienyl titanium, niobium, and tungsten dichlorides are effective regulators of the polymer chain growth in the polymerization of methyl methacrylate under conditions of radical initialization.

Experimental

Commercial Cp_2TiCl_2, $(EtC_5H_4)_2NbCl_2$, and $(Pr^iC_5H_4)_2WCl_2$ (Aldrich) were used. MMA,[10] AIBN,[11] and organic solvents[12] were additionally purified according to the known procedures.

Definite amounts of OMC and the initiator were dissolved in the monomer and the synthesis of the polymer was carried out in evacuated tubes under a residual pressure of 1.3 Pa. The kinetics of polymerization of MMA was monitored by gravimetry and thermography.[13] The polymer was twice precipitated with hexane from its solution in chloroform. The molecular-weight characteristics of the polymer were determined by viscometry[14] and gel permeation chromatography using a set of five Styrogel columns with pore diameters of 10^5, $3 \cdot 10^4$, 10^4, 10^3, and 250 Å (Waters, USA). Tetrahydrofuran served as the eluent. An R-403 differential refractometer (Waters) was used as a detector. For the calibration, narrow-disperse polystyrene standards[15] were used.

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