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Diphenylbutadiene chromium tricarbonyl in radical polymerization of methylmethacrylate

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The synthesis of poly(methylmethacrylate) in the presence of diphenylbutadiene chromium tricarbonyl under radical initiation and temperature conditions that approach those in industry proceeds without autoacceleration and is characterized by a linear increase in the polymer molecular weight with conversion. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: diphenylbutadiene chromium tricarbonyl; methylmethacrylate; controlled radical polymerization

INTRODUCTION

The targeted regulation of kinetic parameters of vinyl monomer polymerization is an important problem in polymer chemistry. It allows the process to be conducted in a controlled mode, i.e. without autoacceleration and with the synthesis of polymers of the desired molecular weight characteristics.[1,2]

Stable radicals and their sources,[3,4] including organometallic additives,[5,6] have been actively employed recently in chain propagation regulators in radical initiation. In particular, α-methylstyrene chromium tricarbonyl and allylbenzene chromium tricarbonyl were reported to influence chain propagation in the polymerization of methylmethacrylate (MMA), styrene and butyl acrylate.[6,7] A regulating effect of the organochromium additives is caused by their action with both, the radicals derived from an initiator and the growing macroradicals to form relatively stable carbon-centered metal-containing radicals that influence the rate of polymerization and molecular weight of the polymers prepared.[5–8]

In this paper, the kinetic parameters of MMA polymerization and the molecular weight characteristics of the polymers obtained in the presence of diphenylbutadiene chromium tricarbonyl (DPC) are discussed. This organometallic additive is of interest to study since it contains two functions: a conjugated butadiene moiety, which is capable of generating a stable allyl-type radical resulting from the addition of a macroradical, and an arenechromium tricarbonyl group, which also provides stability for the radical formed due to delocalization of unpaired electrons.[5–7]

EXPERIMENTAL

DPC was prepared following a published procedure.[9] Its physical constants are in agreement with the literature data. MMA was purified by vacuum distillation before use. The initiator azo-isobutyronitrile (AIBN) was purified by recrystallization from methanol at 50 °C. Nitrosodurene, used as a spin trap, was synthesized according to published methods.[10,11] Di-*tert*-butylperoxytriphenylantimony (DPA) was prepared using a previously published procedure.[12]

Polymerization of MMA was carried out in degassed sealed tubes placed in a thermostatic (glycerol-water mixture) bath. The kinetic study of the polymerization was performed gravimetrically and using a thermometric technique.[13] Purification of the crude polymers from the residual monomer and additives was carried out by reprecipitation of the polymers from ethyl acetate solutions to argon-bubbled hexane. The DPC content in the purified polymers was determined spectrophotometrically by chromium elemental analyses.[14] The molecular weight characteristics of the polymers were estimated by gel permeation chromatography (GPC) in chloroform at 25 °C using a Knauer chromatograph (Germany) equipped with a Phenogel column Linear-2 (Phenomenex, USA) and a Knauer R-2301 differential

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refractometer. Electron spin resonance (ESR) spectra were recorded on an AE-4700 radiospectrometer (USSR) in special tubes. Ions of Mn^{2+} in the crystal cell of MgO were used as standards for magnetic field calibration.

RESULTS AND DISCUSSION

The kinetic study of the polymerization of MMA initiated by AIBN in the presence of DPC showed that the additive exerts a considerable influence on polymer chain propagation. In particular, it reduces both the rate of polymerization and autoacceleration (Fig. 1), the latter being shifted to the high conversion region. An almost complete disappearance of autoacceleration during polyMMA synthesis is observed at 1.5 mol% concentration of DPC. The kinetic data for MMA polymerization in the presence of DPC (Fig. 1a and b) obtained by the gravimetric method are consistent with those detected thermographically. The dependence of the conversion on reaction time is a pronounced S-shape for MMA polymerization with autoacceleration (Fig. 1b, curve 1) and is due to spontaneous uncontrolled growth of the molecular weight. On the contrary, in the presence of DPC this dependence is close to linear (Fig. 1b, curve 2), which is a feature of controlled radical polymerization.[1–3]

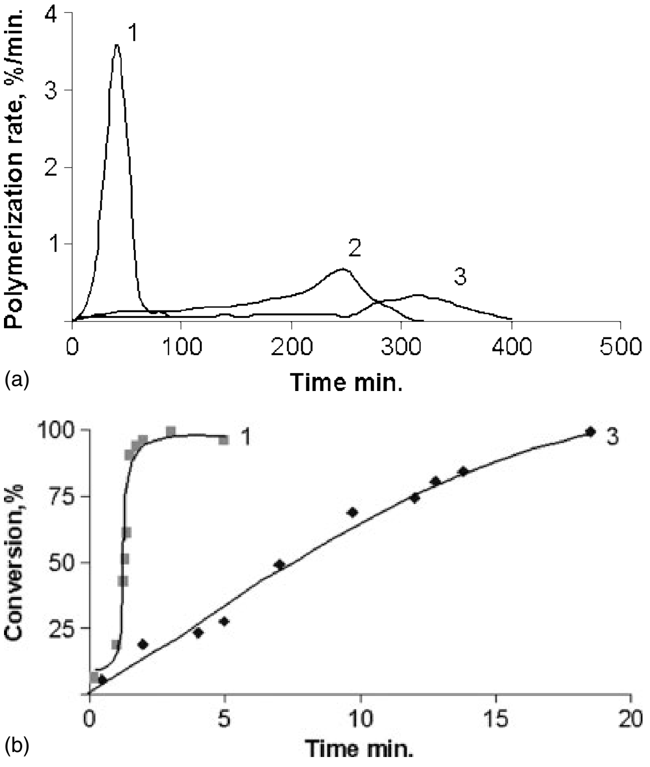
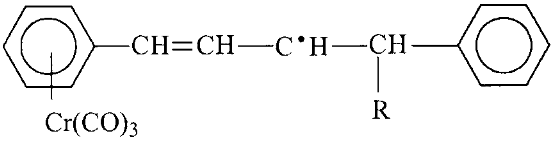


Figure 1. Differential (a) and integral (b) kinetic curves of MMA polymerization in the presence of AIBN (0.1 mol%) and DPC at 70 °C. [DPC]/mol%: (1) 0; (2) 1.0; (3) 1.5.

The difference in the kinetics of polymerization presented above is probably due to the participation of DPC in the chain growth stage. In order to prove this, the nature of an intermediate radical was studied by the ESR method. It was established that during reaction a sterically hindered carbon-centered radical was formed.



$[X^\bullet]$

This radical, fixed by the nitrosodurene spin trap and detected as a nitroxyl adduct (Fig. 2), is generated *in situ* during polymerization on interaction of DPC with the growing macroradical or the radical derived from the initiator according to Scheme 1.

This sterically hindered organic radical is stabilized by means of conjugation of an unpaired electron both with the

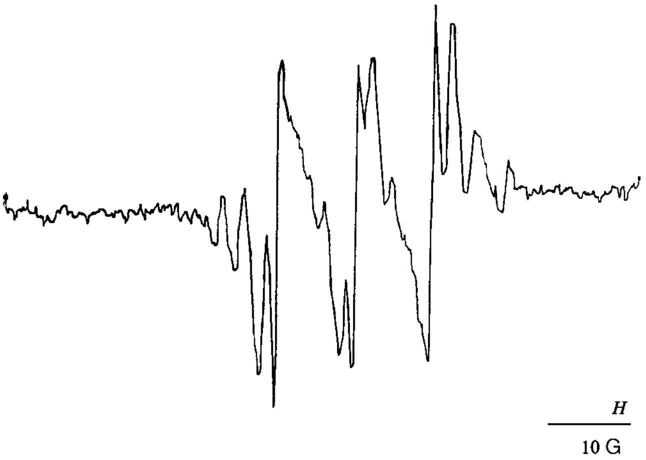
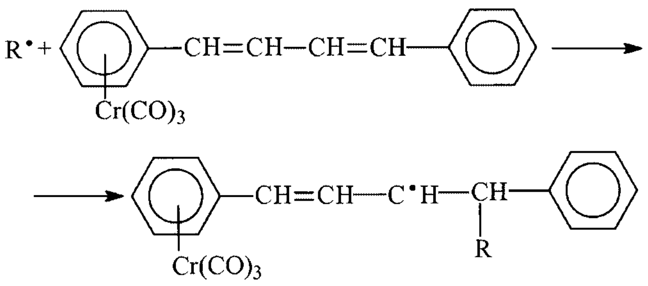
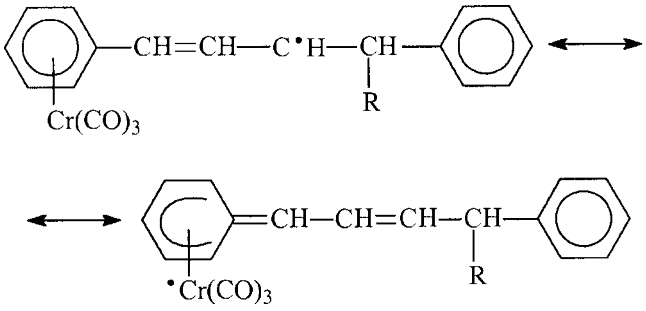


Figure 2. The ESR spectrum of the nitroxyl spin adduct detected in MMA polymerization and generated by means of DPC–DPA system. $T = 25\,^\circ C$. Spin-trap: nitrosodurene (0.2 mol% to MMA). DPC:DPA = 1 : 1 (mol). [DPC] = 0.01 mol mol^{-1} MMA. Solvent: benzene.



Scheme 1. R: a growing radical.



π-bond (so called π–e^- conjugation) and the arenechromium tricarbonyl moiety:

Stable radicals introduced to the polymerizing medium are known to be effective regulatory agents and exert a considerable influence both on the rate of polymerization and the molecular weight characteristics of the polymers obtained.[2,3] According to literature data, diphenylbutadiene (i.e. the organic derivative of DPC) easily gives the corresponding diphenylbutadienyl anions in the presence of *sec*-butyl lithium,[15] and is inert into the 1-cyano-1-methylethyl radical.[16] The data obtained by us indicate that addition of the bulky chromium tricarbonyl group to diphenylbutadiene results in the rearrangement of electron density of the molecule and provides the probability of radical reactions with this compound.

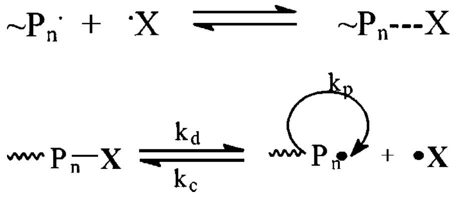
DPC used in various concentrations in the polymerization of MMA as a model polymer system is found not to copolymerize with MMA. Only traces of chromium (less than 0.5 mol%) were detected in the polymer samples prepared at low conversions (up to 10 wt%) in all cases, independent of initial DPC concentrations ranging from 1.5 to 20 mol% to MMA (Table 1). This shows that the MMA–DPC copolymer would not form. These data are in agreement with those of the copolymerization of styrene[15] and MMA[16] with diphenylbutadiene.

It was also found that DPC, similar to diphenylbutadiene,[16] does not polymerize in radical initiation. Furthermore, we failed to prepare polyDPC in ethyl acetate in the presence of AIBN at 70 °C after 50 h.

As indicated above, DPC influences the rate of MMA polymerization owing to its interaction with macroradicals to form stable radicals (Scheme 1). This suggests that the radicals prepared during the reaction effectively regulate the rate of polymerization and the molecular weights of the polymers obtained according to the reversible inhibition mechanism shown in Scheme 2 (top).

Table 1. Number-average molecular weight M_n of polyMMA samples isolated on the initial conversions (up to 10%) versus concentration of DPC in monomer mixture

Initial [DPC] in mixture (mol%)	0	1.5	10	15	20
$M_n \times 10^{-3}$	206	65	45	41	25
[Cr] in polymer (mol%)	0	0.05	0.21	0.26	0.40
M_w/M_n	1.9	2.2	1.8	1.7	1.6



Scheme 2. ~P_n: a growing radical; X: carbon-centered chromium-containing radical.

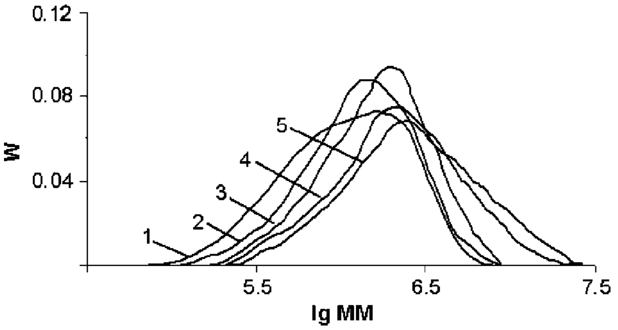


Figure 3. MWD of polyMMA samples synthesized at 70 °C in the presence of AIBN (0.1 mol%) and DPC (1.5 mol%) in various conversions. Conversion/%: (1) 5.3; (2) 27.5; (3) 49.1; (4) 74.0; (5) 83.9.

Figure 3 demonstrates the molecular weight distribution (MWD) curves of polyMMA samples prepared in the presence of DPC. They are gradually shifted towards high molecular weights with conversion. This indicates the realization of the mechanism of controlled chain growth in the polymerization of MMA in the presence of DPC (Scheme 2, bottom).

The analysis of number-average molecular weights M_n of the polymers obtained (Table 2, Fig. 4) leads to the following

Table 2. Molecular weight determinations of polyMMA synthesized in the presence of AIBN (0.1 mol%) and DPC versus polymer conversion; $T = 70$ °C

DPC (mol%)	Polymer conversion (wt%)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
0	90.3	661	1604	2.43
1.5	5.3	65	142	2.18
	19.0	76	159	2.09
	23.3	80	141	1.76
	27.5	92	164	1.78
	49.1	115	200	1.74
	68.7	173	357	2.06
	83.9	183	480	2.62

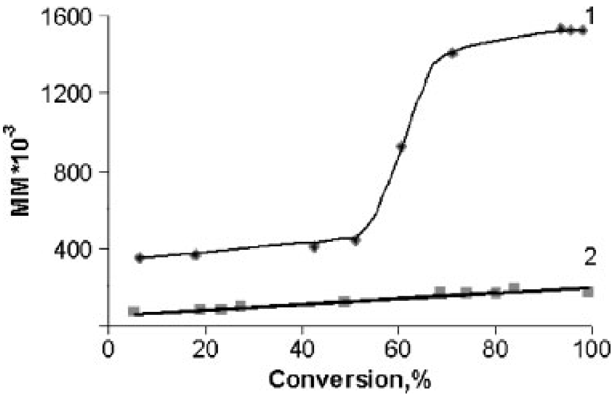


Figure 4. Molecular weight of polyMMA versus conversion: (1) viscosity-average molecular weight; (2) number-average molecular weight. Initiator: AIBN (0.1 mol%). $T = 70\,°\mathrm{C}$. [DPC]/mol%: (1) 0; (2) 1.5.

observations. Upon introduction of the organochromium compound at concentrations comparable to those of the initiator the M_n values increase linearly with polymer conversion. In the absence of the organometallic additive there is a spontaneous uncontrolled growth observed in the molecular weight during polymerization, as shown in Fig. 4 (curve 1).

A linear dependence of polymer molecular weight with conversion is known[2–4] to be one of the main features of 'living' polymerization. This means that, starting from low conversions owing to fragmentary chain growth, a permanent increase in polymer molecular weight takes place during the reaction. It should be noted that exactly the number-average molecular weight increases linearly with conversion.

It was also found that the action of DPC in the polymerization of MMA resulted in a considerable decrease in the molecular weight of the polymers (Tables 1 and 2). As seen for the polyMMA samples, the M_n values slow down with increasing additive concentration (from 1.5 to 20 mol%; Table 1) and the modes of the MWD curves gradually shift to the low molecular weight region (Fig. 5). This indicates that DPC plays a double role in the reaction: first, it controls chain propagation via a reversible inhibition mechanism (Scheme 2); second, it can participate in the chain transfer reaction,[17] simultaneously decreasing the molecular weights of the polymers formed.

It should be noted that, in high conversions, a broadening of the MWD curves (Fig. 3) and increasing polydispersity indexes (Table 2) are observed, which are not characteristic for controlled radical polymerization. This may be attributable to the fact that, together with the 'living' polymer, a non-growing polymer is also formed due to the bimolecular termination of growing chains. This process can proceed simultaneously with 'living' polymerization and is observed, for example, during controlled radical polymerization in the presence of triphenylmethyl[18] and some other sterically hindered carbon-centered radicals, including organometallic ones.[6,7]

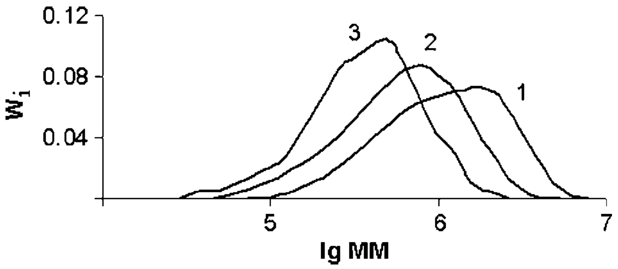


Figure 5. Molecular weight distribution of polyMMA samples synthesized at 70 °C in the presence of AIBN (0.1 mol%) and DPC. [DPC]/mol%: (1) 1.5; (2) 10.0; (3) 20.0.

Thus, the data obtained indicate that DPC is a novel, specific chain propagation regulator for the radical polymerization of MMA at temperatures approaching the optimal conditions of industrial synthesis of polymers.

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