# Kinetic analysis of the radiation induced polymerization of an acrylic acid–silica system

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## Abstract

A kinetic study has been made on the radiation induced polymerization of an acrylic acid–silica system. The effect of temperature and silica on the percentage conversion of monomer to polymer was studied. The rate of formation of polymer at the same temperature in the composite system was found to be faster when compared to bulk acrylic acid system at the same dose. This acceleration showed that the silica had a catalytic effect on the formation of polymer. The kinetic analysis of the conversion curves was made according to equations developed by Magat for nonsteady state polymerization taking place in precipitating media. $k_p/k_t$ ratio determined for polymerization of acrylic acid in presence of silica was found to be much higher than for bulk acrylic acid polymerization. The augmentation in rate is mostly attributed to the orientation effect of silica surface and increased secondary electrons produced in the irradiation of a composite system. © 1998 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Many studies have been reported on the preparation of new types of materials which incorporate the use of polymer with inorganic additives to form composites. In some cases, an accelerated rate of formation of polymer has been observed in the presence of these inorganic additives when compared to the homogeneous polymerization reaction. This increase was attributed to stabilization of the growing polymer radicals on the large internal surface area of the inorganic additives [1].

The bulk polymerization of monomer like acrylic acid, acrylonitrile, vinyl chloride etc. take place in heterogeneous systems due to insolubility of these polymers in their monomers. The kinetic equations developed for homogeneous systems therefore, cannot be applied to polymerizations taking place in these heterogeneous system. The radiation induced bulk polymerization of acrylic acid and acrylonitrile has been thoroughly investigated by Chapiro and his co-workers [2–5]. Their detailed work on bulk polymerization of both acrylic acid and acrylonitrile which exhibit remarkably similar polymerization behaviors has shown that the precipitation of the polymer was not the only factor responsible for the peculiar kinetics. It has been concluded that autoacceleration is determined by the formation of monomer–polymer association complexes. The orientation of monomers around polymers was explained to be due to strong hydrogen bonding in acrylic acid and dipole–dipole interactions of nitrile groups in the case of acrylonitrile. The rate of polymerization of these spatially ordered monomers was observed to be large as compared to random states.

In the present study the kinetics of the radiation induced heterogeneous bulk polymerization of acrylic acid in the presence of silica is re-examined with special emphasis placed on the determination of $k_p/k_t$ values and temperature dependence of this important quantity in heterogeneous polymerization systems. For the determination of $k_p/k_t$ ratio in the polymerization

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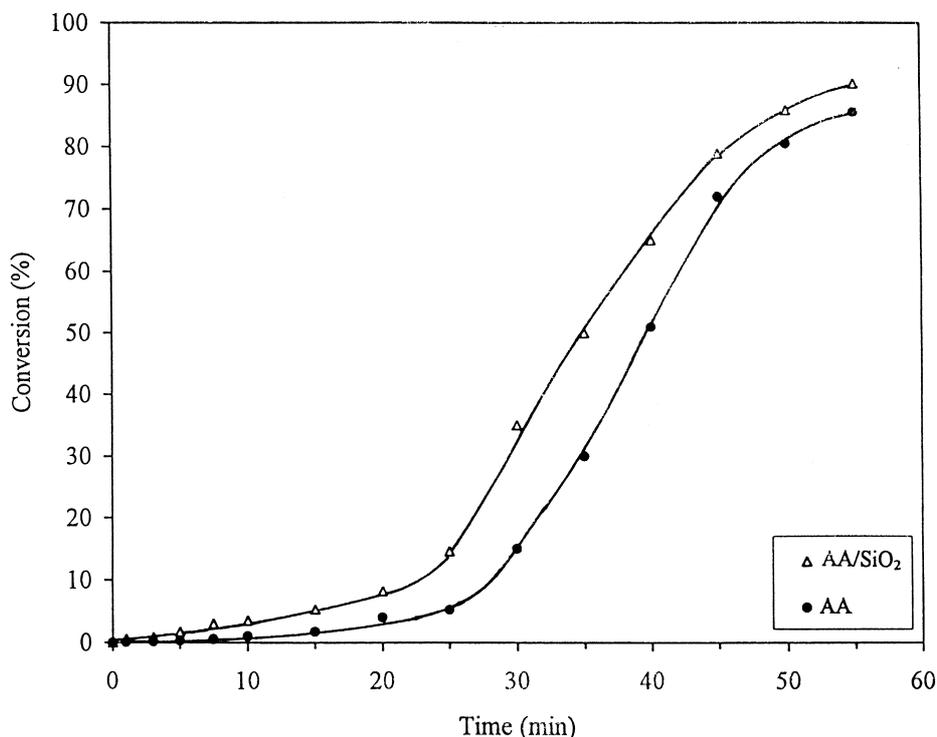
Fig. 1. Conversion curves obtained at 20°C.

of acrylic acid the kinetic approach first developed by Magat was used [6].

## 2. Experimental

Acrylic acid (AA) supplied by BDH Chemical Ltd, U.K. was distilled twice in vacuum and placed in glass tubes, mixed with the silica (97.3% $SiO_2$ by Atomic absorption, density $3 \text{ g/cm}^3$, coarse powder) in 0.35 $AA/SiO_2$ weight ratio and evacuated to $10^{-7}$ mm Hg. Before sealing the glass tubes, the dissolved gas (air) in mixtures was removed by freezing and thawing cycles. After the glass tubes were flame-sealed, mixture were irradiated in Gammacell 220 type $^{60}Co$ $\gamma$ irradiator in temperatures of 20, 30, 40 and 50°C controlled to $\pm1$°C at a dose rate of 0.85 kGy/h. The dose rate was determined by using a standard Fricke dosimeter. After irradiation, the composite product was washed with ether and dried to constant weight in a vacuum oven at 50°C. The conversion of monomer to polymer was gravimetrically determined. Every experimental point is the average result of triple measurements.

The average particle diameter of the silica used in this work was determined to be 15 $\mu$m. The surface area of the same sample was measured to be $1.67 \text{ m}^2/\text{g}$ by using a Malvern Mastersizer instrument.

## 3. Result and discussion

The radiation induced polymerization of acrylic acid in bulk and in presence of silica were investigated at 20, 30, 40 and 50°C, at a dose rate of 0.85 kGy/h. The conversion curves obtained under these conditions are given in Figs. 1–4. The characteristic feature of all these curves is a slow initial rate of conversion, followed by a steep rise and after this autoacceleration a significant drop in the polymerization. This has been observed for polymerization of acrylic acid in presence and absence of silica. As the polymerization rate does not remain constant, a certain type of rate must be selected for quantitative investigation of experimental results. Instead of arbitrarily taking the rate measured at a certain conversion, we have preferred to determine to initial slope of the conversion curves. This enabled us to determine the actual initial reaction rates directly. The initial rates thus determined is given in Table 1. As it is evident from this table, the rate of formation of polymer at a given temperature was found to be faster in the composite system when compared to the
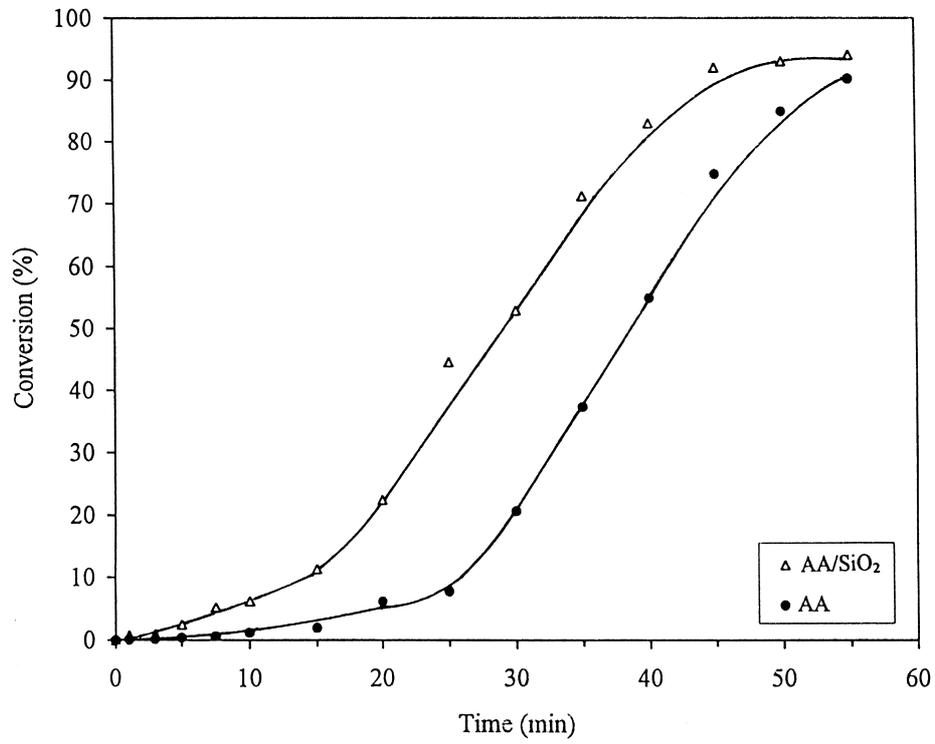
Fig. 2. Conversion curves obtained at 30°C.
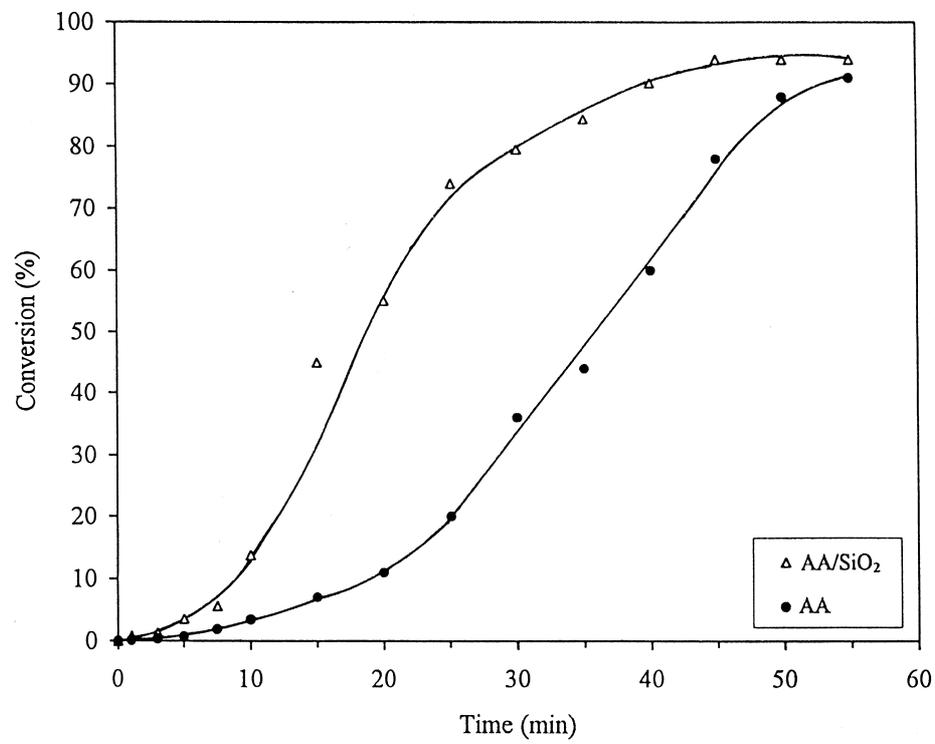


Fig. 3. Conversion curves obtained at 40°C.
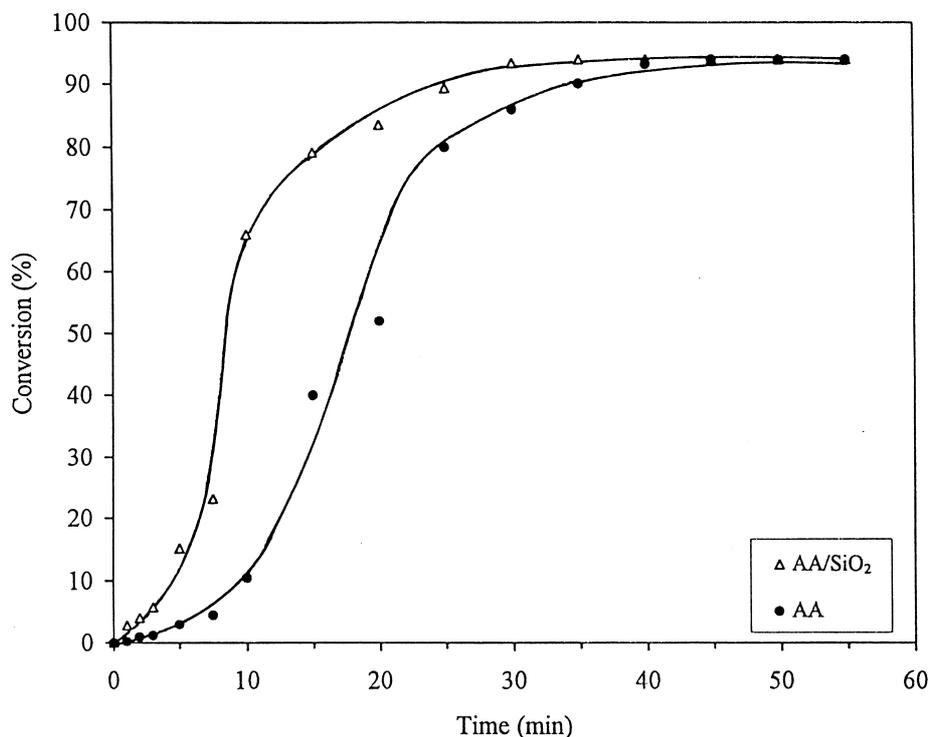
Fig. 4. Conversion curves obtained at 50°C.

bulk acrylic acid system. This acceleration clearly shows that the silica has a catalytic effect on the formation of polymer. This effect decreased with temperature.

In Figs. 1–4 the rates of polymerization after reaching a conversion of ~10% appear to be almost independent of the presence of the silica and the two curves corresponding to polymerizations taking place in the presence and absence of silica become parallel to each other. This is most probably due to propagation of polymerization under similar heterogeneous conditions. As it is known poly(acrylic acid) is insoluble in acrylic acid and its polymerization takes place heterogeneously. In the case of polymerization with silica after about 10% conversion, the surface of silica particles are also covered with poly(acrylic acid) which means that the heterogeneous phase becomes almost a pure poly(acrylic acid) suspension. The two rates beyond this stage are therefore almost identical.

When the kinetics of a reaction is investigated the primary parameters sought are the rate constant and the activation energies. $k_p/k_t$ values for the radiation induced polymerization of acrylic acid in the absence and presence of silica were calculated by using the approach of Magat [6]. The integrated form of the equation for rate of polymerization as proposed by Magat for the analysis of polymerization reactions taking place heterogeneously is written as:

$$-ln M/M_o = k_p/k_t \ln \cos h[(k_a k_t A_o)^{1/2} t]. \tag{1}$$

In the above equation, $M$ and $M_o$ are concentrations of monomer at time $t$ and initially, $k_a$, $k_p$ and $k_t$ are the rate constants for initiation, propagation, termination reactions and $A_o$ is the dose rate. For small amount of conversions, Eq. (1) can be rewritten as [7]:

$$(M_o - M)/M_o = k_p/k_t \ln \cos h[(k_a k_t A_o)^{1/2} t]. \tag{2}$$

When the small powers of series opening of the right hand side of the above equation is rearranged, the final equation can be written as:

$$\Delta M/M_o = 1/2 k_a k_p A_o t^2. \tag{3}$$

Eq. (3) shows that the conversion vs time curves define

Table 1
The change of conversion rates with temperature

| System | Rate (%/min) | | | |
|---|---|---|---|---|
| | 20°C | 30°C | 40°C | 50°C |
| AA | 0.09 | 0.13 | 0.33 | 0.96 |
| AA/SiO₂ | 0.52 | 0.65 | 1.28 | 3.18 |
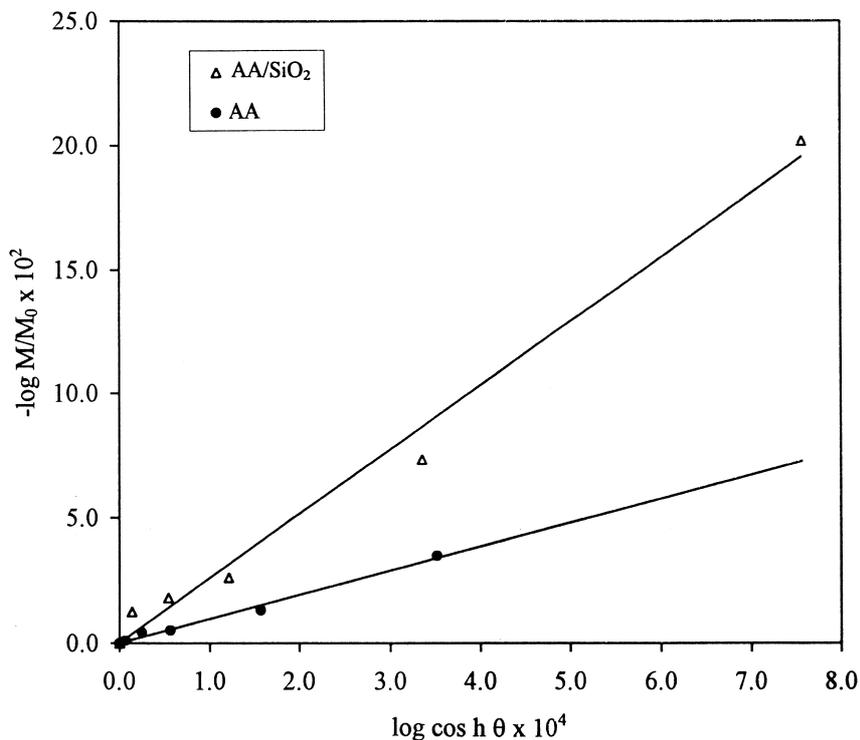
Fig. 5. Plot of log $M/M_o$ vs log cos $h\,\theta$ at 50°C.

a parabola. The initial parts of conversion curves given in Figs. 1–4, up to 20% conversion can be used for the application of Eq. (3). By applying parabolic curve fitting programs to these parts of the curves given in Figs. 1–4 it is possible to determine the factor $(1/2\; k_a\; k_p\; A_o)$ for every temperature. In order to analyze conversion vs time curves according to Eq. (1), however and determine $k_p/k_t$ ratio; the coefficient of time, $(k_a\; k_t\; A_o)^{1/2}$ must be known. The magnitude of this quantity is easily predicted since a factor resembling it, $(k_a\; k_p\; A_o)$ has already been determined from parabolic conversion curves by using Eq. (3). A value chosen for $(k_a\; k_t\; A_o)^{1/2}$ has been multiplied by $t$ and the resulting product $(k_a\; k_t\; A_o)^{1/2}\; t = \theta$ is reused in Eq. (1). For a predicted value of $(k_a\; k_t\; A_o)^{1/2}$ a plot of ln $M/M_o$ vs ln cos $h\theta$ would typically give a curve, after several trials $(k_a\; k_t\; A_o)^{1/2}$ value giving the best linear relation was chosen. After these approximations for every tempera-

ture, ln $M/M_o$ values were plotted against ln cos $h\theta$ [Fig. 5]. When the point of origin is considered together with the other date points the upper data points in Fig. 5 can be described with a line of $r^2 = 0.99$ regression value. A similar approach was applied quite satisfactorily to the heterogeneous polymerization of vinyl chloride by Magat [6] and to the bulk polymerization of acrylic acid [7]. Finally the slopes of these lines are used to determine the $k_p/k_t$ ratio. The results obtained are listed in Table 2. As it is seen the $k_p/k_t$ ratio depends on both temperature and the presence of silica. At every temperature $k_p/k_t$ determined for acrylic acid + silica system is higher than that of pure acrylic acid polymerization. The $k_p/k_t$ ratio changes between 20 and 40°C, by factors of 70 and 4 while the same change reaches values around 170 and 16 between 40 and 50°C for the polymerization of acrylic acid in bulk and in presence of silica respectively. Increment of $k_p/k_t$ ratio by temperature can be explained due to combined effects of thermal and radiation initiated polymerizations taking place of high temperatures. The low $k_t$ value in the heterogeneous media is generally considered to be the main reason for high $k_p/k_t$ ratio. The increase in $k_p/k_t$ ratio with temperature is a generally observed behavior, since reaction rate increases in both homogeneous and heterogeneous systems with temperature. The reason

Table 2
The change of $k_p/k_t$ ratio with temperature

| System | $k_p/k_t$ | | | |
| --- | --- | --- | --- | --- |
| | 20°C | 30°C | 40°C | 50°C |
| AA | 0.0084 | 0.094 | 0.58 | 97.0 |
| AA/SiO$_2$ | 4.7 | 6.9 | 16.2 | 258.7 |
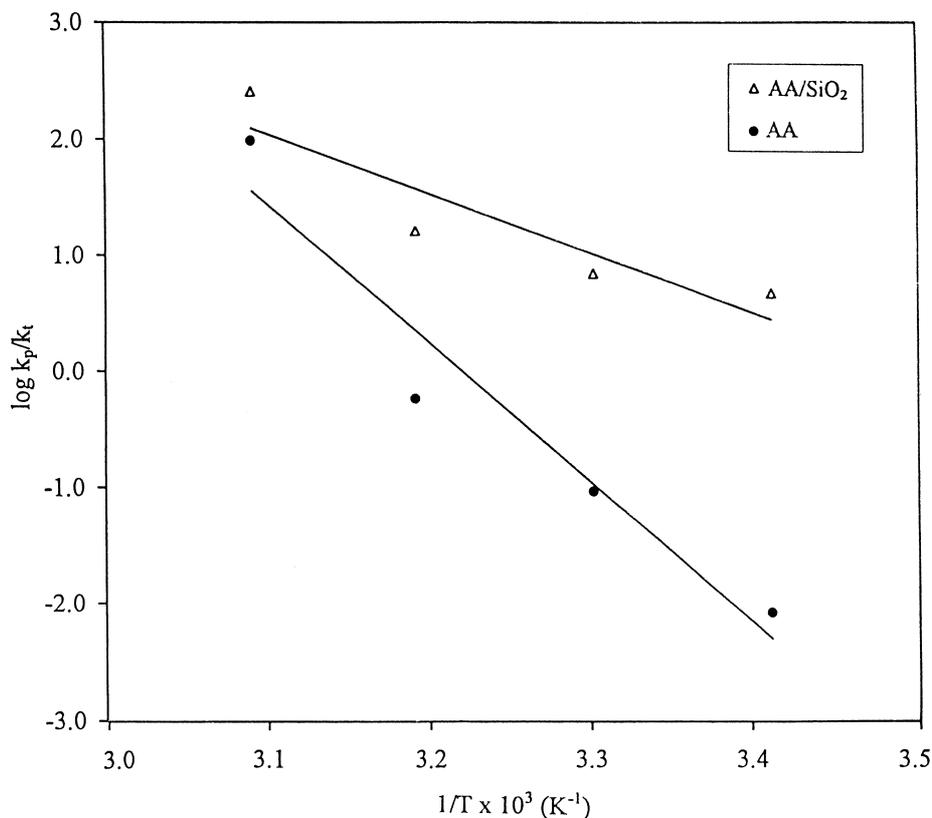
Fig. 6. The change of $k_p/k_t$ ratio with temperature.

for the increase in $k_p$ with temperature can be due to increasing mobility of primary radicals and macroradicals. Another reason of high $k_p/k_t$ ratio observed in the presence of silica is due to the high viscosity of this medium. An increase in viscosity would be expected to reduce the rate constant ($k_t$) for termination and hence, to increase the overall polymerization rate.

It has been considered to visualize the stabilization of the growing radicals within vacant lattice sites on the silica surface. This again presumes that the mutual termination reactions are effectively reduced, thus leading to an increase in the polymerization rate. The chain end radicals may be visualized as being effectively immobilized at vacant sites on the silica surface thus reducing the termination reactions. The reaction between monomer and polymer radicals would then take place at the silica surface. This might lead also to a reduction in the propagation rate constant but this could be easily outweighed by the decrease in the termination rate [1].

It must be considered that the existence of catalytic effects due to the silica interactions may lead to an increase in the initiation or propogations rates, and hence, in the overall polymerization rate. Since polymerization is initiated by $\gamma$-rays in this work, the high electron density of silica as compared to acrylic acid may indirectly increase the secondary electrons during irradiation of the composite system which may cause an increase in the overall polymerization rate, hence, $k_p/k_t$ ratio.

The $k_p/k_t$ ratios obtained at various temperatures were plotted against $1/T$ and the $E_p-E_t$ values calculated from the slope were on these lines [Fig. 6]. The $E_p-E_t$ values for the polymerization of acrylic acid in bulk and in the presence of silica were observed to be 231 and 99 kJ/mol respectively. The activation energy for composite polymerization was found to be approximately 60% less than the bulk activation energy under the same conditions. The presence of the silica was found to have a catalytic influence on the polymerization reaction of acrylic acid. This effect was temperature dependent and decreased as temperature increased.

In this study we have tried to see the effect of the silica on the radiation induced polymerization of acrylic acid. The rate of formation of polymer in composite systems was found to be faster when compared to a bulk acrylic acid system under similar conditions.

This behavior was attributed to the orientation effect of the silica surface and could also be due a catalytic role in the polymerization reactions and stabilization of the polymer radicals. It is also shown that heterogeneous polymerization kinetics as developed by Magat can be applied not only to heterogeneous bulk polymerizations but also heterogeneous composite polymerizations.

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