# ELECTROCHEMICAL SYNTHESIS OF SYNDIOTACTIC POLY-METHYL METHACRYLATE IN TWO PHASIC MEDIA

**P.A.K. Nedungadi, Anil Gupta, S.K. Mukerji & K. Zutshi***

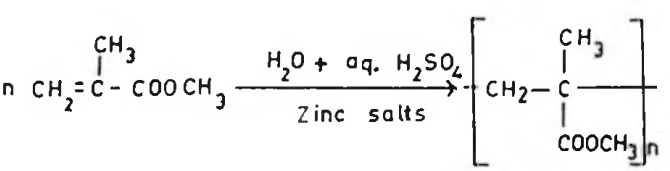
*Electro-organic Synthetic Laboratories, Department of Chemistry, University of Rajasthan, Jaipur-302004*

The synthesis of syndiotactic polymethyl methacrylate (PMMA) has been done electrochemically in mixed biphasic media, consisting of a non-polar phase formed by solution of monomer in a nonpolar liquid like benzene, xylene and carbon tetrachloride and polar phase (water +5 ml sulphuric acid) with added electrolytes (zinc salts). The molecular weight of polymer so obtained is $\approx 10^6$ The syndiotactic polymer was characterised by its NMR spectra in $CDCl_3$ . On the basis of polarization curve, the mechanism of polymerisation has been postulated to be free radical.

Polymethyl methacrylate (PMMA) is valuable in glazing, protective coating, paint base, binders and adhesives [1]. In chemical polymerization of methyl methacrylate, high temperature is necessary but electropolymerization is conducted by adjusting the current and keeping the reaction at constant temperature.

In almost all the studies done so far [2-5], the polymerization of methyl methacrylate has been carried out in a single homogeneous solvent phase containing electrolyte and monomer. Earlier aniline has been polymerised in biphasic medium [6]. The present communication reports, electrosynthesis of PMMA in a biphasic medium consisting of solution of monomer in a nonpolar solvent, like benzene, xylene or carbon tetrachloride and 10% $H_2SO_4$ with added electrolytes. The advantage of this technique lies in the fact that nonpolar phase containing the bulk of monomer traps the radicals formed at electrodes, and therefore is the medium for polymerization, where as, the polar phase, being conducting, acts as the medium for electrolysis. Further, polymers formed remain in the dissolved state in nonpolar phase and do not form a film on the electrode. The polymerization in biphasic media was studied using $ZnCl_2$, $ZnSO_4$ and $Zn(OOC.CH_3)_2$ as supporting electrolytes. In this process, $PbO_2$ which acts as anode, is itself produced electrolytically and in fact is more active, when produced in situ, on the electrode surface when aq. $H_2SO_4$ is added [7,8].

The overall reaction is:




## EXPERIMENTAL

*Materials:* Methyl methacrylate (Fluka), Benzene and carbon tetrachloride (all Ranbaxy), sulphuric acid (BDH), methanol (E. Merck) were used without any further purification.

Zinc chloride, zinc acetate and zinc sulphate (all BDH reagents) were used as such.

*Cell Assembly:* The electrochemical polymerization was carried out in a single compartment cell without any separation between the cathode and anode compartments. The arrangement for bubbling pure and dried $N_2$ gas was provided in the assembly. Lead sheet of working area 1.4 $cm^2$ was used as cathode and anode. The polarization study was made with respect to SCE at 30 $\pm$ 1°C.

*Electrolysis and work up:* The electrolysis was carried out by varying (i) the solvent (ii) the conc. of monomer (iii) the current. The electrolysis was controlled by a regulated power supply (model MP 1026 A) with provision to measure current and voltage drop through the cell.

The electrolysis was carried out at constant temperature and in order to maintain a constant temperature, the cell was kept in a water bath. To keep both the phases in intimate



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contact during electrolysis, the assembly containing the water bath and cell was mounted on a magnetic stirrer and the medium adequately stirred. After filling the cell with reactants, $N_2$ gas was bubbled for 30 min. prior to electrolysis. In order to determine the yield of polymers at certain interval of time, the electrolysis was terminated, the whole of nonpolar phase was precipitated with excess of acidified methanol and resulting white insoluble polymers were subsequently dried in an air oven at 100°C.

The average molecular weight $M_v$ of polymers were determined [9] in benzene using the relation,

$$\eta = 0.94 \times 10^{-4} \bar{M}_v^{0.76}$$

## RESULTS

Experiments showed that the polymerization occurs even in absence of electrolytes but the polymers are produced only to a very small extent over a period of 3-4 hours. The molecular weight of polymers so obtained is also very low. The polymethyl methacrylate obtained by this novel technique was confirmed by its NMR [10] to be syndiotactic. The NMR spectrum of PMMA shows the presence of ester methyl peak ($COOCH_3$) at 3.49 $\delta$ the $CH_2$ group signal at about 1.79 $\delta$ and the $-CH_3$ group signal at about 1$\delta$. The signal obtained at 7.5 $\delta$ is that of residual protons of $CDCl_3$

### Effects of Supporting Electrolytes & Solvent

Table 1 summarises the results of electropolymerization of MMA in benzene, xylene and carbon tetrachloride with zinc salts. Inspection of data presented in the Table-1 shows that $ZnCl_2$ gives a better yield than other zinc salts.

### Effect of Monomer Concentration

The yields of PMMA obtained with different initial monomer concentration at a fixed current of 40 mA for $ZnSO_4$, $Zn(OOC.CH_3)_2$ and $ZnCl_2$ are summarised in Table 2. Data presented in Table-2 shows that with changing monomer concentration, the yield of PMMA is greatly affected.

*Effect of current:* The percentage of conversion of polymer is depicted in Fig. 1, at three different chosen current values (20, 30 and 40 mA), and fixed monomer concentration 1.5 mol/1. From the figure it is seen that the percentage of conversion increases, with increasing current

TABLE 1

ELECTROPOLYMERIZATION OF MMA

Medium-50 ml aq solution + 50 ml non polar solvent (benzene, xylene or $Cl_4$) Electrolyte zinc salt 0.1 mol/l; Temp 30 ± 1°C. [MMA] 1.5 mol/l; Electrolysis at 40 mA; Electrolysis time 60 min

| Zinc salts | Yield in cms, of polymer in | | |
|---|---|---|---|
| | Carbon tetra-chloride | Xylene | Benzene |
| Zinc sulphate | 3.23 | 3.26 | 3.79 |
| Zinc chloride | 4.26 | 4.31 | 4.60 |
| Zinc acetate | 3.00 | 3.03 | 3.61 |

TABLE 2

YIELD OF PMMA WITH MMA CONCENTRATION

Medium 50% benzene; electrolytes zinc salt conc. 0.1 mol/l; Temp 30 ± 1° c; Current 40 mA; Electrolysis for 60 min

| $ZnSO_4$ | | $ZnCl_2$ | | $Zn(OOC.CH_3)_2$ | |
|---|---|---|---|---|---|
| Monomer mol/1 | PMMA yield in gms | Monomer mol/1 | PMMA yield in gms | Monomer mol/1 | PMMA yield in gms |
| 1.20 | 3.01 | 0.75 | 2.49 | 1.00 | 2.46 |
| 1.50 | 3.79 | 1.50 | 4.60 | 1.50 | 3.69 |
| 1.80 | 4.52 | 2.25 | 6.95 | 2.00 | 4.71 |
| 2.10 | 5.23 | 3.00 | 9.01 | 2.50 | 6.10 |
| 2.40 | 6.03 | | | 3.00 | 7.11 |

## DISCUSSION

Biphasic systems are more suitable than the conventional monophasic ones, to synthesise polymers, is evident by the results. The electrodes are kept free of any polymer coating. Polymers are obtained in the soluble form in the nonpolar phase. The polar phase acts to increase the conductance of medium considerably.

The mechanism of polymerization was postulated by studying its polarization curve [11]. Fig.2 shows the plot of current vs cathode potential relative to SCE for electrolysis of solution containing zinc chloride in benzene at

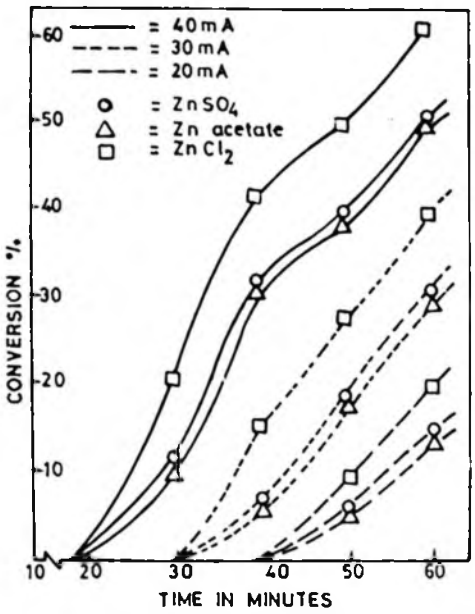



Fig. 1 Polymerization of PMMA in benzene containing solution of Zn salts at different currents. Temp 30 ±1°C; [Zn-salt] = 0.1 mole/1; [MMA] = 1.5 mole/1.

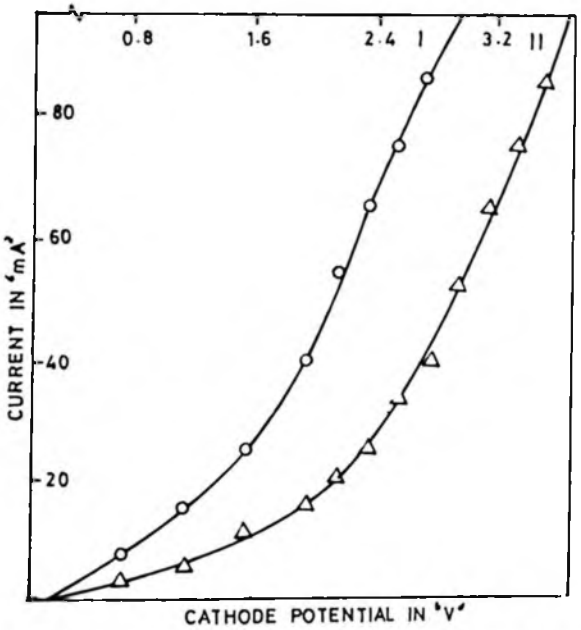



Fig. 2 Plot of current vs. cathodic potential (relative to SCE) for solution $ZnCl_2$ in benzene at 30 ± 1°C. I without MMA and II with 1.5 mole/1 of MMA: [$ZnCl_2$] = 0.1 mole/1.

30 ± 1°C, as model polarisation curve. The polarisation curve reveals that cathodic reduction potential of $ZnCl_2$ is less negative than that of MMA which states that some radical mechanism is operating rather than an anodic mechanism.

The radical may be formed by the scheme shown below:

$$H_2SO_4 + H_2O \rightleftharpoons H_3^+O + HSO_4^-$$

$$H_3^+O + e^- \text{(at cathode)} \longrightarrow H_2^+O + \dot{H} \text{ (radical)}$$

$$M \text{ (monomer)} + \dot{H} \longrightarrow M \text{ (Monomer radical)}$$

The monomer radical, thus formed, diffuses to the nonpolar phase to initiate the polymerization.

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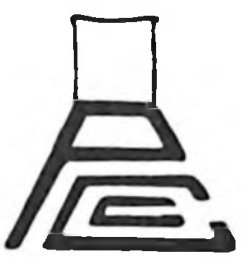
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