JOURNAL OF APPLIED ELECTROCHEMISTRY 9 (1979) 343–349

Evaluation of factors affecting the radical electropolymerization of methylmethacrylate in the presence of HNO_3

G. PISTOIA, O. BAGNARELLI, M. MAIOCCO

Istituto di Chimica Fisica, Universitá di Roma, Rome, Italy

Received 18 May 1978

The electro-initiated polymerization of methylmethacrylate (MMA) in the presence of HNO_3 [1] has been re-investigated in more detail. It has been ascertained that the marked post-polymerization effect is not due to the presence of HNO_3. Indeed, the number of radicals still living at the end of the electrolysis is the most important factor. Oligomers soluble in CH_3OH were formed in this polymerization, their amount depending on both the current density and carbon anode porosity. The polymer tends to accumulate near the electrode forming a barrier which hinders the diffusion of the active species. The gel effect was characterized as a function of electrolysis time and solution viscosity. The $\bar{M}_w/\bar{M}_n$ ratio is equal to 1·9, indicating a low dispersity of the molecular weights. This result, together with the previous results of melt-flow index measurements, indicates that the polymer so obtained may be industrially processed.

1. Introduction

In earlier studies, methylmethacrylate (MMA) was polymerized in $TBANO_3$–MMA [2] and HNO_3–MMA [1] solutions through the anodic formation of nitrate radicals. The latter system proved to be more efficient, especially when the polymerization was carried out with the post-electrolysis technique. Indeed, conversions near to 100% were obtained in HNO_3–MMA when polymerization was allowed to continue after electrolysis [3]. It was suggested that there was a positive structural effect due to the presence of HNO_3 according to Kabanov's interpretation of the living radical polymerization occurring in the H_3PO_4–MMA system [3]. This hypothesis has been re-examined in this study, by investigating the effect of HNO_3 additions to the electrolysis solution and by comparing polymer and oligomers yields with $TBANO_3$ and HNO_3.

Other areas of uncertainty disclosed by the previous works concerned the diffusion and adsorption phenomena at the anode. Therefore, additional experiments have been carried out to shed some more light on these points. The gel effect has also been investigated in more detail as well as the formation of oligomers soluble in CH_3OH.

It had been ascertained that the polymer obtained in HNO_3–MMA solutions has very good flow characteristics [1]. This is a necessary condition for use as a powder processable by the injection moulding technique [4]. A polymer to be processed in this way has, however, to possess another characteristic, i.e. a low $\bar{M}_w/\bar{M}_n$ ratio. This quantity has now been measured and shown to be relatively low, thus confirming that the polymethylmethacrylate (PMMA) may be of industrial interest.

2. Experimental

The purification, storage and purity control of MMA have already been described [2]. 100% fuming HNO_3 was freed from N_2O_4 with a N_2 gas stream.

Graphite electrodes were obtained by machining National Spectroscopic Graphite Rods (AGKS grade L4312 type). Some electrodes were obtained by pelletizing at various pressures graphite

Printed in Great Britain.

powder on a Ag net. Teflon frames were then used to shield Ag edges. Unless otherwise stated, flat graphite electrodes (area 1 cm^2) were used.

All polymerizations were carried out with the post-electrolysis technique in divided cells under dry N_2. The anodic compartment contained 10 cm^3 of a 0·5 M HNO_3–MMA solution, whereas the cathodic compartment was filled with a $LiNO_3$ sat.–DMSO solution. Traps containing pyrogallol solutions and connected to the output of the cells ensured the absence of O_2 when N_2 flow was limited by the increased viscosity of the solutions.

The amounts of polymer existing at a given time at various electrode distances were determined by using a cell with five rubber-capped arms at the anodic compartment. At the end of the electrolysis, a known volume was drawn from one arm with a syringe. The complete procedure was repeated for each arm in order to avoid solution perturbations.

The procedure for polymer recovery has been reported elsewhere [1]. *I–V* curves were obtained galvanostatically by using $Ag/AgNO_3$ sat. as a reference electrode [5]. This was separated from the semi-microanode (graphite rod) by a Luggin capillary. When working with HNO_3–MMA solutions, it was necessary to add $TBAClO_4$ to limit *IR* losses. It had been previously ascertained that ClO_4^- is oxidized at a substantially higher potential than NO_3^- [2].

Viscosity-averaged molecular weights $\bar{M}_v$ were obtained in acetone at 25° C by using Schulz's relation [6]. $\bar{M}_w/\bar{M}_n$ ratio was determined by measuring the molecular weight of a sample ($\bar{M}_v = 180\,000$) with light-scattering and osmotic pressure methods.

3. Results and discussion

HNO_3 tends to form H-bonds with the ester groups of the monomer and of the polymer, as found with the H_3PO_4–MMA system [3]. According to Kabanov [3], this would result in the formation of stabilized long-lived radicals capable of continuous growth. The extraordinary long life of the radicals produced in the HNO_3–MMA system was tentatively attributed to such an effect. There were, however, weak points in this postulate, namely the time independence of the molecular weights and the low HNO_3 concentration present. Kabanov had found that molecular weights increased with time, due to the lack of termination, and used substantially higher acid-to-monomer ratios.

It was observed that the post-polymerization effect was also remarkable in the HNO_3–acrylonitrile system [7], in spite of the fact that structural effects are minimal in these conditions. Indeed, the growing macroradicals precipitate and are heavily occluded by polymer particles, so that H-bondings between the CN groups of the radicals and the hydrogen of HNO_3 are greatly reduced. The post-polymerization in this system was therefore attributed to the low termination rate typical of occluded radicals.

To ascertain if similar considerations could also apply to the HNO_3–MMA system, some additional experiments were carried out. Fig. 1 shows the effect of increasing HNO_3 concentration. In order to separate electrochemical from chemical phenomena, HNO_3 was added to the 0·5 M solutions at the end of the electrolyses. A six-fold increase in HNO_3 concentration (from 0·5–3·0 M) results in a 10% increase in conversion. Further HNO_3 additions even lead to a decrease. This first result seems to indicate that the structural effect of HNO_3, if any, is quite limited in the present system. The decreasing portion of the curve can be attributed to dilution which depresses the gel effect [1, 8].

A careful comparison between $TBANO_3$ and HNO_3 seemed necessary at this point to find out the reasons for their different behaviour.

A possible influence of mass transport was checked by measuring the specific conductivity of both solutions. The 0·5 M $TBANO_3$–MMA solution has a $\chi = 7{\cdot}6 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$, whereas this value for the 0·5 M HNO_3–MMA solution is $3{\cdot}2 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$. Therefore, mass transport

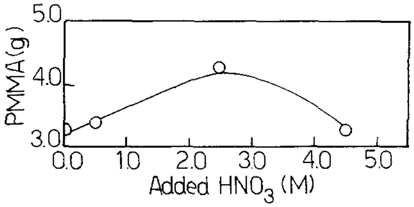

Fig. 1. Yield as a function of HNO_3 addition at the end of electrolysis. 5 mA, 45 min electrolysis, 16 h post-electrolysis.

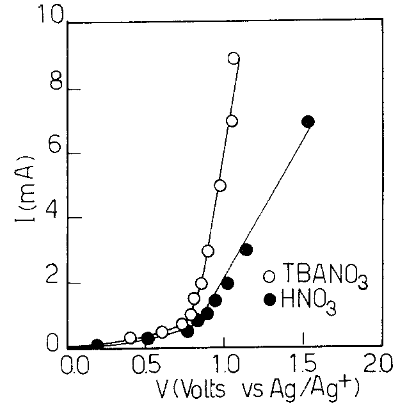

Fig. 2. Current–voltage curves for 0·5M TBANO$_3$ and 0·5 M HNO$_3$ (saturated with TBAClO$_4$) in MMA. Reference electrode, Ag/AgNO$_3$ sat.

Table 2. Effect of different anode materials on yield and molecular weight. 5 mA, 80 min electrolysis, 16 h post-electrolysis

Anode	*Yield (%)*	$\bar{M}_v \times 10^{-3}$
C	81·8	275
platinized Pt	42·5	295
Au	11·1	420
Pt	4·24	680
Al	0·86	290

plays a minor role in this type of polymerization and the difference between TBANO$_3$ and HNO$_3$ has to lie in purely electrodic phenomena.

Current–voltage curves (Fig. 2) show that the oxidation potential of NO_3^- is much the same in the two solutions. From these results it is clear that the difference between the two systems is not at the radical formation stage. Rather, there is thought to be a difference in the propagation step, perhaps due to differences in the double layer configurations created by the nitrate compounds. The adsorption of NO_3^- at the anode brings about the formation of layers of TBA$^+$ or H$^+$. The bulky TBA$^+$ cation is expected to give rise to a more complete barrier which will affect diffusion of radicals away from the anode. Possibly, $\dot{NO}_3$ radicals can still move through this barrier, but radicals which have already reacted with some monomers are bulky enough to be hindered in their diffusion. In these conditions, one may expect radical recombination near the electrode to occur more easily than radical growth by monomer addition. If this were so, low molecular weight compounds would be formed.

This was checked by determining the amount of solid products not precipitated by CH$_3$OH at the end of polymerization. Table 1 shows that the oligomer yield is about five times greater in TBANO$_3$–MMA. As a result, the amount of PMMA formed at the end of electrolysis is substantially less than that found in HNO$_3$–MMA. However, a low initial amount of polymer is not *per se* detrimental for obtaining a high final yield. With HNO$_3$–MMA [2], it was found that even a conversion of 0·22% at the end of an electrolysis could allow a high yield (around 80%) to be obtained. Therefore, it is the enhanced disappearance of small radicals through oligomer formation which lowers the yields in the TBANO$_3$–MMA system. Macroradical disappearance through termination can also be assumed to be more prevalent in this system. Indeed, due to the low conversion, the solution viscosity increases moderately, so that the diffusion controlled termination reactions have some importance [9].

The observed difference between TBANO$_3$ and HNO$_3$ confirms that adsorption is a phenomenon which plays a fundamental role in electroinitiated polymerizations [10, 11]. The effect of using anodes with different adsorbing properties

Table 1. Comparison of TBANO$_3$–MMA and HNO$_3$–MMA systems

System	*PMMA yield** (%)	*PMMA yield*† (%)	*Oligomers yield*‡ (%)
TBANO$_3$–MMA	1·3	25·5	14·6
HNO$_3$–MMA	10·7	89·5	3·1

* 25 mA, 2 h
† 25 mA, 2 h + 16 h post-electrolysis
‡ 10 mA, 1 h electrolysis, 4 h post-electrolysis.

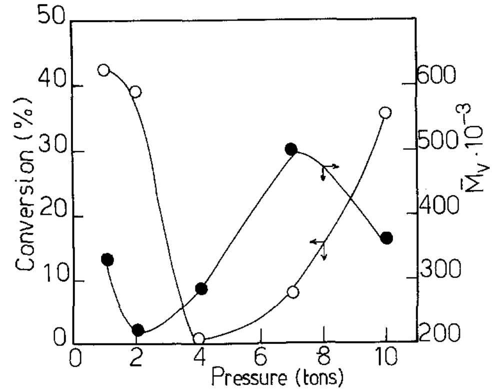

Fig. 3. Influence of C anode porosity on yield and molecular weight. 5 mA, 80 min electrolysis, 16 h post-electrolysis.

on the polymerization of MMA has already been described [1]. We have now reconsidered this effect in post-polymerization conditions (Table 2). Graphite is, as expected, superior to any other material by virtue of its greater adsorbing ability. Platinized Pt is also reasonably efficient, but limited conversions were obtained with the three poorly adsorbing anodes.

We attempted to correlate polymer conversions with the porosity of graphite anodes made by pelletizing C powder at different pressures. The results (Fig. 3) do not follow the expected trend, i.e. increasing yields with increasing porosity. Moreover, Fig. 4 shows that the amount of oligomer formed is a maximum at a pressure of 4 tons, which corresponds to the minimum polymer yield. This behaviour may be due to the pore dimensions at this pressure ensuring that the adsorbed radicals are brought into rapid contact, so favouring their recombination. Smaller and larger sizes of pore may offer the radicals more possibility of desorption.

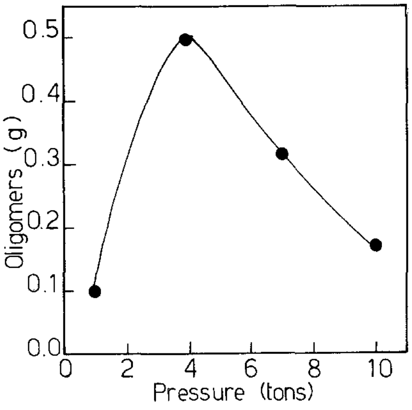

Fig. 4. Amount of oligomer as a function of pressure during anode preparation. 10 mA, 1 h electrolysis, 4 h post-electrolysis.

Table 3. Effect of stirring on yield. 5 mA, 80 min electrolysis, 16 h post-electrolysis (cylindrical anodes)

Conditions	*Yield (%)*
stirred solution*	88·7
unstirred solution	87·3
rotated electrode*	55·2

* 150 rev $\min^{-1}$

For a radical to propagate, it has to possess the ability to diffuse away from the anode. It was hypothesized [1] that the polymer tends to accumulate initially around the anode, thus forming a polymer barrier. This is expected to limit radical diffusion and polymer yield. We have attempted to sketch the 'polymerization profile' by determining the amount of polymer existing at a given moment at various distances from the anode. Fig. 5 shows that the polymer really tends to accumulate near the electrode, even when there was N_2 stirring of the solution. This substantiates the hypothesis of a polymer barrier to be overcome by the radicals.

A moderate mechanical stirring of the solution does not substantially alter the situation, whereas the effect of rotating the anode is negative (Table 3). The latter effect may be related to an enhanced radical recombination due to desorption of radicals and their concentration in layers near the electrode. It has to be noted that in previous

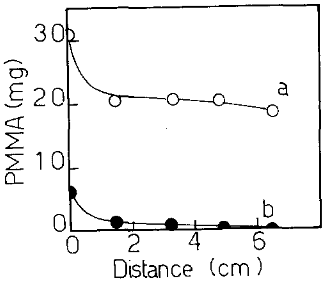

Fig. 5. Amount of polymer as a function of the distance from the anode. Curve a, 30 mA, 1 h, with N_2; curve b, 25 mA, 1 h, without N_2.

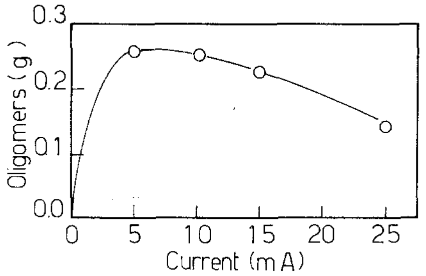

Fig. 6. Oligomer formation as a function of current. 1 h electrolysis, 4 h post-electrolysis.

experiments, moderate stirring of the solution had a negative effect on the yield [1]. This apparent discrepancy may stem from the different experimental conditions (25 mA, 120 min of electrolysis and 5 mA, 80 min of electrolysis for the first and the second experiment, respectively).

The oligomers yield versus current curve (Fig. 6) allows the clarification of the effect of current on polymer yields in post-polymerizations. It was ascertained that polymer conversion is near to 100% at 5 mA and decreases to about 70% 25 mA. In principle, this could be attributed to a greater amount of oligomers formed at higher currents. This can now be excluded and the former hypothesis, i.e. limited diffusion due to high solution viscosity, may be considered valid.

The importance of the amount of radicals and, therefore, of polymer formed during the electrolysis was directly evidenced by electrolysing HNO_3–MMA solutions for different times (Fig. 7). Short electrolysis periods produce low concentrations of macroradicals, so that the increase in viscosity and the gel effect are limited. Conversely, too long periods raise the viscosity to the point where diffusion of the monomer itself (especially through the polymer barrier surrounding the anode) becomes inefficient. Burnett [12] has compared this situation to that existing in the bulk polymerization of acrylonitrile. A polymer network surrounds the macroradicals and eventually reaches such a degree of entanglement as to prevent any reaction with the slowly diffusing monomer.

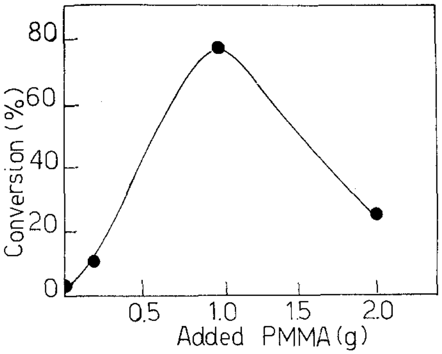

Fig. 8. Influence of pre-added PMMA on yield. 5 mA, 10 min electrolysis, 16 h post-electrolysis.

A further confirmation of the influence of viscosity on the yields was obtained by experiments in which the initial viscosity of the solutions was varied by additions of preformed PMMA (Fig. 8). A limited increase in viscosity is profitable for the onset of the gel effect. Beyond a certain value, limited diffusion and the polymer network reduce the capability of the radicals to add monomers. For the present system, conversions exceeding 10% at the end of the electrolysis produce negative effects.

The gel effect observed in conventional radical polymerizations of MMA is characterized by increasing molecular weights [8]. In our previous

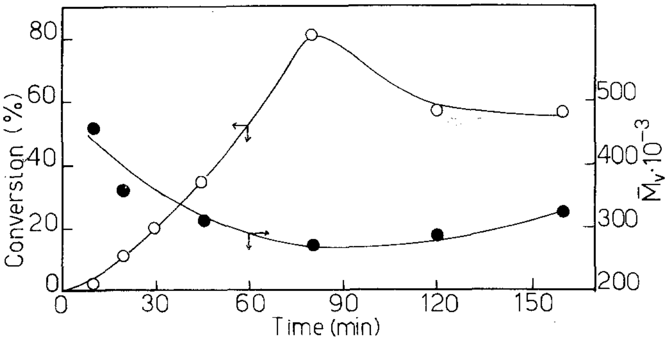

Fig. 7. Influence of electrolysis time on yield and molecular weight. 5 mA, 16 h post-electrolysis.

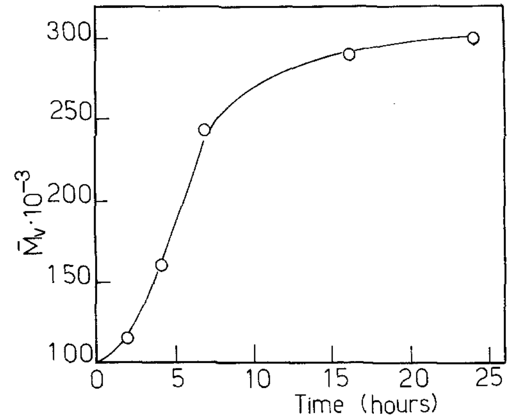

Fig. 9. Variation of molecular weight with post-electrolysis time. 5 mA, 2 h electrolysis.

experiments of post-polymerizations with the HNO_3–MMA system (1·5 mA, 2 h of electrolysis) [1], we found a constant $\bar{M}_v$ with time. By repeating rhe experiments at 5 mA, the expected sigmoidal trend of the $\bar{M}_v$–time curve was obtained (Fig. 9). The acceleration period, leading to a reduced R_t/R_p ratio, is soon established, this enabling the polymer to double its mean chain length in five hours. The constant $\bar{M}_v$ value at 1·5 mA had evidently been produced by the balance of opposing effects.

The effect of the C anode area and its shape on the polymerization were also investigated. Fig. 10 shows that the yields are affected only to a small extent by the electrode surface, i.e. the polymerization is relatively insensitive to current density variations. Anyway, the shape of this curve seems to be the result of two opposing effects, as better indicated by the variation of the molecular weights. These increase considerably for surfaces greater than 3·0 cm^2, possibly due to a reduced recombination rate of adsorbed radicals on a larger surface.

Table 4. Effect of anode shape on yield. 5 mA, 80 min electrolysis, 16 h post-electrolysis

*Anode**	*Yield (%)*
flat, multiple (4 pieces)	89·2
cylindrical	87·3
flat, pierced	81·7
flat, rough	81·6
flat	77·9
flat, channelled	68·9

* Electrodes have ‘smooth’ surfaces except where indicated.

The electrode shape influences polymer yield to a certain extent (Table 4). However, the effect of shape cannot be isolated from the complicated situation existing around the anode. For instance, in Table 4, cylindrical electrodes show a better performance than flat electrodes. However, at 25 mA the reverse is true, indicating that the final yields are the result of the balance of various factors.

Finally, the polydispersity ratio was determined. A sample of $\bar{M}_v = 180\,000$ has a $\bar{M}_w/\bar{M}_n$ value of 1·9. PMMA (Vedril) produced by Montedison (Milan, Italy) has a $\bar{M}_w/\bar{M}_n$ equal to 1·7–1·8. Therefore, the value found for our sample may be considered satisfactory. The melt-flow indices are similar to those of industrial PMMA [1], so it may be concluded that PMMA obtained by radical electropolymerization in HNO_3–MMA may be industrially processed with the injection moulding technique [4].

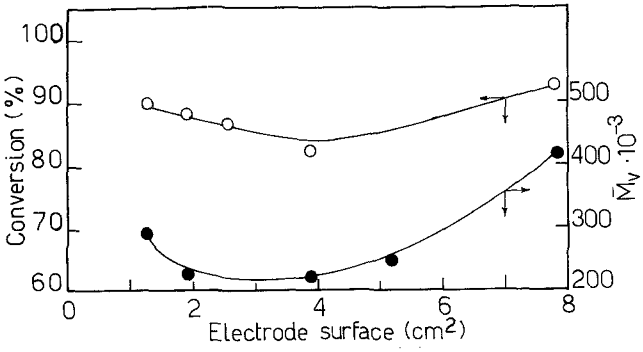

Fig. 10. Influence of anode surface area on yield and molecular weight. 5 mA, 80 min electrolysis, 16 h post-electrolysis. Cylindrical electrodes.

The optimum experimental conditions for simultaneously leading to high polymer yields and good $\bar{M}_v$ values are: flat C anode (rough surface), 25 mA, 2 h of electrolysis, about 16 hours of post-electrolysis. In these conditions, PMMA was obtained with 90% conversion and $\bar{M}_v = 100\,000$. Quite possibly, as indicated by previous results [1], a slightly lower current (around 20 mA) may further improve the yield, while $\bar{M}_v$ should remain well below 200 000.

Acknowledgement

Work carried out with the financial support of the Consiglio Nazionale delle Ricerche (CNR) of Italy.

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