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Anodic polymerization of methyl methacrylate in CH_3OH-H_2SO_4 solutions

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The electro-initiated polymerization of methyl methacrylate (MMA) in CH_3OH–H_2SO_4 solutions occurs at the anode through the oxidation of H_2SO_4 to radicals. Variations of the composition of the solution and of the current density result in the presence of maxima in the conversion curves. Only at low current densities do the kinetic curves have the characteristic shapes typical of the presence of the gel effect. A peculiar post-polymerization effect has been observed, in which conversions exhibit a minimum as a function of current. The values of the average molecular weights are strongly dependent on the current and are therefore controllable.

1. Introduction

The electro-initiated polymerization of MMA through a radical mechanism has been investigated by both cathodic and anodic processes. The former have mainly been studied in acid solutions and are now related to the cathodic decomposition of the MMA peroxide [1–3]; the formation of hydrogen radicals is no longer taken as responsible for such polymerization [4–6]. The anodic reaction has almost exclusively been concerned with the use of acetate compounds giving the Kolbe reaction; little information is available on the polymerization induced by radicals obtained from anions other than CH_3COO^-. The possibility of using anions such as PF_6^-, ClO_4^- or NO_3^- was briefly discussed by Nakahama *et al.* [7].

The formation of polymer at the anode when using sulphuric acid solutions has been reported with reference to acrylonitrile [8, 9]. In this work, polymethylmethacrylate (PMMA) was obtained in CH_3OH–H_2SO_4 solutions through the anodic oxidation of HSO_4^- on a platinum electrode. The features of this polymerization are compared with those of the cathodic polymerization of MMA in H_2O–H_2SO_4 solutions [3]. In the latter process, PMMA was obtained with fairly high yields and with molecular weights generally too high to make it interesting from an industrial point of view. This shortcoming is often encountered in the radical polymerization of MMA; in this work, the conditions which would enable PMMA with limited molecular weight to be obtained were also sought.

2. Experimental

2.1. *Materials*

MMA was purified by fractional distillation under reduced pressure in a stream of dry N_2 free from O_2. The presence of N_2 was seen to be a determining step for obtaining MMA absolutely free from peroxide; the absence of the latter was checked by both chemical and electrochemical tests (see below). Distilled MMA was stored in the dark at 4° C and was used within 24 h from distillation.

96% H_2SO_4 was used without further purification; its impurity level being too low for a secondary catalytic activity [3]. 100% H_2SO_4 was obtained from fuming H_2SO_4 (7% SO_3) after evacuation under N_2 of the excess SO_3 contained in it.

2.2. *Apparatus and procedure*

The CH_3OH–H_2SO_4–MMA solutions were prepared at room temperature under a N_2 atmosphere. No spontaneous polymerization was seen to occur for some days. As previously reported

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[3, 10], use of H_2O instead of CH_3OH may give rise to a considerable spontaneous formation of PMMA.

The polymerizations were made at 25° C in two-compartment cells having a low porosity glass disc in the middle. The anodic compartment was filled with 10 cc of a solution which, unless otherwise indicated, had the following composition: CH_3OH, 3·5 cc; H_2SO_4, 3·5 cc; MMA, 3·0 cc. A CH_3OH–H_2SO_4 solution was put in the cathodic compartment. Platinum cathodes and anodes (area, 1 cm^2) were used. Pb, Ni, Ag, Zr and Al were also tested as anodes; PMMA was obtained only with the latter, whereas the remarkable corrosion shown by the other materials prevented any appreciable formation of polymer.

For currents higher than 50 mA, the temperature increase due to heating effects was no longer negligible. The temperature of the bath was accordingly lowered so as to ensure that the current flow would only raise the solution temperature to 25° C. Purified N_2 was bubbled at constant rate for 20 min before the beginning of the electrolysis and was maintained throughout the polymerization.

Yields were determined by adding H_2O to the polymerizing solution; hydroquinone was also added to avoid undesirable post-polymerization phenomena. PMMA was subsequently washed to neutral pH, dissolved in acetone to free it from residual traces of the solution components, reprecipitated with H_2O, filtered and dried at 60° C. The % conversion was obtained from the ratio between the amount of polymer formed and the initial amount of monomer. Saturated calomel was used as a reference electrode for measuring the variation of the anode potential at fixed current.

The viscosity-averaged molecular weights $\bar{M}_v$ were obtained by determining the intrinsic viscosity of PMMA in acetone at 25° C and using the relation [11]:

$$[\eta] = 7{\cdot}5 \times 10^{-5}\,\bar{M}_v^{0{\cdot}70}\ (\mathrm{dl\,g^{-1}})$$

The PMMA obtained was completely soluble in acetone, thus indicating the absence of detectable amounts of cross-links.

3. Results and discussion

In order to avoid overlapping of different radical initiating reactions, the presence of the MMA peroxide, which was responsible for initiation in H_2O–H_2SO_4 [3], had to be carefully excluded. The Barnes test [12], based on the use of a saturated solution of KI, did not reveal the presence of the peroxide. A CH_3OH–H_2O–MMA solution was then electrolysed in the cathodic compartment at 25 mA: no polymer was recovered, thus confirming the result of the chemical test.

3.1. *Mechanism of initiation*

In the system under investigation, the radical formation may be attributed to the oxidation of H_2SO_4. Indeed, at the anode potentials used in this work (above 2 V versus SCE) CH_3OH is not adsorbed on the platinum electrode and does not give oxidation reactions [13]. On the contrary, H_2SO_4 is strongly adsorbed [14] in these conditions, thus further reducing the possibility of adsorption of CH_3OH. MMA may be adsorbed on platinum also in the presence of H_2SO_4 [8], but it does not show any disposition towards oxidation [15], as also demonstrated by its inability to give rise to a cationic polymerization. The anodic oxidation of HSO_4^- (which is the stable anion at high acid concentration [16]) probably gives rise to $HSO_4^{\bullet}$ radicals, as suggested by Hickling and Jones [16] for aqueous solutions of $(NH_4)_2SO_4$ or H_2SO_4. According to Tsvetkov, concentrated aqueous H_2SO_4 gives $SO_4^{\bullet -}$ at the anode thus initiating the radical polymerization of acrylonitrile [8]. The formation of $S_2O_8^{2-}$ by coupling of these radicals has been reported [8, 16, 17].

We attempted to ascertain the presence of $H_2S_2O_8$ by electrolysing both CH_3OH–H_2SO_4 and CH_3OH–H_2SO_4–MMA solutions. The results of the tests have left doubts concerning the presence of this compound. However, after a prolonged electrolysis of a CH_3OH–H_2SO_4 solution and subsequent addition of MMA, polymer was recovered. This indicates the formation of an active species, relatively stable in the above solution, coming from the mutual reaction of the radicals generated from H_2SO_4.

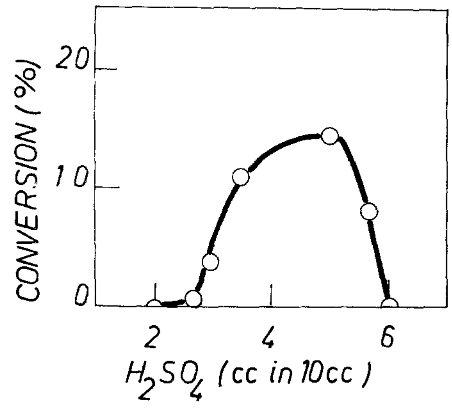

Fig. 1. Influence of the concentration of H_2SO_4 on the conversion. MMA, 3·0 cc; 96% H_2SO_4, as indicated; CH_3OH, the amount necessary to obtain 10·0 cc. Electrolyses carried out at 25 mA for 3 h.

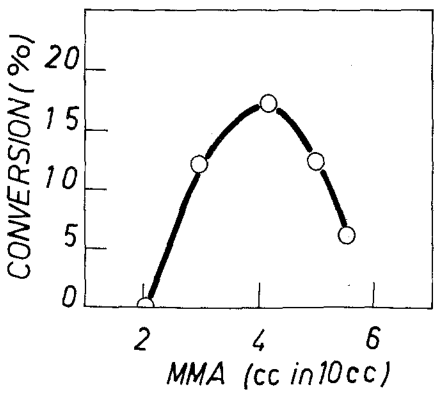

Fig. 2. Influence of the concentration of MMA on the conversion. 96% H_2SO_4, 3·5 cc; MMA, as indicated; CH_3OH, the amount necessary to obtain 10·0 cc. Electrolyses at 25 mA for 4 h.

*Table 1. Specific conductivities at 18°C of solutions of different compositions**

Vol. H_2SO_4 (cc)	*Vol.* CH_3OH (cc)	*Vol.* MMA (cc)	$\chi \times 10^{-3}$ (Ω^{-1} cm^{-1})
3·0	4·0	3·0	18·3
5·0	2·0	3·0	16·5
6·0	1·0	3·0	29·4
3·5	3·5	3·0	20·4
3·5	2·5	4·0	16·3
3·5	1·0	5·5	9·48

* Measured at 1 KHz between unplatinized platinum electrodes

3.2. *Influence of H_2SO_4 concentration*

As shown in Fig. 1, the concentration of 96% H_2SO_4 must be kept within a certain range to obtain polymer. At low acid concentrations, the efficiency of the reaction initiating the polymerization is too low. At high acid content (more than 5 cc, i.e. 9·4 M) the polymer formation decreases markedly and, finally, no polymer is recovered at a concentration of 11·3 M.

As suggested by Tsvetkov and Koval'chuk [8], who observed the same trend with the H_2O–H_2SO_4–acrylonitrile system, a change in the character of the electrode reaction is possible, resulting in the formation of inactive species. It is also known that in concentrated aqueous H_2SO_4 the anodic process produces $H_2S_2O_8$ within a certain concentration range and H_2SO_5 above this range.

Anyhow, the possibility that such a pattern would be related to the conductivity of the solutions was checked. From Table 1 it may be seen that the specific conductivity of the solution more concentrated in H_2SO_4 is quite high, thus excluding the possibility that the lack of conversion for this solution may be due to the presence of excess uncharged ion-pairs [16].

3.3. *Influence of MMA concentration*

The curve of Fig. 2 also shows that the concentration of MMA has to be limited to obtain PMMA with satisfactory yields. The decrease noticed at high MMA concentrations can be related to the rapid decrease in conductivity observed when the ratio MMA/CH_3OH is raised (Table 1). The number of uncharged ion-pairs incapable of migrating to the anode [16] becomes large enough to reduce considerably the efficiency of the radical formation and, therefore, of the polymerization reaction.

However, it has also to be noted that a high monomer concentration results in a large number of radicals adsorbed on the electrode [18], so that their recombination rate becomes significant. The same hypothesis was made for acrylamide radicals anodically obtained in the system CH_3COONa–acrylamide–H_2O–glycol [19].

3.4. *Influence of water addition*

Water addition is expected to have a dual effect on the polymerization: (a) a negative effect on the

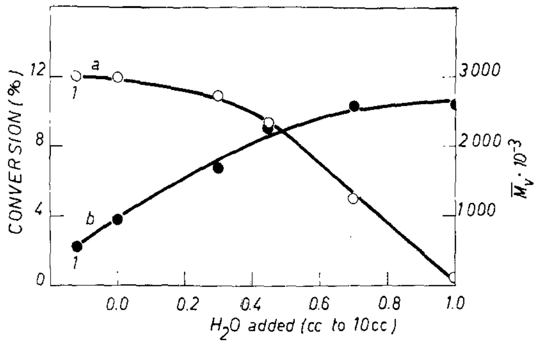

Fig. 3. Formation of PMMA (a) and molecular weights (b) as a function of H_2O added. Points 1 refer to 100% H_2SO_4. Electrolyses carried out at 25 mA for 4 h.

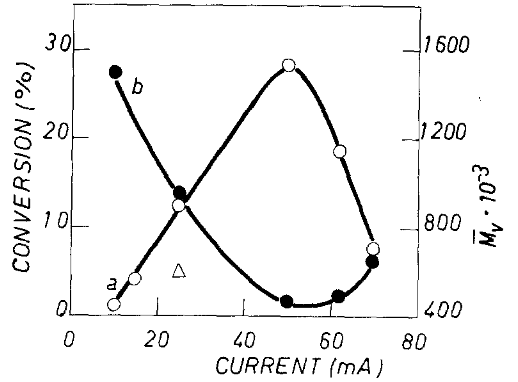

Fig. 4. Formation of PMMA (a) and molecular weights (b) as a function of current. Δ, $\bar{M}_v$ with 100% H_2SO_4. Electrolysis time, 4 h.

formation of radicals due to the concurrent anodic reaction producing O_2 and (b) a positive effect on the reactivity of the sulphuric radicals [20]. Fig. 3 shows that the first effect prevails, but only when a sufficient amount of water is added. At low water contents, the two effects tend to balance, this being also due to the limited extent of O_2 evolution in the presence of adsorbed H_2SO_4 and MMA.

The molecular weights increase markedly with water content due to the lower concentration of initiating radicals formed when the discharge of water also takes place at the anode. However, as will be pointed out later, other factors may contribute to the higher $\bar{M}_v$ values obtained in H_2O-containing solutions.

3.5. *Influence of the current*

Fig. 4 shows that above 50 mA a sharp decrease in conversion occurs. As will be later confirmed by the kinetic curves, at high currents the polymerization reaction has a rapid start followed by a premature stop. This cannot be explained by the onset of the 'gel effect' (Tromsdorff effect), frequently observed in the radical polymerization of MMA and accurately described by some authors [21–23]. Indeed, at the conversions observed (below 20% for currents higher than 60 mA), the extent of the gel effect may only positively affect the polymerization through a reduction of the termination reaction [21]. Only at high conversions (above 60%) can the system become so gelled that the addition of monomers to the growing macroradicals is hindered to the point where the propagation rate falls to low values.

The possible destruction of the sulphuric radicals due to an increase of the anode potential, was checked during a galvanostatic electrolysis at 25 mA for 20 h. It was observed that the potential increased by about 0·3 V within a few minutes (probably due to the adsorption phenomena) and then remained fairly constant with time. The presence of undesirable reactions is thus unlikely.

However, it has to be noted that, as the electrolysis goes on, the solution becomes more and more viscous. This is particularly so around the anode, because the polymer formation is mainly localized in the layers near the anode surface due to radicals' adsorption [18, 19]. Under these conditions, diffusion of active species (primary radicals and the products of their reactions with monomers) from the electrode towards the bulk of the solution becomes difficult.

Attempts to obtain some more information on the diffusion phenomena by mechanical stirring of the solution were thwarted by the rapid increase of the viscosity which prevents any efficient stirring. By bubbling N_2 the solution was stirred for relatively longer times, although less efficiently; also in this case, the increased viscosity limited the possibility of detecting a dependence of diffusion phenomena on the rate of gas bubbling.

The trend shown by the molecular weights as a function of the current seems to confirm the existence of concentration gradients for the active species. Below 50 mA, the $\bar{M}_v$ decrease as usually observed in polymerizations of this type, but above 50 mA they start to increase; this may again be connected with a lower number of initiating radicals in the bulk of the solution.

The molecular weights decrease in the range 10–50 mA much more sharply than those found with the cathodic polymerization of MMA [3]. This effect is obviously desirable, in that it allows a better control of the average chain length.

At 25 mA, a $\bar{M}_v$ value was also determined for a solution containing 100% H_2SO_4; the value is considerably lower than that obtained with 96% H_2SO_4 and confirms a pattern found throughout this work, i.e. lower $\bar{M}_v$ are obtained in anhydrous solutions.

3.6. *Conversion/time curves*

The kinetic curves of Fig. 5, obtained at various currents and with both 96 and 100% H_2SO_4, allow a better understanding of the features of this polymerization. As one could anticipate from the curve of Fig. 4, a high current density does not lead to high yields. Indeed, the polymerization process starts rapidly at 25 and 62 mA, as shown by the conversions after 1–2 h, but soon the propagation rate tends to zero and conversions lower than 30% are obtained. As stated before, the diffusion of the active species from the anode to the bulk of the solution may become rate-determining, this becoming more evident after about 8 h with the levelling off of the curves.

Comparison of the curves made at 25 mA with both 96 and 100% H_2SO_4 indicates that in the early stages of the polymerization the absence of water is beneficial. However, at later stages the small amount of water contained in 96% H_2SO_4 leads to slightly higher conversions. This may be explained by considering the positive effect of water on the efficiency of the sulphuric radicals [20]. Furthermore, the conductivity of the H_2O-containing solutions is slightly higher so that the efficiency of the reaction producing radicals should be a little increased for these solutions.

It may be noted that the curve obtained at 62 mA levels off at a conversion lower than that attained at 25 mA. This is not surprising if the assumption is made that at 62 mA the radicals produced at later stages cannot diffuse through the polymer surrounding the electrode.

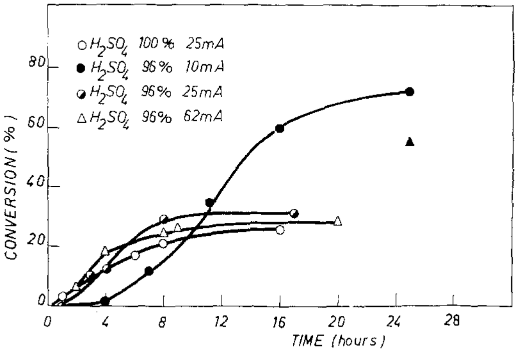

Fig. 5. Conversion/time curves at various currents. ▲, 100% H_2SO_4 (at 10 mA).

The curve obtained at 10 mA confirms that higher yields may be obtained when the rate of radicals' formation is limited. This curve has the typical shape observed when a noticeable gel effect takes place in solution. After an induction period, a long rising portion is visible in which the termination rate is greatly reduced [21]. After about 60% conversion, the propagation rate tends to decrease, i.e. the gel effect reduces markedly the possibility of residual monomers encountering the growing radicals buried in the polymer network.

According to the gel effect theory, the molecular weights should continuously increase as the termination rate is decreased [21, 22]. We have measured $\bar{M}_v$ for the curve made at 10 mA at various time intervals (4, 7, 16 and 25 h); the values were practically constant, the average $\bar{M}_v$ being $1{\cdot}56 \times 10^6$. This may be explained on the basis that, unlike conventional polymerizations in which the concentration of initiating radicals is constant, when current flows continuously through the solution the concentration of radicals increases with time (although with decreasing rate due to diffusion phenomena). The latter effect would lead to shorter chains as the electrolysis proceeds, as was indeed observed with the polymerization of ethyl acrylate in methanol solutions [24] in the absence of a gel effect. Evidently, in the present system the two opposite effects (gel effect and continuous radical formation) balance each other, so that almost constant $\bar{M}_v$ are obtained as a function of time.

The $\bar{M}_v$ of a solution containing 100% H_2SO_4, electrolysed at 10 mA for 25 h, was found to be $9{\cdot}8 \times 10^5$. With 96% H_2SO_4, $\bar{M}_v$ was $1{\cdot}6 \times 10^6$. This confirms that the presence of H_2O raises the molecular weights. The gel effect is indeed favoured in this case and this gives rise to higher rates and molecular weights.

On the basis of the kinetic features of the present system, it may be stated that the primary electrode reaction (radical formation) is only one of the factors determining the course of the polymerization. Other factors connected with the diffusion of monomer, polymer and active species formed at the anode play a very important role. Furthermore, adsorption phenomena may considerably influence the anode–solution interface and, therefore, the course of the polymerization.

Comparisons with the analogous kinetic curves for the polymerization of MMA in H_2O–H_2SO_4 solutions [3] show that in the present system the polymerization is slower. This may be connected with the fact that different active species are present in the two systems; furthermore, in the former, water favours the reactivity of the radicals formed at the cathode. Experiments in which H_2O was replaced by CH_3OH resulted in slower cathodic polymerizations; however, the cathodic process is still faster than the anodic one examined in this work.

3.7. *Post-polymerization effect*

A remarkable post-polymerization effect was reported by Palit for MMA in H_2O–MMA–CH_3COONa solutions [25]. However, it was also reported that the yields in a N_2 atmosphere were less than those found when residual air was present. This clearly indicates that in this system MMA peroxide is present and plays a major role in the polymerization.

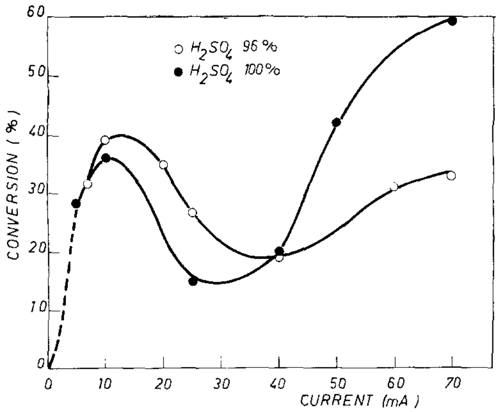

Fig. 6. Conversion with the post-polymerization effect as a function of current. 1 h of electrolysis followed by 15 h in the absence of current (under N_2).

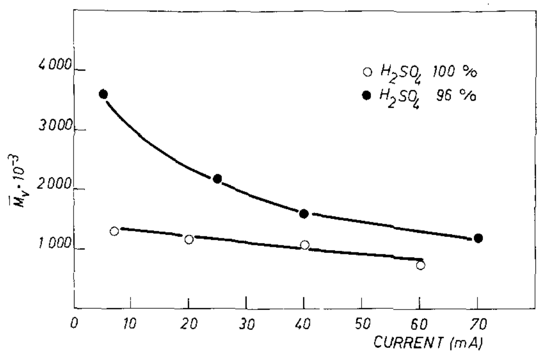

Fig. 7. Influence of the current on the molecular weights of PMMA obtained with the post-polymerization effect.

We have examined the existence of a post-polymerization effect at various current densities and in the absence of MMA peroxide. Fig. 6 refers to the conversions obtained when the indicated currents were passed for 1 h, and the systems were then left for 15 h under N_2 in the absence of current. The shapes of the curves are really surprising, especially as the number of radicals formed after 1 h of electrolysis increases as the current increases. Indeed, Fig. 5 shows that, after 1 h, conversions increase in the order: $10 < 25 < 62$ mA. Furthermore, the molecular weights (Fig. 7) continuously decrease with current and this confirms the presence of more radicals as the current is increased.

A more detailed investigation of this phenomenon is necessary. Meanwhile, the trend could possibly be attributed to variations of the ratio between the number of active species and their ability to diffuse away from the anode. The conversions obtained with this effect are fairly high. Furthermore, the yields increase with time: after 1 h of electrolysis at 10 mA, followed by 47 h in the absence of current, a conversion of 64% was obtained (it was 36% after 16 h).

The molecular weights obtained with the post-polymerization effect are higher than those found with continuous electrolyses, which is explained by the lower number of radicals generated in the first case. Lower values are again obtained with the anhydrous solutions, the differences being particularly marked at low currents.

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