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Radical Polymerisation of Methylacrylate Initiation by the Azidoadamantane / Copper Bromide System

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Summary

A new initiating system, azidoadamantane/CuBr, for the radical polymerisation of methylacrylate was found. Polymerisations occur as well at 50°C in toluene solution as in bulk at 70°C. A kinetic study seems to show a monomer consumption of first order in monomer concentration. However, despite a polydispersity index lower than 2, the value and the constancy of Mn during the whole polymerisation time gave an indication of a non controlled polymerisation. This is assumed to be due to the double role played by the azide function: strong complexing agent for copper ions and radical initiatior for the polymerisation, so that the presence of an additional ligand, i.e. bipyridine, is not necessary.

Introduction

For many years, we were involved in the use of pseudo-halide as reactive function in macromolecular synthesis, particularly azide function R-N_3. It was shown that the organic azide/Lewis acid (LA) combinations, in the presence or in the absence of an electron donor, initiated the cationic polymerisation of olefins. For instance, in the case of isobutene, the polymerisation is "living'' using a strong Lewis acid, i.,e, $TiCl_4$, BCl_3, and the presence of an electron donor is necessary [1] whereas with a weak LA ($AlEt_2Cl$), its presence is not needed [2]. Whatever the systems, the polymers presented an azide terminal end. In the mean time, it was shown that the azide group can be used as reactive function in polycondensation [3].

It was sometimes mentioned in the literature that organic isothiocyanates, the NCS function of which behaves as pseudohalide, could be also initiators for the radical polymerisation of methylacrylate (MA) and probably via an ATRP process [4]. It could be interesting to determine whether azides, which are also classified as pseudohalides, are initiators for the radical polymerization of MA. In this preliminary paper, the investigation of such a possibility is carried out and is dealing with the polymerisation of MA initiated by azidoadamantane (AZAD) / Copper Bromide (CuBr) in the presence and in the absence of a ligand, bipyridine (BP).

Experimental

MA was washed with a NaOH solution (1 M) and then several times with H_2O. It was dried over $CaCl_2$ and distilled. CuBr was washed first with acetic anhydride and then with MeOH. BP was used as received. A typical polymerization was carried out as follows. In a flask equipped with a magnetic stirrer, were introduced CuBr (0,1 g, 4,6 10^{-2} M), AZAD (0,12 g, 4,5 10^{-2} M), BP (0,11 g, 4,7 10^{-2} M) MA (5 ml, 3,7 M) and toluene (10 ml) and closed with a septum. The mixture was flushed with N_2 for 1 hour and placed in a regulated oil bath. At the end of the polymerization, the system was cooled and the reaction medium precipitated in MeOH. The polymer was dissolved in THF and passed through a silica gel column, precipitated again in MeOH and dried. Mn was determined by SEC with polystyrene standards.

Results and Discussion

Table 1 presents the results of a study of the polymerization yield with time. The comparison of the theoretical molar mass Mn_{th} with the experimental one Mn shows that the concentration of active centres was very low (at least 10^2 times lower with respect to the $[AZAD]_0$ introduced). On the other hand, the polydispersity index I_p = Mw/Mn is relatively low, corresponding to a relatively narrow molar mass distribution (1,27-1,49).

The Ln ($[M]_0/[M]$) versus polymerization time plot (Fig 1) gives a straight line indicating the possibility of a reaction of first order relatively to monomer concentration, most probably with a stationary state of active species concentration, and thus k_{app} can be determined: $k_{app} = 0,09\ hr^{-1} = 2.5\ 10^{-5}\ s^{-1}$.

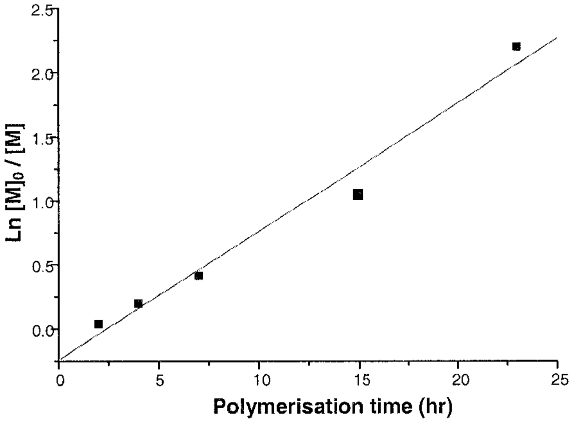


Fig 1. Ln ($[M]_0$ / [M]) versus polymerization time plot in the polymerisation of MA initiated by AZAD/CuBr/BP system in toluene solution ($[M]_0$ = initial monomer concentration, [M] being the monomer concentration at time t).

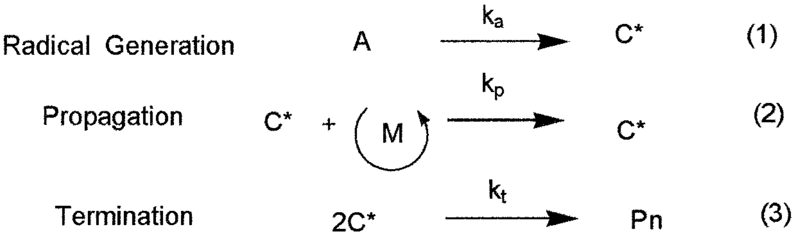
However, the fact that Mn remains constant with the conversion (during the whole time of polymerization, instead of a linear increase), shows a non controlled polymerization behavior. This point will be discussed later. It is easy to calculate an apparent efficiency of the initiating system assuming no transfer for run 5. This apparent efficiency is hardly higher than 2 %, which illustrates the low rate of radical production in this system.

Table 1 - Polymerization of MA initiated by AZAD/CuBr/BP in toluene solution at 50°C.

N°	t (hr)	Conversion (%)	$10^{-5}Mn_{SEC}$ ($g.mol^{-1}$)	I_p=Mw/Mn
1	2	4	2,1	1,47
2	4	18	2,5	1,27
3	7	34	2,5	1,30
4	15	65	2,4	1,49
5	23	89	2,6	1,35

T = 50°C, [MA] = 3,7M, [AZAD] = 4,5 10^{-2}M, [BP] = 4,7 10^{-2}M, [CuBr] = 4,6 10^{-2}M.

The uncontrolled polymerization follows the classical radical process (scheme I, transfer not indicated) :



Scheme I : Standard polymerization process where C* is the active centre including as well the first generated radicals as the growing chains and Pn is the dead polymer.

From the relation (2), the rate of polymerization is :

$$R_p = - d[M] / dt = k_p [C^*] [M]$$

$$Ln ([M_0] / [M]) = k_{app} t = k_p [C^*].t$$

$$[C^*] = k_{app} / k_p$$

where [C*] is the concentration of the active centers.

The k_p value of MA is to be estimated. A k_p expression { $10^{7,2}$ exp (-17,3 / RT)} has been found for n-butylacrylate which corresponds to a value of k_p = 2,5 10^4 M^{-1} s^{-1} at 50°C from reference [5]. The question is to know to what extent this value can be used for the polymerization of MA in the same situation. Indeed, a k_p expression of 2,4 10^6 exp (-22,3 / RT) can be found for methylmethacrylate and of 3,4 10^6 exp (-23,3 / RT) for n-butylmethacrylate [8]. These two values which are close from each other support the assumption made here that n-butylacrylate and methylacrylate have similar k_p values. Thus, [C*] can be roughly estimated, [C*] = 10^{-9} M, which is much lower than $[AZAD]_0$.

It was assumed that the uncontrolled polymerization came from the behaviour of azide function with respect to copper atom. This latter can give a very strong complex (even shifting out the ligand BP). Thus, the interest of the presence of the ligand, i. e. BP, was questionable. To elucidate this point, a series of polymerizations was carried out in bulk at 70°C as presented in table 2.

Experiments 6, 7, 8 are standard polymerizations which show that thermal polymerization, AZAD alone or CuBr alone cannot initiate the MA polymerization in our experimental conditions. On the other hand, MA polymerization occurred with the AZAD/CuBr combination and thus the presence of the ligand, i.e BP, is not essential. This is an indication of the possible double role played by the azide : radical source and complexing agent.

Table 2 - Polymerisation in bulk of MA initiated by AZAD/CuBr at 70°C.

N°	[AZAD] (M)	[CuBr] (M)	t (hr)	Conversion (%)	$10^{-5}Mn_{SEC}$ (g.mol^{-1})	$Ip=M_w/M_n$
6	0	0	6	0	-	-
7	0,22	0	6	0	-	-
8	0	0,22	6	0	-	-
9	0,22	0,22	1	14	2,4	1,5
10	0,22	0,22	1,5	18	1,9	1,7
11	0,22	0,22	2	23	1,9	1,6
12	0,22	0,22	4	56	1,6	1,8
13	0,22	0,22	6	63	2,1	1,6

[MA] = 11.12 M

Again, the linear regression of Ln ($[M]_0/[M]$) against polymerization time (not shown) , with $k_{app} = 0{,}165\ hr^{-1} = 4.6\ 10^{-5}\ s^{-1}$, can be interpreted as showing a quasi-stationary state of active center concentration and a kinetic of first order in monomer concentration. [C*] can be estimated through the calculation mentioned above : $[C^*] = 10^{-9}$ M, using $k_p = 3.7\ 10^4\ M^{-1}\ S^{-1}$ calculated from the expression given by ref. [5]. It is worth noting that the constancy of Mn (1,6-2,4 10^{5} g/mol) indicates again an uncontrolled polymerization.

For the sake of comparison, extracting the data obtained by Matyjazewski et al [6] in the polymerization in bulk of MA initiated by methyl-2-bromopropionate/dinonylbipyridine/CuBr at 90°C, [C*] can be evaluated with $k_{app} = 1\ 10^{-4}\ s^{-1}$ and with $k_p = 5{,}45\ 10^{4}\ M^{-1}\ S^{-1}$ determined also from the expression given by ref. [5]; Thus, $[C^*] = 1{,}8\ 10^{-9}$ M. It can be surprising that the active species concentration is lower when the initiator (AZAD) and the CuBr concentrations have been both increased by a factor of 5. This is probably due to the fact that here the active species concentration is governed by a kinetic effect (quasi stationary state of active species concentration), and to the fact that termination rate is favored by an increase of temperature. It can be estimated that in first approximation that azidoadamantane and methyl-2-bromopropionate induced similar values of [C*]. This similarity is probably fortuitous since for the former the active species concentration is resulting from a kinetic effect, while for the latter it results from an equilibrium between dormant and active species.

The high values of Mn and the polydispersity index I_p near to 1,5 as well in toluene solution as in bulk show a termination reaction occurring mostly by recombination of the growing chains [7].

From these results some informations can be pointed out : Azide function can be used as initiator for MA radical polymerization and also as a very strong complexing agent for copper atom so that the polymerization is not controlled. The assumption of a strong complex between azide and copper atom is supported by the existence of stable complexes such as $[HB(3,5(CF_3)_2PZ)_3]CuAZAD$ (PZ=Pyrazolyl) mentioned in the literature [9] where the copper atom is coordinated to the terminal nitrogen atom of the AZAD ligand. However, since the polymerization is apparently not controlled, there is no equilibrium between the complex and and the constituents.

An another explanation of the polydispersity index lower than two is to assume that polymerization initiation occurs via a new process such as a 1,3 dipolar cycloaddition leading to the corresponding triazoline adduct giving a diradical which can initiate the polymerization of MA. It is worth noticing that a bifunctional initiator can give polymers with polydispersity index in the 1.5 range. However in this case, a kinetic analysis which is not going to be described in details here can easily show that the polymerization degree cannot be constant throughout the whole reaction, taking into account the usual behavior of the monomer used in this study.

It is presently difficult to assert the structure of the radical initiator due to the high molar mass of the collected polymer: adamantyl radical or radical formed through a triazoline intermediate. Work is continuing to determine which one of these two explanations can account for these observations, and to investigate the fate of the azide group.

Whatsoever, our work shows that using the organic azide-copper bromide mixture, which constitutes a completely new initiating system of radical polymerization, a complexing agent of copper ions is not needed, and this fact can be considered as an interesting aspect of this system. This polymerization process apparently dominated by termination by recombination can also constitute an aspect of high synthetic value.

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