Synthesis of aminotelechelic polymers with the redox system $TiCl_3/NH_2OH$ in hydrochloric aqueous phase:
2. Polymerization of methylmethacrylate. Relation functionality/molecular weight/yield

Brigitte Serre, Serge Rubio, Joseph Sledz and François Schué
Laboratoire de Chimie Macromoléculaire, Université des Sciences et Techniques du Languedoc, 34060 *Montpellier, Cedex, France*

and Gilbert Chapelet-Letourneux
Centre de Recherche ELF, 69360 *Saint-Symphorien d'Ozon, France*

(*Received* 17 *March* 1980)

Aminotelechelic poly(methylmethacrylates) of which number average molecular weight $\bar{M}_n$ is less than 7×10^3 are synthesized with the redox system $TiCl_3/NH_2OH$ in hydrochloric aqueous phase. Functionality, molecular weight and yield are discussed on the basis of initiation, propagation and termination reactions. These considerations justify the influence of various factors such as the addition time of the $TiCl_3$ solution, the molar ratio $MMA/TiCl_3$ and the nature of the reducing ions. The evolution of molecular weights determined by g.p.c. confirms the interpretation of the results.

INTRODUCTION

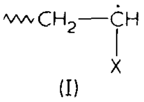
According to some studies[1-4] concerning the polymerization of methylmethacrylate (MMA) initiated by the system Ti^{3+}/NH_2OH in aqueous phase, it appears that MMA polymerizes easily. High molecular weights are obtained, the lowest one (23 200) being reached for a molar ratio $MMA/NH_2OH = 71{:}1$. The termination reaction occurs mainly by addition of an amino radical $\cdot NH_2$:

$$H_2N{-}R_{n-1}{-}R\cdot + \cdot NH_2 \rightarrow H_2N{-}R{-}NH_2$$

No reference is made to termination reactions by coupling or disproportionation.

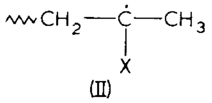
Therefore, before discussing our results, it is important to recall briefly the termination reactions involved during the radicalar polymerization of acrylic monomers.

In *Table 1* are given, according to Bamford and Tipper[5], the percentages of coupling at 25°C for different monomers. It appears that radicals giving 100% coupling have the structure (I); radicals giving both coupling and disproportionation reactions have the structure (II).



$\sim\!\sim CH_2{-}\dot{C}H(X)$

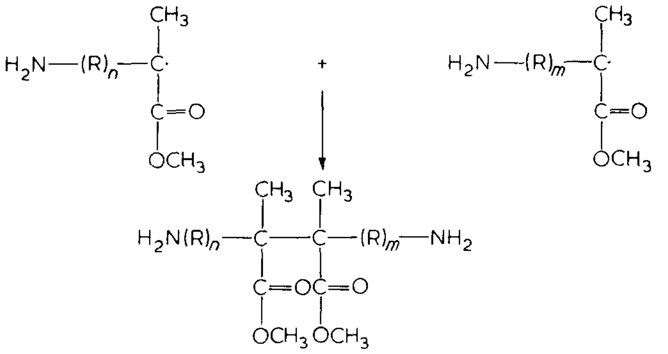
(I)



$\sim\!\sim CH_2{-}\dot{C}(X){-}CH_3$

(II)

The presence of a methyl group in the structure (II) introduces a steric hindrance being opposed to coupling.



But the possibility of hydrogen transfer must be considered to explain the disproportionation reaction.

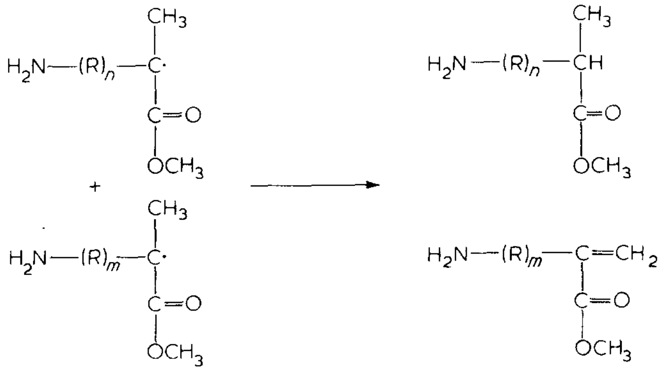


Table 1 Percentage coupling at 25°C for given acrylic monomers (according to Bamford and Tipper[5]). The percentage is given by the following equation:

$$100\,\frac{k_{tc}}{(k_{tc}+k_{td})}$$

where k_{tc} = termination rate constant by coupling and k_{td} = termination rate constant by disproportionation

Monomer	Percentage of coupling
Methylmethacrylate	32
Ethylmethacrylate	32
n-Butylmethacrylate	25
Methylacrylate	100
Ethylacrylate	100
Methacrylonitrile	35

From that study it appears that the disproportionation reaction is preponderant in the polymerization of MMA.

In order to synthesize some polymethylmethacrylates (PMMA) of low molecular weight ($10^3 \leqslant \bar{M}_n < 6.10^3$) by polymerizing MMA with the system Ti^{3+}/NH_2OH, we have used a molar ratio monomer/$TiCl_3$ = 10:1; an excess of hydrochloric hydroxylamine with respect to Ti^{3+}, so minimizing the following secondary reaction:

$$Ti^{3+} + \cdot NH_2 + H^+ \rightarrow Ti^{4+} + NH_3$$

— a hydrochloric aqueous solution (HCl, N) as polymerization solvent. The MMA concentration is 0.05 molar in order to get a homogeneous medium; the redox system exhibits good water solubility.

A homogeneous medium and an effective stirring assume the reproducibility of the experiments. But water is a non solvent of PMMA. The initiation of the polymerization occurs in solution. When the growing macromolecular chain reaches a given degree of polymerization, it precipitates in an active state. From then, two different states of the active macromolecular chains coexist: a mobile state in solution and a rigid state in the precipitate. Because of the low mobility of the precipitated macromolecular radical, the termination reactions by coupling are still more improbable and the propagation reaction is favoured and high molecular weight polymers are therefore obtained.

So, polymerizing MMA with the redox system Ti^{3+}/NH_2OH in aqueous phase, two types of products are synthesized. The g.p.c. spectra show a bimodal distribution. We will now examine the influence of various factors on the functionality, the molecular weight and the yield of the polymers.

EXPERIMENTAL

With the free radical polymerization being sensitive to the presence of oxygen, it is necessary to work under an inert atmosphere. For that reason each solution was previously saturated with nitrogen for approximately 30 min.

Monomer purification

Methylmethacrylate (Fluka, purum) was successively washed with a 10% KOH solution and distillated water. The organic phase was dried several times over calcium chloride, then distilled over calcium hydride under reduced pressure (boiling temperature ≃ 50°C under 15 mm of mercury). The purified methylmethacrylate was stored at −30°C.

Preparation of the redox solutions

Titanium trichloride ($TiCl_3CH$), (Stauffer Chemical Company) was handled in a gloves box under a nitrogen atmosphere. Aqueous hydrochloric acid solutions (HCl, N) were used ($[TiCl_3] = 1.3$ mol l^{-1}) because of their good stability in air and for easy handling ot $TiCl_3$. The same method was applied to preparation of VCl_3, $FdCl_2$ and $CoCl_2$. The necessary amount of hydroxylamine hydrochlorate (Prolabo) was weighed before each run and solubilized in an aqueous hydrochloric acid solution (HCl, N).

Polymerization and polymers characterization

(*1*) *Polymerization:* 400 ml of an aqueous hydrochloric solution (HCl, N) containing 6×10^{-3} mol of hydroxylamine hydrochlorate and 3×10^{-2} mol of methylmethacrylate are introduced in a one litre glass reactor. That mixture is homogeneous. The $TiCl_3$ solution (200 ml; 3×10^{-3} mol of $TiCl_3$) was added dropwise to the medium under vigorous magnetic stirring. The reducing solution was added over a period of one hour ($t_1 = 60$ min); the polymerization takes place at room temperature (temperature ≃ 20°C) and the solution was stirred for one more hour ($t_2 = 60$ min) after the complete addition of the reducing solution. At the contact of the oxidizing solution, the violet colouration of $TiCl_3$ disappears instantaneously. The non-water soluble polymer precipitates. At the end of the run, the polymer is separated by filtration and washed several times with distilled water; it is finally dried under vacuum (10^{-6} mm of mercury) and a white powder is obtained.

The polymer is then treated with an aqueous KOH solution under magnetic stirring in order to deliver the amino function. Lastly, the telechelic polymethylmethacrylate is washed with distilled water and dried under 10^{-6} mm of mercury.

(*2*) *Characterization: molecular weights:* (a) Gel permeation chromatography: G.p.c. measurements have been performed on a Waters Associates apparatus (ALC/GPC 201) at room temperature. The standardizing was carried out using polystyrenes of which $\bar{M}_n$ values were 800, 2200, 17500, 35000, 110000 and 233000 respectively. Four micro-styragel columns (100, 500, 10^3 and 10^4 Å) and tetrahydrofuran as solvent were utilized. (b) Tonometry: The tonometric $\bar{M}_n$ values have been determined on a Mechrolab type 301 apparatus, at 37°C in toluene as the solvent. The standardizing was realized using benzyl.

Microstructure: The tacticity of polymethylmethacrylate was determined by protonic nuclear magnetic resonance on a Varian HA 100 apparatus (solvent: O-dichlorobenzene; temperature: 120°C; reference: TMS).

Functionality: (1) nitrogen analysis: The nitrogen dosing was performed on a CARLO ERBA C-H-N-O apparatus. After weighing some aminotelechelic polymethylmethacrylate (less than one mg), the sample was introduced in a pyrolyzer by means of an automatic distributer. Then, the nitrogen oxides formed are reduced to nitrogen. The separation of nitrogen from water and carbon dioxide is realized by chromatography, each

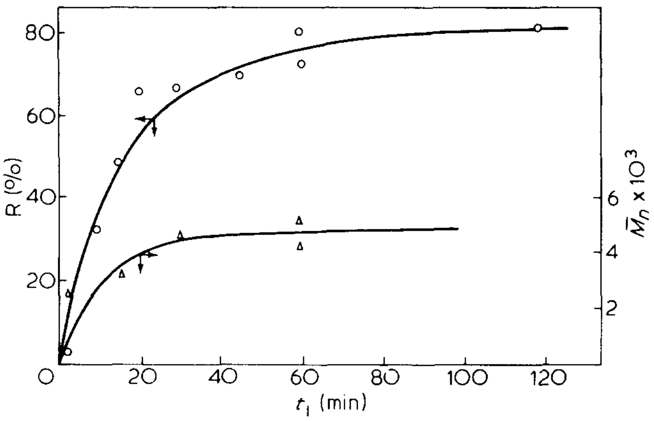


Figure 1 Variations of the polymer yield (R %) and the tonometric molecular weight $\bar{M}_n$ as a function of the addition time of the $TiCl_3$ solution ($MMA/TiCl_3$ = 10/1 $NH_2OH/TiCl_3$ = 10/1; temperature = 20°C; $TiCl_3 = 5 \times 10^{-3}$ mol l^{-1})

compound being detected through its thermal conductivity. A calculator integrates each signal and the results are given after standardizing the apparatus. (2) Polycondensation: The average functionality was determined knowing the percentage of nitrogen contained in the polymer and the tonometric number average molecular weight $\bar{M}_n$. Polycondensation is an easy method to verify that functionality.

For instance, the first step of the condensation between aminotelechelic polymethylmethacrylate and sebacic acid dichloride is given by the following reaction:

$$\begin{array}{c} m\,H_2N\text{-(-PMMA-)-}NH_2 + m\,ClCO\text{-(-}CH_2\text{-)}_8\text{-}COCl \\ \big\downarrow -2m\,HCl \\ H_2N\text{-((-PMMA-)-}NH\text{—}CO\text{-(-}CH_2\text{-)}_8\text{-}CO\text{-)}_m\text{-}Cl \end{array}$$

We carried out the polycondensation on an aminotelechelic polymethylmethacrylate of which the tonometric $\bar{M}_n$ value and the average functionality were 8300 and 1.1 respectively.

One g of polymer is dissolved in 20 ml of acetone and 10 ml of ethylene tetrachloride containing one ml of sebacic acid dichloride are slowly added, over 30 min under vigorous stirring, to this solution at room temperature. After four hours reaction, the solution is precipitated in ether and the polymer dried under vacuum (10^{-6} mm of mercury). Its tonometric $\bar{M}_n$ value is equal to 17500 justifying the experimental functionality of 1.1.

INFLUENCE OF THE ADDITION TIME OF THE $TiCl_3$ SOLUTION

In this study we have chosen an additional one hour stirring time after complete addition of the reducing solution. According to Kakurai *et al.*[3,4] the polymerization is complete after reaction time of 30 min.

Figure 1 shows the variations of the polymer yield (R in %) and of the number average molecular weight $\bar{M}_n$ (tonometric determination) as a function of the addition time (t_1) of the $TiCl_3$ solution. For a fast addition of the reducing solution, the polymer yield and the molecular weight, $\bar{M}_n$, have low values.

In order to explain these results we utilized the hypothesis of Pinazzi *et al.*[6], relative to the existence of a local overconcentration of amino radicals.

In this local overconcentration zone the large amount of initiator favours the initiation at the expense of the propagation reaction. Low molecular weight products are therefore obtained. Moreover, the high concentration of amino radicals leads to an enhanced possibility of termination by these radicals, increasing the average functionality (*Figure 2*):

$$H_2N \rightarrow R_m\cdot + \cdot NH_2 \rightarrow H_2N - R_m - NH_2$$

The combination of two $\cdot NH_2$ radicals leading to N_2H_4 must be also considered. That reaction seems probable because the dissociation energy of the nitrogen–nitrogen bond in N_2H_4 is important (60 kcal per mol). For a slow addition of the reducing solution, the polymer yield and the number average molecular weight increase. Indeed, in comparison to the case of a fast addition, the amino radical concentration is not high, favouring the propagation reaction and thus high molecular weight polymers are synthesized.

The g.p.c. chromatograms of several samples show a distribution which is bimodal (*Figure 3*). That distribution may be attributed to the coexistence of two different active states for the growing macromolecular chain: a mobile state in solution and a rigid state in the precipitate. Thus the high molecular weight polymers arise from the precipitated phase and the low molecular weight polymers from the solution. The curves (*Figure 3*) at fast addition time show a maximum in the low molecular weight field and a shoulder in the high molecular weight field; however by increasing addition times the results are inverted. These observations agree with the above considerations.

The tacticity determined on two PMMA samples obtained for low and high addition times of the reducing solution gives the following values: isotactic 6%; atactic 30%; syndiotactic 64%. A classical free-radical polymerization of MMA leads to polymer of identical tacticity.

In all the experiments an additional stirring time (t_2) of one hour after complete addition of the $TiCl_3$ solution was carried out in order to avoid an incomplete polymerization.

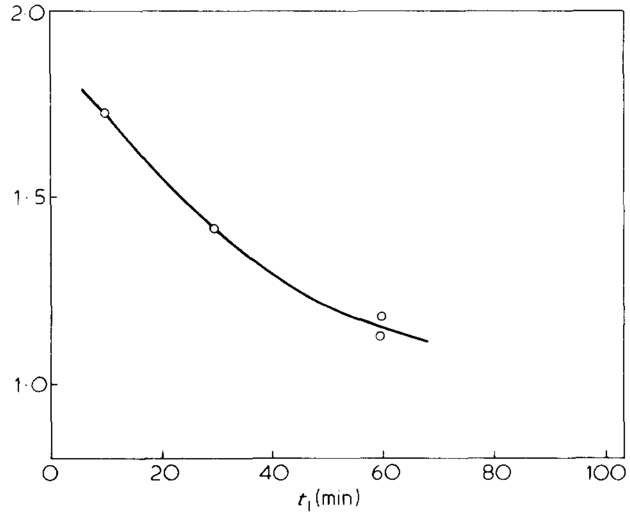


Figure 2 Variation of the functionality f with the addition time of the $TiCl_3$ solution

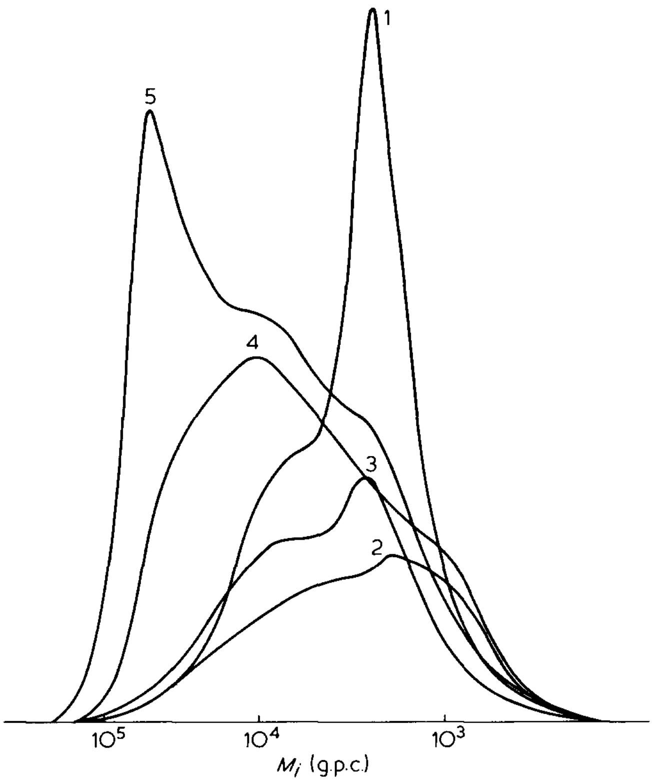


Figure 3 Variation of the molecular weights distribution as a function of the addition time of the $TiCl_3$ solution: (1) 2 min; (2) 15 min; (3) 45 min; (4) 60 min; (5) 120 min

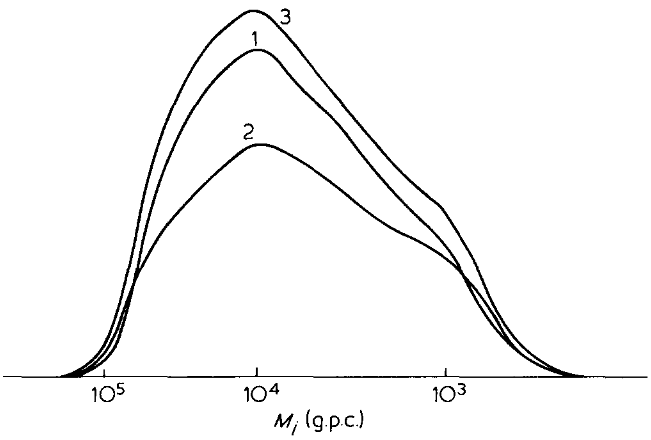


Figure 4 Variation of the molecular weights distribution as a function of the hydroxylamine concentration: $[NH_2OH]$ = (1) 2.5×10^{-1}; (2) 10^{-2}; (3) 4.9×10^{-2} mol l^{-1}

INFLUENCE OF THE HYDROXYLAMINE CONCENTRATION

The polymerization takes place only in presence of hydroxylamine, but in order to minimize any secondary reactions an excess of Ti^{3+} is necessary.

Varying the molar ratio $NH_2OH/TiCl_3$ from 1 to 10 (with $TiCl_3$ = constant = 5×10^{-3} mol l^{-1}), the polymer yield does not depend on the hydroxylamine concentration; for instance, the yield approaches 72% (weight) for a molar ratio $MMA/TiCl_3$ equal to 10 (at 20°C; $t_1 = 60$ min). The g.p.c. curves do not show any change in the molecular weight distributions (*Figure 4*). The average functionality is about 1.2.

In the next experiment we have kept the molar ratio $NH_2OH/TiCl_3$ equal to 2. That value is high enough to get, at any one time an excess of hydroxylamine with respect to $TiCl_3$, but also that the value is low enough in order to remove all the remaining hydroxylamine by washing the polymer. The last remark is important because the functionality has been determined by dosing nitrogen in the polymer (see Experimental section).

INFLUENCE OF THE MOLAR RATIO $MMA/TiCl_3$

Keeping the monomer amount constant, a decrease in the initiator ($TiCl_3$) concentration involves an increase in the polymer yield and of the number average molecular weight (*Figure 5*). Moreover, the g.p.c. curves show a developing of the high molecular weights at the expense of the low molecular weights by varying the ratio from 0.5 to 20 (*Figure 6*). Simultaneously the functionality decreases (*Figure 7*).

The following explanation is proposed: a low ratio corresponds to an important initiator concentration. Therefore the initiation and the termination reactions with the amino radical are favoured; a high ratio corresponds to a reduction of amino radicals in the medium, favouring the propagation step.

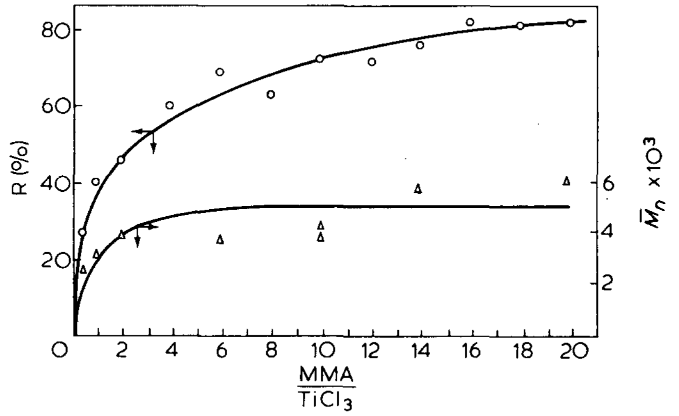


Figure 5 Variations of the polymer yield (*R* %) and the tonometric molecular weight $\bar{M}_n$ as a function of the molar ratio $MMA/TiCl_3$ ($[MMA] = 5 \times 10^{-2}$ mol l^{-1}; $NH_2OH/TiCl_3$ = 2:1; t_1 = 60 min; temperature = 20°C)

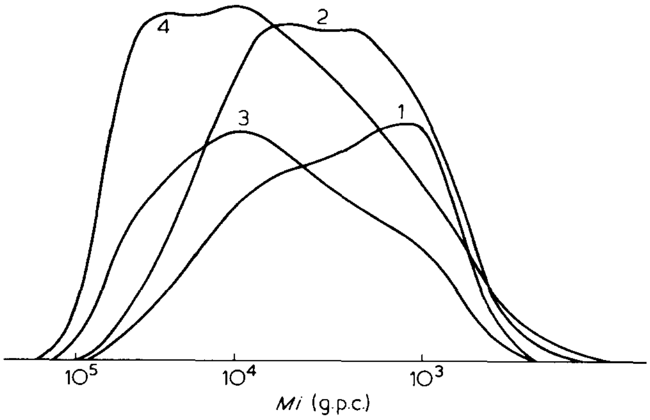


Figure 6 Variation of the molecular weights distribution as a function of the molar ratio $MMA/TiCl_3$ ($MMA/TiCl_3$ = (1) 0.5; (2) 2; (3) 10; (4) 20)

INFLUENCE OF THE TEMPERATURE

The polymer yield and the number average molecular weight increase with the temperature (*Figure 8*) and on the g.p.c. curves (*Figure 9*) the maximum is shifted to the high molecular weights. This result needs some more investigation to find a valuable explanation.

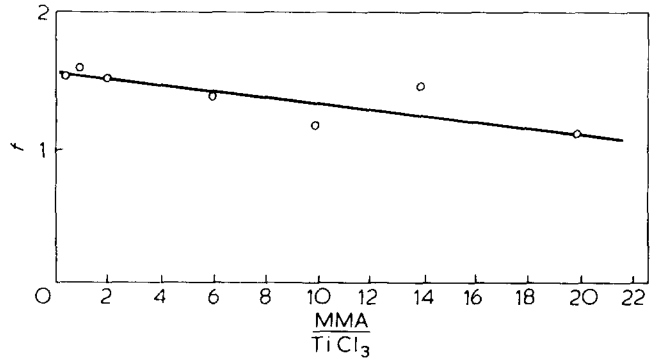


Figure 7 Variation of the functionality with the molar ratio MMA/TiCl$_3$

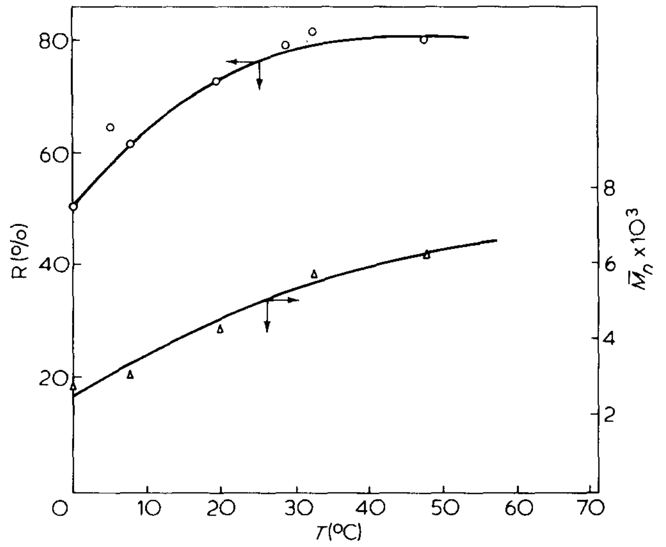


Figure 8 Variations of the polymer yield (R %) and the tonometric molecular weight $\overline{M}_n$ as a function of the temperature (MMA/TiCl$_3$ = 10: 1; NH$_2$OH/TiCl$_3$ = 2 : 1; [TiCl$_3$] = 5 x 10^{-3} mol l^{-1}; t_1 = 60 min)

INFLUENCE OF THE NATURE OF THE REDUCING ION

The following reducing ions were used: Ti^{3+}, V^{3+}, Fe^{2+} and Co^{2+}. In order to obtain telechelic polymers, the reducing solution is added rapidly (10 to 20 s) to the medium. In that way, the termination reaction with the amino radical is favoured.

PMMA appears immediately with TiCl$_3$, after some minutes in the case of VCl$_3$ and several days in the case of FeCl$_2$; CoCl$_2$ presents a low potential and after 2 h reaction the polymerization does not take place (*Table 2*).

With the fast addition of the reducing solution, VCl$_3$, good yields are obtained. Therefore it seemed worthwhile to study the influence of the molar ratio MMA/VCl$_3$ on the monomer conversion, the molecular weights and the functionality. The variations were similar to those observed for TiCl$_3$ (*Figure 10*). The propagation reaction is favoured with decreasing the concentration of initiator M^{n+}, consequently the polymer yield and the molecular weight increase. Finally when the ratio MMA/VCl$_3$ varies from 1 to 10, the functionality decreases from 1.3 to 1.1.

CONCLUSIONS

A particular interest has been borne to the polymerization of methylmethacrylate with the redox system TiCl$_3$/NH$_2$OH in acid aqueous phase. The homogeneity of the medium is initially conditioned by the solubility of the monomer and then by the low polymer solubility. The

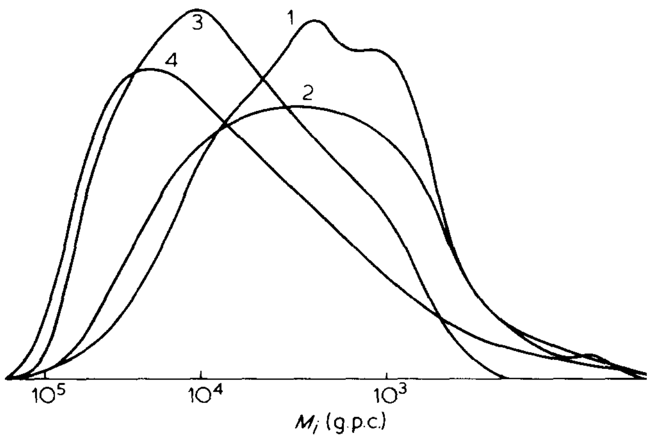


Figure 9 Variation of the molecular weights distribution as a function of the temperature: (1) 0°C; (2) 8°C; (3) 20°C; (4) 48°C

Table 2 Influence of the nature of the reducing ion M^{n+} on the polymer yield (R %) the molecular weights ($\overline{M}_n$, $\overline{M}_w$) and the functionality (f). Experimental conditions: NH$_2$OH/M^{n+} = 2 : 1; MMA/M^{n+} = 10 : 1; [MMA] = 5 x 10^{-2} mol l^{-1}; [M^{n+}] = 5 x 10^{-3} mol l^{-1}; [NH$_2$OH] = 10^{-2} mol l^{-1}; t_2 = 120 min, but for FeCl$_2$ (one week)

M^{n+}	Potential (volts)	R %	$\overline{M}_n$ (tonometry)	f	G.p.c.		
					$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
Ti^{3+}	−0.40	3	2500	1.15			
V^{3+}	−0.20 pH = 0	78	8300	1.10			
Fe^{2+}	+0.75 pH ⩽2	2			1800	8100	4.5
Co^{2+}	+1.83 pH = 0	0					

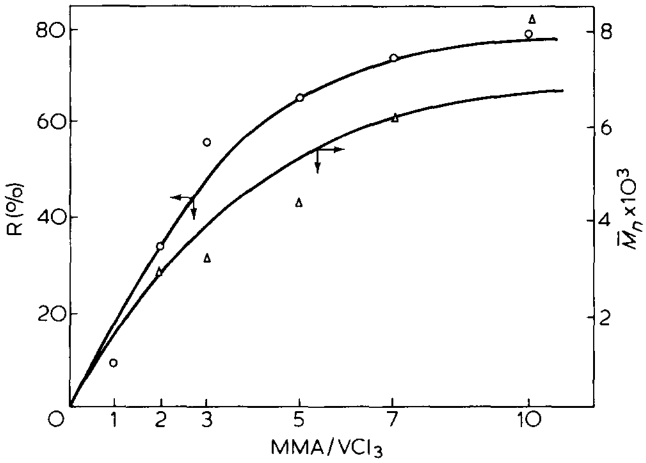


Figure 10 Variations of the polymers yield (R %) and the tonometric molecular weight $\bar{M}_n$ as a function of the molar ratio MMA/VCl$_3$ (NH$_2$OH/VCl$_3$ = 2:1; [MMA] = 5×10^{-2} mol l^{-1}; $t_1 \simeq 15$ s; t_2 = 120 min)

originality of the published papers is often limited to the synthesis of high polymers and to some kinetic aspects, disregarding any mechanism of the polymerization which also proceeds in the heterogeneous medium.

We have synthesized some low molecular weight aminotelechelic polymethylmethacrylates ($10^3 < \bar{M}_n < 7 \times 10^3$) under experimental conditions assuming that these conditions are reproducible. Functionality, molecular weight and yield are discussed on the basis of initiation, propagation and termination (by coupling, disproportionation and amino radical addition) reactions.

At a given time, the polymerization allows the coexistence of precipitated and soluble active macromolecular chains. In the precipitated state, the termination by coupling seems less probable, favouring the propagation; thus high molecular weight polymers are obtained but their average functionality is tending to 1. However, the termination by coupling is more probable in solution than in the precipitated state and low molecular weight polymers with high functionality are formed. The bimodal distribution observed by g.p.c. and the low functionality of the high molecular weight polymers and the high functionality of the low molecular weight polymers justify our hypothesis. A further fractionation of the polymer and the determination of the functionality of each fraction will undoubtedly support our conclusions.

A local amino radical overconcentration favours the initiation at the expense of the propagation and permits the termination with the radical itself therefore polymer yield and molecular weight will be low, but the functionality will tend to a maximum value.

Increasing the addition time and/or diluting the TiCl$_3$ solution, in other words suppressing the local overconcentration, average(s) the functionality and the molecular weight to low and high values respectively. The termination with the amino radical may be disregarded, the disproportionation being favourable towards the coupling reaction. Therefore, it seems evident that each increase in the amino radicals concentration leads to polymers of higher functionality, but lower molecular weight and yield.

Table 3 Influence of the temperature on the polymer yield (R %), the molecular weight ($\bar{M}_n$) and the functionality (f). Experimental conditions: MMA/TiCl$_3$ = 10:1; MMA = $5 \cdot 10^{-2}$ mol l^{-1}; NH$_2$OH/TiCl$_3$ = 2:1; NH$_2$OH = 10^{-2} mol l^{-1}; t_1 = 60 min; t_2 = 60 min and $\bar{M}_n$ expressed in equivalent of polystyrene

				G.p.c.		
t °C	R %	$\bar{M}_n$ tonometry	f	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
0	50	2800	1.35	1550	5500	3.5
20	72	4300	1.17	3300	12 750	3.8
48	79	6200	1.02	2850	14 400	5.0

These considerations seem to justify the influence of various factors like the addition time of the TiCl$_3$ solution, the molar ratio MMA/TiCl$_3$, etc, are supported by the evidence from the g.p.c. curves. However, the temperature effect still remains to be explained. The tacticity of polymethylmethacrylate synthesized through the redox system TiCl$_3$/NH$_2$OH (6% isotactic; 30% atactic; 64% syndiotactic) corresponds to a classical free radical polymer whose degree of polymerization increases by decreasing the temperature. However, we observed the reverse phenomenon which is also effective through photopolymerization and this result is evidence for the interference of another mechanistic aspect. However, at temperatures favouring the disproportionation termination, the functionality must decrease, and this is what we effectively observe (*Table 3*).

This work, discussed on the basis of the initiation, propagation and termination (by coupling, disproportionation and amino radical addition) reactions, presents a new face in comparison to the studies of Kakurai *et al.*[3,4]. Indeed, Kakurai *et al.* have synthesized high aminotelechelic polymers ($\bar{M}_n > 23 \times 10^3$) with correct functionality ($f = 1.78$ for $\bar{M}_n = 23\,200$); however they worked in a field favourable for secondary reactions (i.e. a molar excess of TiCl$_3$ with respect to NH$_2$OH); moreover, their results are only justified on the basis of termination with the amino radical.

It might also be interesting to consider the polymerization of MMA initiated with the amino radical issuing from N$_2$H$_4$ decomposition by irradiation, in order to compare the capacities of the three systems, N$_2$H$_4$ (+radiation), H$_2$O$_2$ (+radiation and TiCl$_3$/NH$_2$OH.

ACKNOWLEDGEMENTS

The authors would like to thank Jean-Pierre Ferrand for his technical assistance. This work was supported in full by ELF ERAP Grant No 2155.

REFERENCES

1 Rubio, S., Serre, B., Sledz, J., Schue, F. and Chapelet-Letourneux, G. *Acc. Chem. Res.* in press
2 Davis, P., Evans, M. G. and Higginson, W. C. E. *J. Chem. Soc.* 1951, 2563
3 Kakurai, T., Iwai, S. and Noguchi, T. *Kobunshi Kagaku* 1966, **23**, (252), 279
4 Kakurai, T., Sugata, T. and Noguchi, T. 1968 ibid **25**, (274), 120
5 Bamford, C. H. and Tipper, C. F. H. 'Free-radical polymerization' Elsevier, volume 14 A, (1976)
6 Pinazzi, C., Lenain, J. C., Brosse, J. C. and Legay, G. *Makromol. Chem.* 1976, **177**, 3139