Kinetics and Mechanism Studying of Graft Copolymerization of Acrylic Monomers on PVC

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Abstract

Polyvinyl chloride was first dehydrochlorinated by LiCl in DMF at 353 K and then grafted with methylmethacrylate using benzoylperoxide as free radical initiator in an inert atmosphere. Studies were carried out to determine the optimum graft condition such as initiator, monomer and polymer concentration.

It was found that the percentage of grafting and rate of grafting were all dependent to some extent, on the concentration of the initiator, monomer and polymer, reaction time and temperature. The kinetics of the graft polymerization of MMA onto PVC was studied by gravimetry.

The following rate expression observed:
$$Rg = K[MMA]^{0.977}[DHPVC]^{0.545}[BPO]^{0.545}$$
Suitable mechanism is suggested. The dehydrochlorination and the graft copolymer were characterized by FT-IR spectroscopy.

The overall activation energy is found to be 37.44 KJ/mol, within the temperature range 40-70 ºC.

Introduction

Graft copolymerization of polyvinyl chloride (PVC) with various vinyl monomers by free radical and ionic initiators is well known (Eastman Kodak, 1952; Minuosia, *et al.,* 1968; Williams, 1967; Stauffer, 1972; Rao & Santappa, 1968; Bhemerzynshi *et al.,* 1981; William, 1962). The current studies are conducted to develop suitable means to increase the extent of grafting on PVC. Sharma and Varma reported

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the use of dehydrochlorinated PVC in nitrobenzene for grafting of styrene (Sharma & Varma, 1980). The grafted methods that were commonly used are based on dehydrochlorination of PVC for increasing the number of radical sites in an alkaline medium and increase the extent of grafting while using methyl methacrylate (MMA) as the comonomer were reported by Saroop (Saroop *et al.,* 1988). Vigo and Uliana investigated vinyl acetate and 2-hydroxyethylmetacrylate (HEMA) grafted onto PVC via chemical and radiation methods (Vigo & Uliana, 1893; Vigo & Uliana, 1989).

In the present study, the effects of benzoyl peroxide (BPO) as a free-radical initiator and monomer concentrations on the graft polymerization of methyl methacrylate on to dehydrochlorinated poly (vinylchloride) (DHPVC) were studied.

The graft polymerization was kinetically studied and the percentage of grafting as a function of various parameters, a reaction scheme and an expression for the polymerization rate have been proposed and activation energy and order of reaction were determined.

Experimental
Materials
Suspension-polymerized PVC sample (fluka k value 1 g/100ml, at 25ºC 55-57) MMA (BDH-LR grade) was first washed with 5% NaOH to remove inhibitor and then with distilled water to remove Traces of Alkali. It was then dried over anhydrous Na_2SO_4 and distilled under reduced pressure.

Benzoyl peroxide (BPO) was purified by dissolving in chloroform at room temperature and precipitated by addition of methanol.
LiCl 98% was dried at 80ºC. Cyclohexanone and DMF (Merck) and methanol (Merck), reagents used were of pro analysis grade.
Preparation of DHPVC
PVC (3g), LiCl (13.75) and DMF (300 ml) were fed to a round bottom flask fitted with a reflux condenser.
The dehydrochlorination proceed for 3 h at 70ºC, and then precipitated by methanol.

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The dehydrochlorinated material was washed with distilled water to remove all traces of LiCl and dried under vacuum. The product is referred as dehydrochlorinated PVC (DHPVC).

FT-IR spectra measurement

Polyvinyl chloride and dehydrochlorination polymers were characterized by FT-IR (8 101 M shimadzu) spectroscopy. Figures 1-2 demonstrates the differences between PVC alone and after dehydrochlorination of polyvinyl chloride.
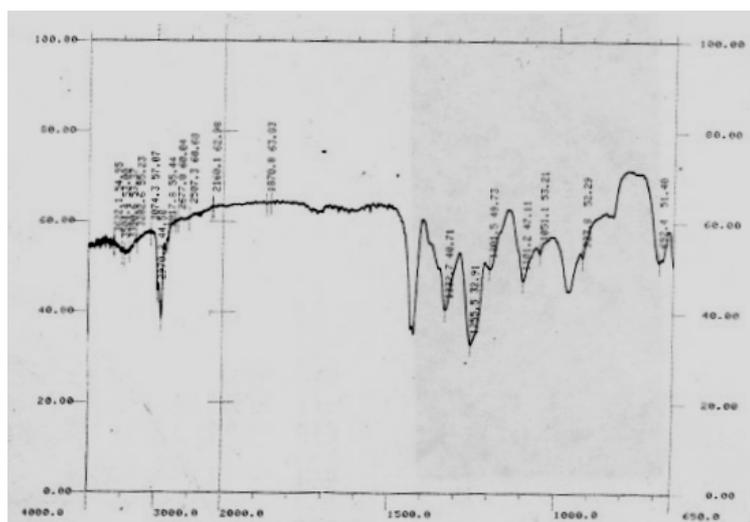

Figure 1 - FT-IR Spectra of PVC

The appearance of absorption band at 1675 cm-1 in the (DHPVC) identified, the formation of sequences of conjugated double bonds (long polyene sequences) in the PVC chains.

Graft polymerization

DHPVC (1g) was dissolved in cyclohexanone (15 g). The solution was then stirred and heated to 70ºC in an argon atmosphere. When the desired temperature was reached a known amount of MMA (1g) containing a known quantity of BPO was added with continuous stirring. The reaction was then carried out for predetermined time (3h). The mixture was then cooled and poured into excess well- stirred methanol.

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The precipitation polymer was filtered and washed, several times with methanol, then dried at 50ºC under vacuum for 7-8 hr. The precipitate would be a mixture of grafted copolymer of pvc-g-PMMA and PMMA. Poly(MMA) was removed by soxhlet extraction using benzene. The remaining solid (PVC- g-PMMA) was dried under vacuum and subsequently characterized.
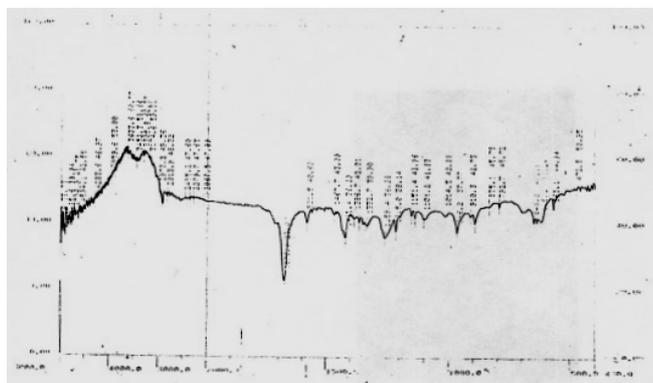

Figure 2 - FT-IR Spectra of DHPVC

Infra red spectra measurement

Infra red spectra of the polymer sample was taken after the reaction. The carbonyl band has its highest absorption at 1740 cm-1 (Fig. 3).

In the grafted polymer was not present vinyl absorption band. This testified the existence of grafting.
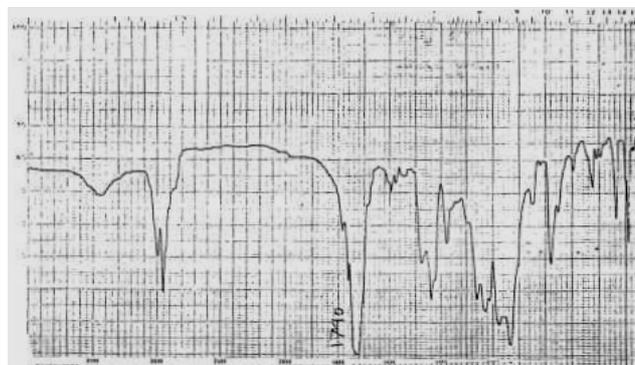
Figure 3 - I.R Spectra of the graft copolymer MMA on to DHPVC

Estimation of extent of grafting

Gravimetry

The grafting parameters were evaluated from the mass of the sample before and after grafting.

The percentage of graft yield was calculated according to the following relationship:

$$\text{\%PMMA in graft} = \text{Graft yield (\%)} = \frac{\text{dry weight of grafted PDHPVC - dry weight of original DHPVC}}{\text{dry weight of original DHPVC}} \times 100$$

Results and Discussion

Effect of initiator, monomer and DHPVC concentration

The grafting reaction may be influenced by the concentration of initiator, monomer and DHPVC and reaction time.

Effect of reaction time

The effect of reaction time on MMA grafting on DHPVC is shown in Figure 4. The time ranged from 1 to 6 hr keeping other parameters constant studied at 70 ℃.

The percentage of graft yield is linear with time up to 3 hr. However, with increase of reaction time to 3hr, the value of grafting increased to 32% at which maximum grafting was observed. When the reaction time was further increased, there was decrease in % graft.

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Figure 4- Effect of reaction time on % grafting [DHPVC]=66.67 g/lit, [MMA]=0.666 M, [BPO]=2.75×10-2 M, T=70 ⁰C

Effect of initiator concentration

Graft copolymerization was studied by changing the concentration of BPO from, 1.65×10-2 - 4.65 ×10-2 M at constant MMA and DHPVC concentration on the graft (%) is shown in Figure 5. The perusal of results indicates that, with increasing initiator concentration in this range, the graft yield increase.
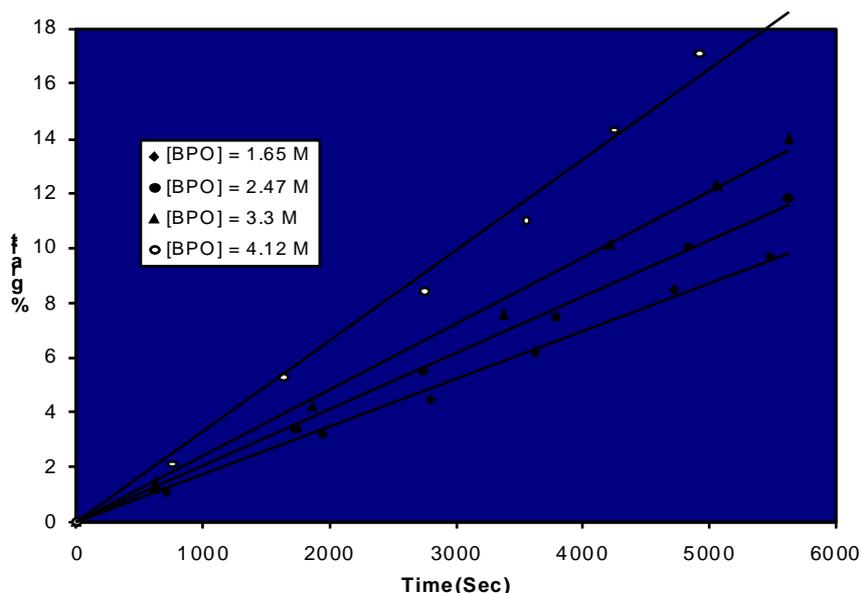

Figure 5 - Effect of initiator concentration on % graft at fixed concentration of [MMA] =1 M and [DHPVC]=66.7 g/lit, T = 70 ⁰C

Effect of MMA concentration

The grafting has been studied at the monomer concentration within the range of 0.4-2 M at constant initiator and DHPVC concentrations on the graft (%) is shown in Figure 6. It is observed that with increasing monomer concentration, the graft yield increases.
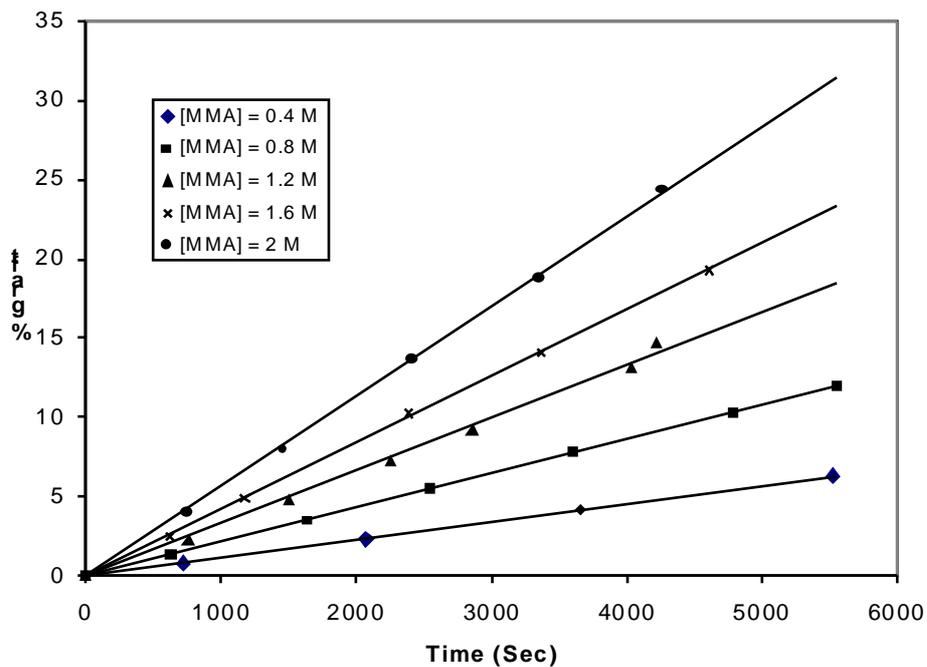
Figure 6 - Effect of monomer concentration on % graft at fixed concentration of [BPO] =2.75×10^{-2} M and [DHPVC]=66.7 g/lit, T = 70 ºC

Effect of DHPVC concentration

The dependence of grafting on the amount of DHPVC was studied in the range of 26.7-80 g/l at constant initiator and monomer concentrations on the graft (%) are shown in Figure 7. It is observed that with increasing DHPVC concentration, the graft yield increases.
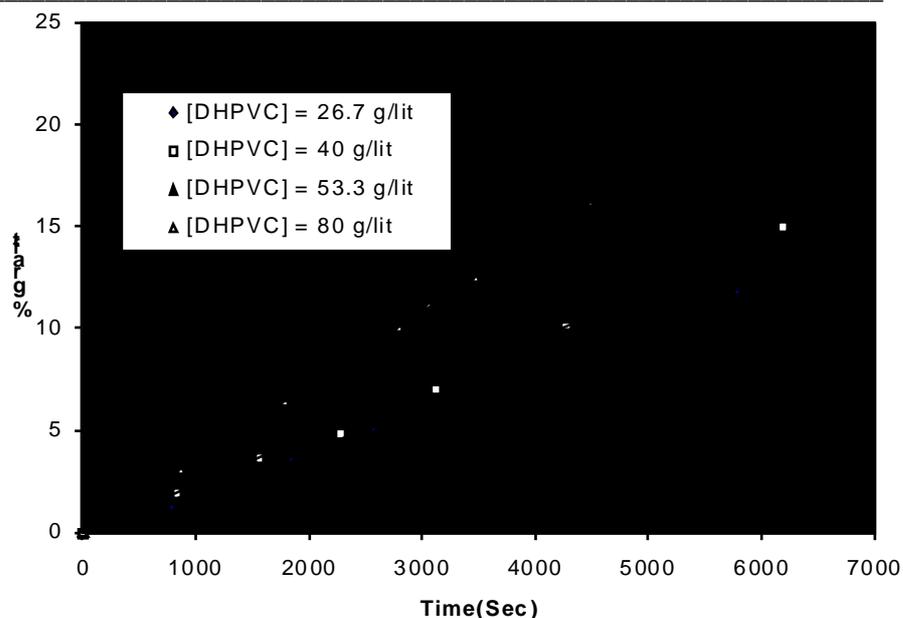
Figure 7 - Effect of DHPVC concentration on % graft at [MMA]=1M, [BPO]=2.75×10^{-2} M, T = 70 ºC

Kinetics of Graft polymerization

The rate of graft polymerization (Rp: grafted monomer mol/L Sec) depends on the concentration of initiator, monomer and DHPVC as following:

$$Rp = K[MMA]^{?\ddagger}[BPO]^{?\ddagger}[DHPVC]^{?\ddagger}$$

The plot of ln (Rp) vs. Ln [BPO] is linear and plotted in Figure 8. The slope of line is 0.5446, which suggests that the order of the reaction with respect to initiator is 0.5.

The plot of Ln (Rp) vs.Ln[MMA] is linear and plotted in Figure 9. The slope of line is 0.9766 and indicating that the order of the reaction with respect to monomer is one.

The plot of Ln (Rp) vs. Ln [DHPVC] is linear and presented in Figure 10. The slope of line is 0.5447,which suggests that the order of the reaction with respect to DHPVC is 0.5.

Therefore:

$$Rp= K[MMA]^{0.977} [BPO]^{0.545} [DHPVC]^{0.545}$$
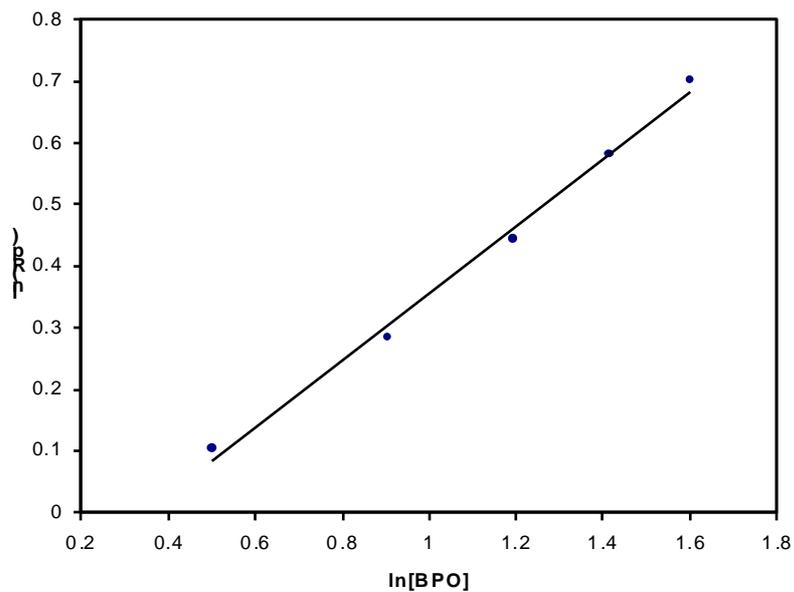
**Figure 8 - Plot of Ln (Rp) vs. Ln [BPO] at fixed concentration of MMA and DHPVC.**
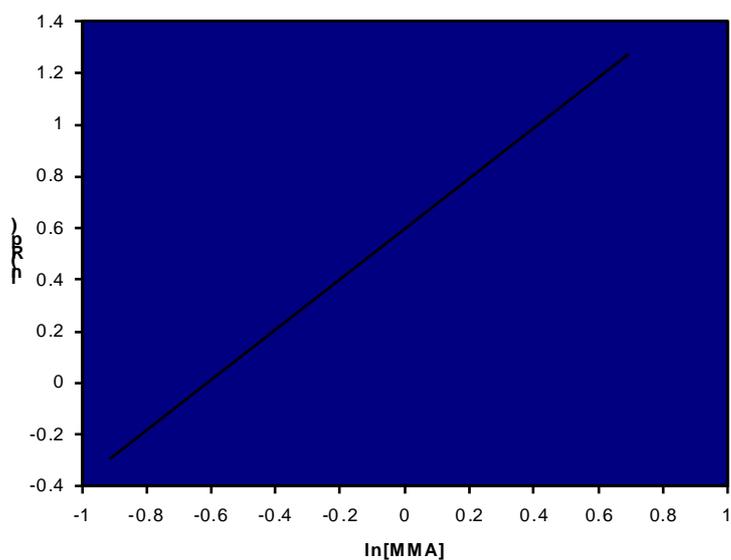
**Figure 9 - Plot of Ln (Rp) vs. Ln [MMA] in the constant conditions.**
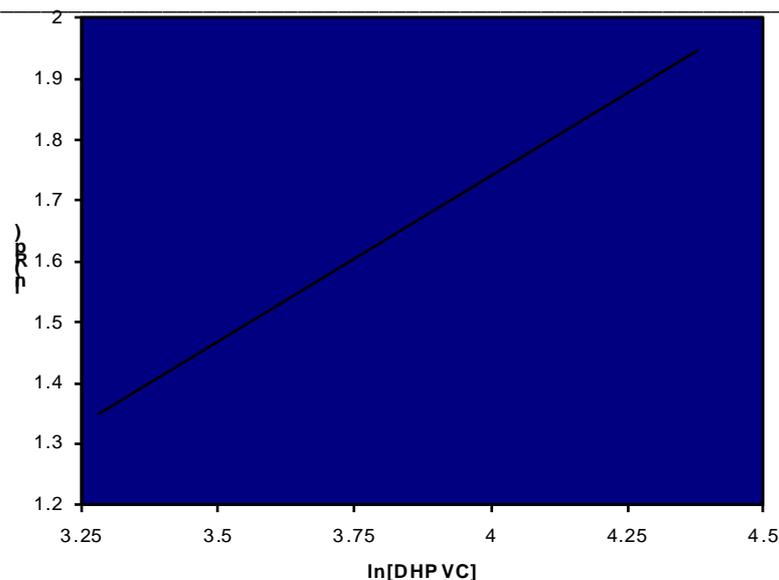
Figure 10 - Plot of Ln (Rp) –Ln[DHPVC] in the constant conditions.

Effect of temperature

The grafting reaction was carried out at 40-65 ºC in the constant conditions (see Fig.11).There is gradual increase in the extent of grafting as the temperature of dehydrochlorination is expected to provide more reactive sites along the polymer chains thus increasing extent of grafting.

The plot of Ln(Rp) vs. 1/T is linear and activation energy was obtained as 37.44 KJ mol^{-1} (Fig. 12).

Mechanism

The mechanism of grafting on PVC by BPO for a free radical inititor is suggested as follow:

Initiation:

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1) $I \xrightarrow{kd} 2R^{\bullet}$

2) $R^{\bullet} + D \xrightarrow{k_i} D^{\bullet}$

3) $D^{\bullet} + M \xrightarrow{k_i'} DM^{\bullet}$

4) $R^{\bullet} + M \xrightarrow{k_i''} M^{\bullet}$

Propagation:

5) $DM_n^{\bullet} + M \xrightarrow{kg} DM_{n+1}^{\bullet}$

6) $M_n^{\bullet} + M \xrightarrow{k_h} M_{n+1}^{\bullet}$

Termination :

7) $DM_n^{\bullet} + DM_n^{\bullet} \xrightarrow{kt} graft\ copolymers$

8) $M_n + M_n \xrightarrow{k_t'} \mathbf{hom}\ opolymer$
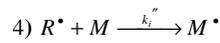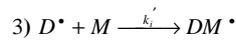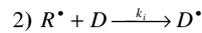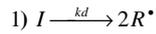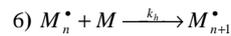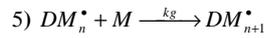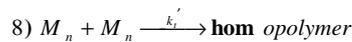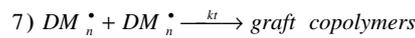
Here D is the dehydrochlorinated PVC; M is the monomer; M. is the monomer radicals; I is the initiator. D. is the DHPVC macroradical. K represents the rate constant of a reaction step: K_t and K_t' are rate constant of mutual termination of free radicals. With considering steady state approximation, for our mechanism the following results is found

9) $\dfrac{d[DM_n^0]}{dt} = K_i'[D^{\bullet}][M] - K_t[DM_n^{\bullet}]^2 = 0$

10) $\dfrac{d[D^{\bullet}]}{dt} = K_i[R^{\bullet}][D] - K_i'[D^{\bullet}][M] = 0$

from eq.(9,10) we have Eq .(11).

11) $[DM_n^{\bullet}] = K_i^{0.5}.K_t^{-0.5}[R^{\bullet}][D]$

12) $\dfrac{d[R^{\bullet}]}{dt} = 2K_d[I] - K_i[R^{\bullet}][D] - K_i''[R^{\bullet}][M] = 0$

The $K_i''[R^{\bullet}][M])$ (is depends to homopolymerization and graft polymerization is suggested undepended to homopolymerization. Now Eq. (12) becomes:

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$$13) \frac{d[R^\bullet]}{dt} = 2\,K_d[I] - K_i[R^\bullet][D] = 0$$

$$14) \frac{d[R^\bullet]}{dt} = 2K_d f_D[1] - K_i[R^\bullet][D] = 0$$

fD(fD=α[D]) is fraction of initiator witch is consumed in the graft copolymerization[12].By using Eq. (14) determined the value of [R]:

$$15)\ [R^\bullet] = \frac{2K_d?[2]}{K_i}$$

As an approximation, the rate of polymerization may be taken as that of propagation. Therefore, we may write the rate of polymerization as:

16) Rg= Kg[DMn.][M]

By replacing the value of [R.] from Eq. (15) and (DMn.) from Eq. (11) to Eq. (16) we have:

$$17)\ R_g = K_g K_i^{0.5} K_t^{-0.5} (\frac{2K_d?[1]}{K_i})^{0.5}[D]^{0.5}[M]$$

or:

18) Rg= K[M][D]0.5[l]0.5 , when $K = K_g K_t^{-0.5}(2K_d?)^{0.5}$

These results have shown that, the rate of reaction, obtained from our proposal mechanism is compatible with experimental results.
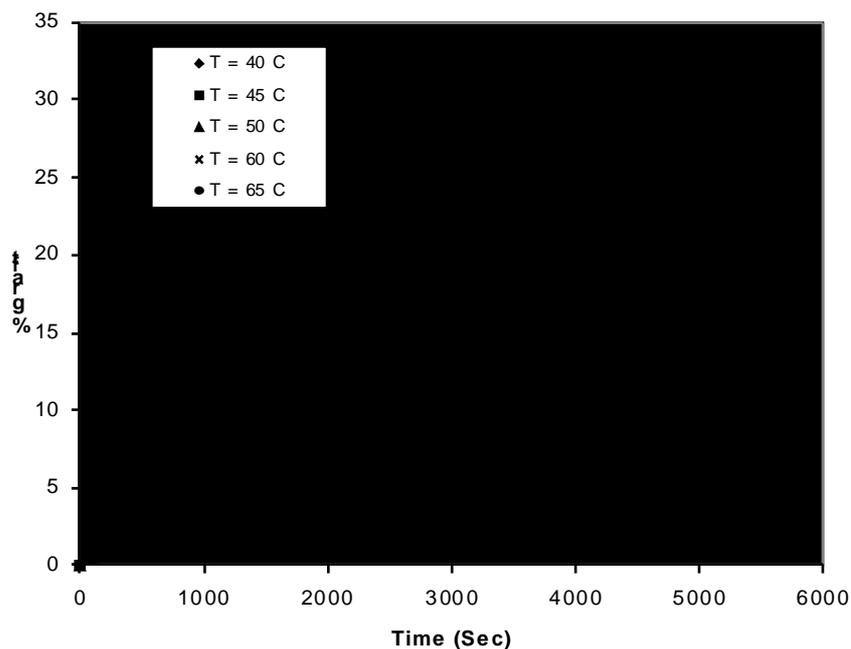
Figure 11 - Effect of reaction temperature on the graft yield at : [DHPVC]=66.67 g/l , [MMA]=1M, [BPO] = 2.75×10^{-2} M
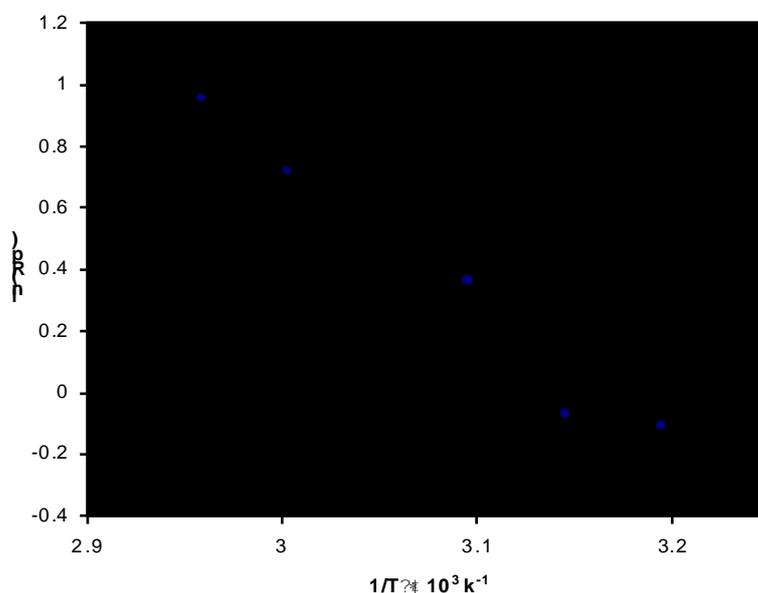

Figure 12 - Plot of Ln(Rp) vs. I/T in the constant conditions

Conclusion

Grafting of MMA on DHPVC has been successfully demonstrated. It was shown that dehydrochlorination of PVC facilitates grafting. Under the reaction conditions chose, the reaction time for optimum grafting was determined. BPO can initiate the graft copolymerization of DHPVC with MMA efficiently, and the graft yield and Rp can be adjusted by changing the reaction conditions, such as Temperature, concentration of monomer, initiator and DHPVC.

Under the experimental condition, a suitable rate equation was proposed and the overall activation energy was determined.

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