Kinetics of Polymerization of Vinyl
Monomers Initiated by Dimethylaniline-
Tosyl Chloride System

H KOTHANDARAMAN* & N ARUMUGASAMY
Department of Polymer Science, University of Madras, Madras
600025
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The polymerization of acrylamide and methacrylamide initiated
by a new binary system of N,N-dimethylaniline (DMA)-p-
toluenesulphonyl chloride (TsCl) has been investigated in
acetonitrile medium at 50°C. The rate of polymerization shows first
order dependence in [monomer] and square root dependence each
on [DMA] and [TsCl]. A suitable kinetic scheme has been
proposed.

A number of binary systems having N,N-
dimethylaniline (DMA) as one of the components have
been used as initiators in vinyl polymerization 1–4. The efficacy of yet another new binary initiator system of
DMA and p-toluenesulphonyl chloride (TsCl) for vinyl
polymerization has now been investigated. Under the
experimental conditions employed, neither DMA
nor TsCl functions individually as an initiator.

The polymerization of acrylamide and methacry-
lamide was carried out in the absence of light under
nitrogen blanket in acetonitrile at 50°C. The polymer
was precipitated at regular time intervals by adding an
excess of a non-solvent and the conversion of the
monomer was determined gravimetrically.

That the polymerization with DMA-TsCl initiator
system occurred by a free radical mechanism was
revealed by the following observations: (i) hy-
droquinone inhibited the polymerization; and (ii) no
polymerization occurred in the presence of air.

The rate of polymerization studied over wide
concentration range of the monomers and the initiator
was proportional to [DMA]^{1/2} and [TsCl]^{1/2} and first
order in [monomer].

The activation energy was calculated to be 30.3 kJ
mol^{-1} for the polymerization of acrylamide in the
temperature range of 35 to 55°C and 40 kJ mol^{-1} for
the polymerization of methacrylamide in the
temperature range of 40 to 60°C.

In view of the fact that polyacrylamide and
poly(methacrylamide) absorb in the same region as
DMA, spectral studies of poly(methyl acrylate) were
carried out. The UV spectrum of poly(methyl acrylate)
obtained with the DMA-TsCl system in dioxane,
showing absorption maxima around 255 and 300 nm
was similar to that of DMA. Thermally polymerized
methyl acrylate did not display these bands in the UV
spectrum. This observation indicates the presence of
end groups similar to those present in DMA (probably
the N-methylanilinomethyl group).

A plausible mechanism of polymerization using
DMA-TsCl initiator system is shown in Scheme I. DMA and TsCl react to give the initiating radicals
through the formation of the intermediate (I). This
type of adduct had earlier been isolated from trimethylamine and benzene sulphonyl chloride by
Horner5.

\[
\text{C}_6\text{H}_5\text{N}-(\text{CH}_3)_2 + \text{CH}_2\text{C}_6\text{H}_4\text{SO}_2\text{Cl} \xrightarrow{K} \left[\text{C}_6\text{H}_5-N^-\text{SO}_2-\text{C}_6\text{H}_4-(\text{CH}_3)^+ \right] \text{Cl}^- \quad (I)
\]

\[
\text{I} \quad \xrightarrow{k_d} \quad \text{C}_6\text{H}_5\text{N}^+ - \text{SO}_2 - \text{C}_6\text{H}_4 - \text{CH}_3 + \text{Cl}^- \quad \text{CH}_3 \quad \text{CH}_3
\]

\[
\text{R}^* + \text{M} \quad \xrightarrow{k_t} \quad \text{RM}^* \\
\text{RM}^* + \text{M} \quad \xrightarrow{k_p} \quad \text{RM}_2^* \\
\ldots \ldots \ldots \ldots \\
\text{RM}_m^* + \text{RM}_n^* \quad \xrightarrow{k_t} \quad \text{R} \left[\text{M}_m \right] \left[\text{M}_n \right] \text{R} \quad \text{Polymer}
\]

Scheme 1

Scheme 1 leads to rate Eq. (1)

\[
R_p = -\frac{d[M]}{dt} = k_p \left[ \frac{2k_d}{k_t} \right]^{1/2} [M]^{1/2} [\text{DMA}]^{1/2} [\text{TsCl}]^{1/2} \ldots (1)
\]

When DMA and TsCl were mixed either in the
presence or in the absence of monomer a blue colour
slowly developed which absorbed around 600 nm,
indicating complex formation.

Making the usual assumptions of the steady state
kinetics involving termination by mutual combination
of radicals, the overall rate constants $k_p\sqrt{2k_d/k_f} / K^{1/2}$ were calculated to be $3.048 \times 10^{-2}$ and $1.77 \times 10^{-3}$ mol$^{-1}$ dm$^3$ s$^{-1}$ for the polymerization of acrylamide and methacrylamide respectively at 50°C.

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References