Effect of C-Ethoxycarbonyl-N-phenyl-nitrilimine on Radical Polymerization of Methyl Methacrylate

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The kinetics of polymerization of methyl methacrylate (MMA) has been studied under N₂ atmosphere in the presence of a 1, 3-dipole, (C-ethoxycarbonyl-N-phenyl-nitrilimine, ECPN) and α, α'-azobisisobutyronitrile (AIBN) employing dilatometric technique at 60°, 65° and 70°C. ECPN, which acts as weak retarder, reduces the average degree of polymerization (Pn) appreciably. The orders of reaction in [ECPN], [AIBN] and [MMA] have been evaluated as 0.15 ± 0.07, 0.67 and 1.06, respectively. The rate of polymerization (Rp) increases with polymerization temperature and the overall energy of activation is computed as 83.0 and 67.0 kJ mol⁻¹ in the presence and absence of ECPN.

1, 3-Dipolar compounds have been used for the synthesis of a number of polycyclic heterocycles. In recent publications we have reported the kinetics of polymerization of vinyl monomers such as methyl acrylate and styrene in the presence of methylnitrile ylid (a 1, 3-dipolar compound). The present investigation is a follow up of earlier reports from our laboratory.

Methyl methacrylate (MMA), α, α'-azobisisobutyronitrile AIBN and solvent were purified before use. C-Ethoxycarbonyl-N-phenyl-nitrilimine (ECPN) was prepared in situ according to the method given by Huisgen.

The reaction mixture containing monomer, AIBN, ECPN and benzene (inert solvent) was injected into a modified dilatometer and progress of the reaction was monitored with the help of a cathetometer as meniscus movement and was converted into percentage conversion (C) using master graph.

The rate of polymerization (Rp) was calculated employing Eq. (1):

$$R_p \text{(mol dm}^{-3} \text{s}^{-1}) = \frac{1.498 \times 10^{-3} \times C}{t} \quad \ldots (1)$$

where t = polymerization time in min.

The intrinsic viscosity [η] of polymers, measured in benzene at 32°C using an Ubbelohde viscometer, was converted into $\tilde{P}_n$ using Eq. (2):

$$\log \tilde{P}_n = 3.342 + 1.13 \log [\eta] \quad \ldots (2)$$

The percentage conversion is not much affected (<5% conversion) using twelve-fold variation of [ECPN] from $1.02 \times 10^{-3}$ to $12.24 \times 10^{-3}$ mol dm⁻³ at 60°, 65° and 70°C. This indicates that ECPN acts as weak retarder. The plot of log $1/R_p$ against log [ECPN] is linear with a slope = 0.15 ± 0.7, which is also the order of reaction in [ECPN]. The values of $\tilde{P}_n$ decrease from 847.0 to 418.0, 397.0 to 200.0 and 92.0 to 58.0 at 60°, 65° and 70°C, respectively, at [ECPN] = $1.02 \times 10^{-3}$ mol dm⁻³. Beyond this [ECPN] there is no further decrease in $\tilde{P}_n$.

The Rp increases with the increase in the polymerization temperature and the energy of activation of the system, computed from Arrhenius plot, is 83.0 kJ mol⁻¹ at [ECPN] = $1.02 \times 10^{-3}$ mol dm⁻³. In the absence of ECPN, $E_a$ = 67.0 kJ mol⁻¹.

The effect of varying [AIBN] on the polymerization of MMA has been studied in the presence and absence of ECPN. The value of AIBN exponent increases from 0.50 to 0.67 in the presence of ECPN confirming its retarding effect.

The presence of ECPN can affect either (i) rate of initiation ($R_i$), (ii) rate of propagation ($R_p$) or (iii) rate of termination ($R_t$). No appreciable change in the rates of decomposition of AIBN is noted in the presence and absence of ECPN, indicating that ECPN does not affect $R_i$. This is further confirmed by the fact that ECPN does not act as an inhibitor even at higher concentrations.

The plot of log ($R_p/R_{po}$) and log ([η]/[η₀]) where $R_p$ and [η] are the rate of polymerization and intrinsic viscosity of the polymers respectively in the presence of ECPN and $R_{po}$ and [η₀] are the corresponding values in the absence of ECPN shows that $R_i$ is not affected by ECPN. This fact is further confirmed by the IR and PMR spectra of polymers which do not give any indication of ECPN incorporation in the polymer backbone.

The Rp increases with increase in [MMA]. The monomer exponent value, calculated from the slope of linear plot between log $R_p$ and log [MMA], is 1.06, which is also the order in [MMA].

The above observation clearly indicate that this 1, 3-dipole can be used to diminish average degree of polymerization of polymers without affecting conversion to a great extent.

Notes

Based on kinetic investigations, it is concluded that ECPN retards rate of propagation ($R_p$) of MMA by combining with a monomer or polymer radical (R') to produce a resonance stabilized radical X'. Non-incorporation of ECPN in the polymer backbone leads...
to the conclusion that radical $X'$ reacts with $R'$ to form the polymer (RH) and inactive species $X(X' + R'\rightarrow X + RH)$.

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References