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Phase Transfer Catalyzed Polymerization of Acrylonitrile Initiated by Potassium Persulfate–N, N, N-Trimethylhexadecan-1-Ammonium Chloride in Diphase System: A Kinetic Study

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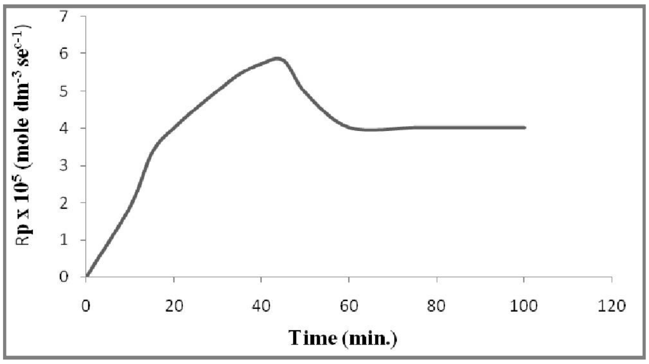
ABSTRACT

The polymerization of acrylonitrile (AN) has been studied under phase transfer reaction condition. The suitable reaction conditions and the kinetics of free radical polymerization of acrylonitrile using N, N, N-trimethylhexadecan-1-ammonium chloride (TMHDAC) - potassium peroxydiphosphate (PDP) as free radical initiator have also been assessed and discussed. The influence of concentrations of the monomer, initiator, catalyst, variation of temperature and solvent polarity on polymerization rates were determined and verified with the experimental results. Based on these results a suitable kinetic mechanism has been proposed. The reaction order with respect to monomer, initiator and phase transfer catalyst concentrations were found to be 1, 0.5 and 0.5 respectively. Herein, the polymer products yield with improved properties and checked by various instrumental studies viz., UV, IR, ^{1}HNMR, ^{13}CNMR and viscosity measurements.

Graphical Abstract



Steady state rate of polymerization

Keywords: Phase transfer catalysis, Peroxydiphosphate (PDP), Acrylonitrile, Mechanism of free radical polymerization, Spectral studies.

INTRODUCTION

A new chemical technology was introduced in 1960s, named as phase transfer catalysis (PTC) and used as a synthetic tool for the synthesis of a variety of organic compounds with industrial importance. Phase transfer agents [**1**] such as crown ethers and ammonium salts were found to be responsible for the reaction between a substrate soluble in the organic solvent and the ionic reagent insoluble in the solvent. It was found an effective method for the preparation of a large number of industrial processes, [**1-3**] including the preparation of pharmaceuticals, amino acids, epoxides and pesticides etc., The scientist Regen [**4**] has developed a newer technique called triphase catalysis, due to its easy and quantitative catalyst recovery and simplified product work-up through considerable advantages over other techniques. Mathias *et al.* [**5**] has reported a class of heterogeneous reactions similar to PTC systems, called as inverse PTC in which the PT agent transfer the reactant species from the organic phase to the aqueous phase and the main reaction occurs in the aqueous phase, The most significant recent application of PTC to polymer science in the free radical polymerization catalysis as discovered and developed by Rasmussen *et al.* [**6-7**] Many scientists explored Rasmussen works for various condensation, anionic, free radical, and chemical modifications of polymers. [**7-10**] Further, the PTC assisted free radical polymerization of vinyl monomers by using peroxomono sulphate and peroxydisulphate as free radical initiators have also been reported. [**11-21**] After, the discovery and the synthesis of peroxydiphosphate (PDP), many scientists have been used PDP as a free radical initiator for the polymerization of water soluble vinyl monomers in various redox systems. [22-24] From the above evidences and thorough literature survey, it may be revealed that, the polymerization of using vinyl monomers with PDP coupled with phase transfer agents has not been studied so far. This prompted us, to investigate the use of potassium peroxydiphosphate as an initiator for the polymerization of oil-soluble monomers in presence of water–ethyl acetate diphase conditions. A systematic study for the kinetics of phase transfer catalyzed free radical polymerization of acrylonitrile using peroxydiphosphate–N, N, N-trimethylhexadecan-1-ammonium chloride (TMHDAC) as an initiator has been studied.

MATERIALS AND METHODS

Materials: The monomer, acrylonitrile (AN). Sd.fine Chemicals was freed from the inhibitor, distilled and used for polymerization studies. The free radical initiator potassium peroxydiphosphate (PDP), Sigma, USA was purified by crystallization from deionized water. The quaternary ammonium salt, TMHDAC was used as a high purity supplied by Sigma, USA, for this study. Ethyl acetate and methanol were purified by using standard procedures. Sulphuric acid was used as a high purity analytical grade. Polymerization reactions were carried out in the presence of nitrogen atmosphere at 50±0.10°C, under unstirred condition, in a long pyrex glass polymerization apparatus with a provision of gas inlet and outlet.

Experimental procedure for the polymerization of vinyl monomers: The polymerization experiments were conducted in the polymerization tubes thermostated at 50 (±) 0.1°C. The aqueous phase containing phase transfer catalyst, acid (H_2SO_4) and organic phase containing monomer acrylonitrile (AN) in the desired solvent (ethyl acetate) were taken in a polymerization tube and flushed with purified nitrogen gas to ensure inert atmosphere for 45 min. The calculated amount of deaerated PDP solution, which was also thermostated at experimental temperature, was added to the polymerization tube quantitatively and simultaneously starting the stop watch. The polymerization tubes were then carefully sealed by rubber gaskets to ensure an inert atmosphere. The polymerization reactions were arrested by pouring the reaction mixture into ice cold methanol–water mixture containing traces of hydroquinone in various experiments [**10-18**]. The precipitated polymers in each experiment were filtered through sintered glass crucibles (G.4) washed with water and methanol and dried in a vacuum oven at 60 (±) 0.1°C. The rates of polymerization (Rp) were calculated from the weight of the polymers (w) obtained by using the following equation.

$$R_p = 1000 \times w / V.\ t.\ M$$

Where R_p-Rate of Polymerization, w-Weight of Polymer, V-Total volume of the polymerization mixture, t-Reaction time in seconds, M-Molecular weight of the monomer.

In each system, temperature variations (in the range, 40 to 60°C) experiments were also carried out, to evaluate the thermodynamic parameters.

RESULTS AND DISCUSSION

Steady state rate of polymerization: The steady state rate of polymerization was first determined from its rate of polymerization (Rp) at different time intervals and recorded as 75 min (Table1 and Figure 1). Initially, the Rp was first increased with time and reached a maximum, thereafter, it was decreased and attain as a steady state i.e., Rp remains constant. The reaction time was fixed as 75 min to carry out the experiments for variation of other parameters like variation of [monomer], [PTC], [initiator] and temperature etc.,

Table 1. Steady state rate of polymerization

Time (min)	Rp x 10^5 (mole $dm^{-3}sec^{-1}$)	Time (min)	Rp x 10^5 (mole $dm^{-3}sec^{-1}$)
10	1.92	50	5.82
20	3.35	60	4.95
25	4.01	75	4.02
30	4.53	80	4.02
35	5.01	90	4.02
40	5.45	100	4.02
45	5.73	--	--

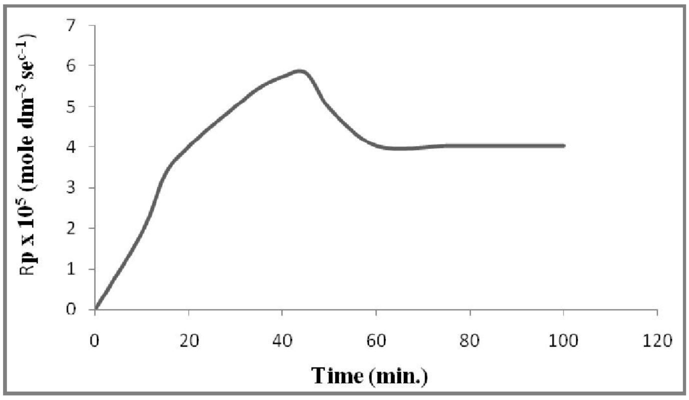
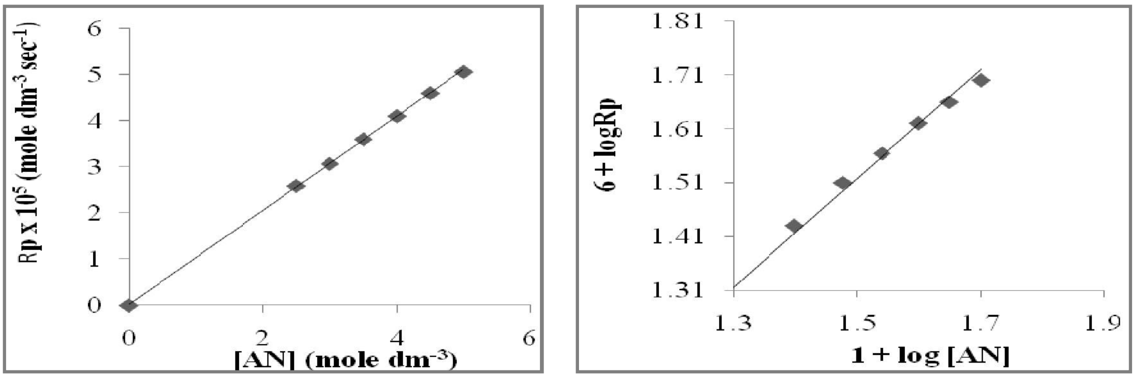


Figure 1. Steady state rate of polymerization.

Effect of [monomer] on the rate of polymerization (Rp): The effect of monomer concentration on the Rp was studied by varying acrylonitrile concentration in the range from 2-5 mole dm^{-3} at fixed concentrations of initiator, phase transfer catalyst and acid. The rate of polymerization was found to be increased with an increase in monomer concentration (Table 2, Figure 2a and 2b). The order with respect to monomer has been deduced from a slope of the linear plot of log Rp vs.log [AN] and found to be unity. The first order dependence may also be due to occlusion phenomenon [19] occur during polymerization. The same order dependence was reported in the phase transfer catalyzed polymerization of acrylonitrile using $K_2S_2O_8$ as an initiator by Balakrishnan *et al*. [9], Umapathy *et al.* [14] have also reported the same order of dependence of monomer for the phase transfer catalyzed polymerization of butyl methacrylate using $K_2S_2O_8$ as an initiator. Yoganand *et al*. [17] have also observed the same kinetical results for the despite phase transfer catalyst assisted free radical polymerization of methylmethacrylate using water soluble $K_2S_2O_8$ as an initiator.

Table 2. Effect of [monomer] on Rp

[AN] (mole dm^{-3})	1+ log [AN]	Rp x 10^5 (mole dm^{-3} sec^{-1})	6 + log Rp
2.0	1.3010	2.05	1.3117
2.5	1.3979	2.59	1.4132
3.0	1.4777	3.07	1.4871
3.5	1.5400	3.50	1.5441
4.0	1.6000	4.02	1.6042
4.5	1.6500	4.60	1.6628
5.0	1.7000	5.04	1.7024



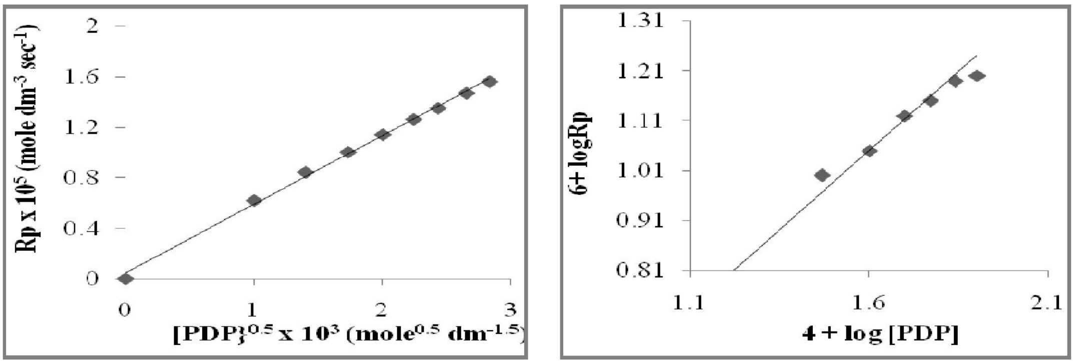
(a) . [AN] vs.Rp x 10^5 (b). 1 + log [AN] vs. 6 + log Rp

Figure 2. Effect of [monomer] on Rp.

Effect of [initiator] on the rate of polymerization (Rp): The effect of initiator concentration of Rp was studied by carrying out the polymerization reactions at various initiator concentrations in the range of 0.001 mole dm^{-3} to 0.008 mole dm^{-3} at fixed concentrations of monomer, phase transfer catalyst and acid. Rp was found to increase with an increase in concentrations of the initiator. A plot of Rp vs. $[K_2P_4O_8]^{0.5}$ is linear passing through the origin confirming the above observation (Table 3 and Figure 3a) and the fractional reaction order (0.5) was obtained for the bilogarithmic plot of log Rp vs. log [PDP] (Figure 3b). The same order dependence of initiator was reported by Savitha *et al.* [16] for the synthesis of new phase transfer catalyzed free radical polymerization of ethyl methacrylate. Umapathy *et al*. [15] have reported the same kinetical observations for the kinetics and mechanism of phase transfer catalyzed free radical polymerization of methyl acrylate. Recently, Thangaraj *et al.* [25] were found the same order dependence of [PDP] on the rate of polymerization of butyl methacrylate (BMA) initiated by TMHDAC system.

Table 3. Effect of [initiator] on Rp

[PDP] X 10^3 (mole dm^{-3})	$[PDP]^{0.5}$ x 10^3 (mole $^{0.5}$dm$^{-1.5}$)	4 + log [PDP]	Rp x 10^5 (mole dm^{-3}sec^{-1})	6 + log Rp
1	1.000	1.0000	0.65	0.8129
2	1.414	1.1010	0.80	0.9031
3	1.730	1.4771	0.95	0.9777
4	2.000	1.6021	1.15	1.0607
5	2.240	1.6995	1.25	1.0969
6	2.450	1.7782	1.35	1.1303
7	2.650	1.8451	1.45	1.1614
8	2.830	1.9071	1.55	1.1903



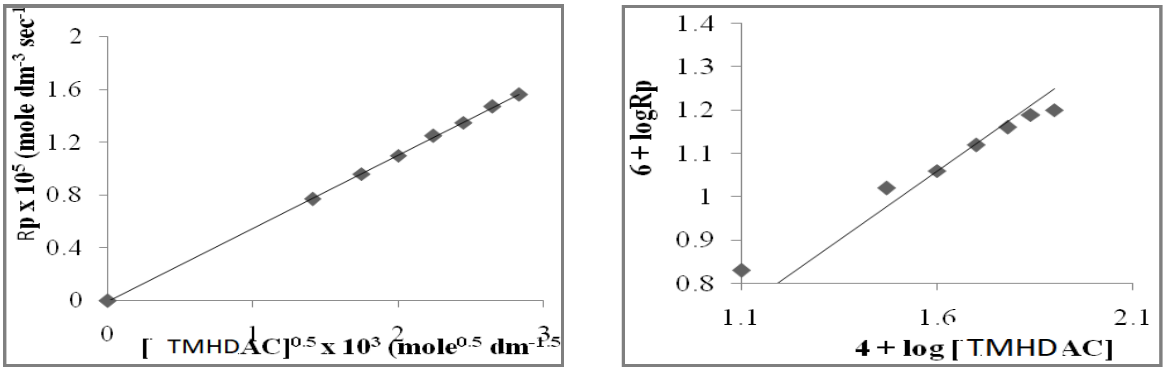
(a). [PDP]$^{0.5}$ x 10^3 vs. Rp x 10^5 (b). 4 + log [PDP] vs. vs 6 + log Rp

Figure 3. Effect of [initiator] on Rp.

Effect of [Catalyst] on the rate of polymerization (Rp): The effect of concentration of phase transfer catalyst, [TMDHAC] on Rp was studied by carrying out the reaction at 0.001 mole dm^{-3} to 0.008 mole dm^{-3} at fixed concentrations of monomer, initiator and acid. Rp was found to be increase with an increase in concentration of the phase transfer agent. A plot of Rp vs. [TMHDAC]$^{0.5}$ is linear passing through the origin confirming the above observation [Table 4 and Figure 4a]. A plot of 4 + log [TMHDAC] Vs 6 + log Rp (Figure 4b) was found to be linear passing through the origin have slope value 0.5 confirm the fractional reaction order. A similar order with respect to [PTC] has been reported for the free radical polymerization of methylmethacrylate by using the various initiator systems [15, 18, 19].

Table 4. Effect of [catalyst] on Rp

[TMHDAC] x 10^3 (mole dm^{-3})	[TMHDAC]$^{0.5}$ x 10^3 (mole $^{0.5}$ dm$^{-1.5}$)	4 + log [TMHDAC]	Rp x 10^5 (mole dm^{-3} sec $^{-1}$)	6 + log Rp
1	1.000	1.0000	0.64	0.8062
2	1.414	1.1010	0.78	0.8921
3	1.730	1.4771	0.96	0.9823
4	2.000	1.6021	1.14	1.0569
5	2.240	1.6990	1.26	1.1003
6	2.450	1.7782	1.35	1.1303
7	2.650	1.8451	1.46	1.1644
8	2.830	1.9031	1.56	1.1931



(a). [TMHDAC]$^{0.5}$ x 10^3 vs. Rp x 10^5 (b). 4 + log [TMHDAC] vs. 6 + log Rp

Figure 4. Effect of [catalyst] on Rp.

Effect of temperature on the rate of polymerization (Rp): The effect of temperature on the rate of polymerization (Rp) was studied at different temperatures in the range of 40°C to 60°C at a fixed concentration of monomer, initiator, catalyst and acid. Rp was found to increase with an increase in temperature (Table 5 and Figure 5). The same kinetical observations were reported by Rasmussen *et al*. [6, 7] for the polymerization of acrylonitrile using the $K_2S_2O_8$-crown ethers. The same order was also proposed for the polymerization of vinyl monomers in the various initiator systems [17, 22, 26]. From a plot of 8 + log Rp vs.1/T, Energy of activation was calculated (Ea = 5.26 k Cal mole^{-1}). From the Arrhenius plot, the various thermodynamic parameters were also calculated, (ΔH = 3.98 kcal mole^{-1}, ΔS = -0.0621 kcal mole^{-1} K^{-1} and ΔG = 24.04 kcal mole^{-1}).

Table 5. Effect of Temperature on Rp

T°C	TK	$\frac{1}{T}$ x 10^3 (K^{-1})	Rp x 10^5 (mole dm^{-3}sec^{-1})	8 + log Rp
40	313	3.1949	3.13	3.4955
45	318	3.1447	3.36	3.5263
50	323	3.0959	4.02	3.6000
55	328	3.0488	4.63	3.6656
60	333	3.0030	5.32	3.7259

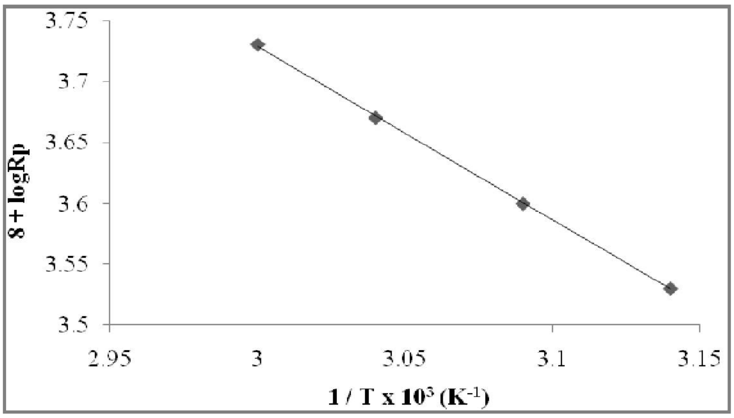


Figure 5. Effect of Temperature on Rp.

Effect of solvent polarity on the rate of polymerization (Rp): The effect of solvent on Rp was examined by carrying out the polymerization in three different solvents, viz., ethyl acetate, cyclohexane and toluene (Table 6). It was found that the rate of polymerization decreased in the following order - Ethylacetate > Cyclohexane > Toluene.

Table 6. Effect of Solvent polarity on Rp

Solvent	Rp × 10^5 (mole dm^{-3} sec^{-1})
Ethylacetate	4.02
Cyclohexane	3.81
Toluene	3.61

Since, the quaternary peroxydiphosphate $[Q_2P_2O_8]^{2-}$ (or) $[QH_2P_2O_8]^-$ is an ionic pairs, it may be transferred to the organic medium to a greater extent with the increasing dielectric constant of the medium. In addition, the increase in dielectric constant of the medium would favor separation of ions and enhance the rate of propagation and retard the rate of termination. Hence, there will be an increase in the rate of polymerization with an increase in dielectric constant of the organic medium [23, 24].

Effect of acid and ionic strength on rate of polymerization (Rp): A variation in acid and ionic strength has no significant change in the rate of polymerization.

Mechanism and rate law: To explain the experimental observations a suitable mechanism has been proposed. PTC transfers the reactive species, PO_4^{2-}, from the aqueous to the organic phase containing the monomer and initiates the reaction. Acrylonitrile induces the decomposition of the initiator and produced radial ions. This initiation is followed by the propagation and termination.

Phase Transfer

$$Q^{+}_{(w)} + [H_3P_2O_8^{-}]_{\,w)} \overset{K}{\rightleftarrows} \underset{\text{Complex}}{[Q.H_3P_2O_8]_{(o)}} \qquad ...(1)$$

Decomposition of Complex

$$[Q.H_3P_2O_8]_{(O)} + e^{\theta}_{solvent} \xrightarrow{kd} Q^{+} + 3H^{+} + 2PO_4^{\bullet 2-} \qquad …(2)$$

(Where $PO_4^{\bullet 2-} = R^{\bullet}$)

Initiation

$$R^{\bullet} + M \xrightarrow{ki} RM_1^{\bullet} \qquad ...(3)$$

Propagation

$$RM_1^{\bullet} + M \xrightarrow{kp} RM_2^{\bullet}$$

$$RM^{\bullet}_{(n-1)} + M \xrightarrow{kp} RM_n^{\bullet} \qquad …(4)$$

Termination

$$RM_n^{\bullet} + RM_n^{\bullet} \xrightarrow{k_t} \text{Polymer} \qquad …(5)$$

Applying the steady state approximation to the species $R^{\bullet}$ and $RMn^{\bullet}$ we can derive the following expression for the rate of polymerization.

Considering the equation (1),

$$[Q\ H_3P_2O_8]_{[o]} = K\,[Q^{+}]_w\,[H_3P_2O_8^{-}]_w \qquad …(6)$$

Rate of initiation

$$Ri = ki\,[R^{\cdot}]\,[M] \qquad …(7)$$

$$d[R^{\cdot}]/dt = 2kd\,[QH_3P_2O_8]_{[o]} - ki\,[R^{\cdot}]\,[M] = 0$$

$$[R^{\cdot}] = 2kd\,[Q\ H_3P_2O_8]_{[o]} /\ ki\,[M] \qquad …(8)$$

Substituting the value $[Q\ H_3P_2O_8]$ from equation (6), into the equation (8),

$$[R^{\cdot}] = 2kd\ K\ [Q^{+}]_{w}\,[H_3P_2O_8^{-}]_{w} / ki\ [M] \qquad \ldots(9)$$

Substituting for $[R^{\cdot}]$ in equation (7),

$$Ri = 2kd\ K\ [Q^{+}]_{w}\ [H_3P_2O_8^{-}]_{w}\ [M]\ [ki] / [ki]\ [M]$$

$$= 2kd\ K\ [Q^{+}]_{w}\ [H_3P_2O_8^{-}]_{w} \qquad \ldots(10)$$

Rate of termination

$$Rt = kt\ [RM_n^{\cdot}]^{2} \qquad \ldots(11)$$

At steady state, the rate of initiation is equal to the rate of termination in the free radical polymerization.

$$Ri = Rt$$

$$2kd\ K\ [Q^{+}]_{w}\ [H_3P_2O_8^{-}]_{w} = kt\ [RM_n^{\cdot}]^{2}$$

$$[RM_n^{\cdot}] = \{2kd\ K / kt\}^{1/2}\ [Q^{+}]^{1/2}\ [H_3P_2O_8^{-}]_{w}^{1/2} \qquad \ldots(12)$$

The overall rate of polymerization Rp,

$$Rp = -\,d\,[M] / dt = kp\ [RM_n^{\cdot}]\ [M \qquad \ldots(13)$$

Substituting the value $[RM_n^{\cdot}]$ from equation (12) into the equation (13)

$$Rp = -\,d\,[M] / dt$$

$$Rp = kp\ \{2kdk / kt\}^{1/2}\ [Q^{+}]_{w}^{1/2}\ [H_3P_2O_8^{-}]^{1/2}\ [M \qquad \ldots(14)$$

The total concentration of $[H_3P_2O_8^{2-}]_{total}$ ion can be given as,

$$[H_3P_2O_8^{2-}]_{total} = [H_3P_2O_8^{-}]_{w} + [Q.H_3P_2O_8]_{(o)} \qquad \ldots(15)$$

Substituting the value, $[Q.H_3P_2O_8^{-}]_{[o]}$ from the equation (6), into the equation (15),

$$[H_3P_2O_8^{-}]_{total} = [H_3P_2O_8^{-}]_{w} + K\ [Q^{+}]\ [H_3P_2O_8^{-}]_{w} \qquad \ldots(16)$$

$$[H_3P_2O_8^{-}]_{w} = [H_3P_2O_8^{-}]_{total}\ /\ 1 + K\ [Q^{+}]_{w} \qquad \ldots(17)$$

Substituting $[H_3P_2O_8^{-}]_{w}$ from equation (17) into the equation (14),

$$Rp = -d\,[M] / dt$$

$$Rp = kp\ \{2kd\ K / kt\}^{1/2}\ [Q^{+}]_{w}^{1/2}\ [H_3P_2O_8^{-}]_{total}^{1/2}\ [M]\ /\ 1 + K\ [Q^{+}]_{w} \qquad \ldots(18)$$

Equation (18), explains most of the observed kinetic data. If, $1 >> K\ [Q^{+}]_{w}$ we have,

$$Rp = -d\,[M] / dt$$

$$Rp = kp.\ \{2kd\ K / kt\}^{1/2}\ [Q^{+}]_{w}^{1/2}\ [H_3P_2O_8^{-}]_{total}^{1/2}\ [M]$$

The above equation explains the experimental observations, i.e., Rp is directly proportional to the half power of [Initiator] and [Catalyst] and unity on [monomer].

Instrumental analysis of the obtained polymer: The kinetics and the growth of the polymer PAN can be confirmed by the following instrumental analysis.

UV Spectroscopy: An UV spectrum of the sample (Figure 6) may be taken, by taking wave length (nm) along X-axis and absorbance along Y-axis. A sharp intense peak at 269 nm indicates the functional identity of the polymer. i.e., the presence of cyanide functional group attached with alkenyl group in the polymer. This can be confirmed with the spectral studies of polymers by Jack D. Graybeal [27] Manas chanda [28] and Kalsi [29].

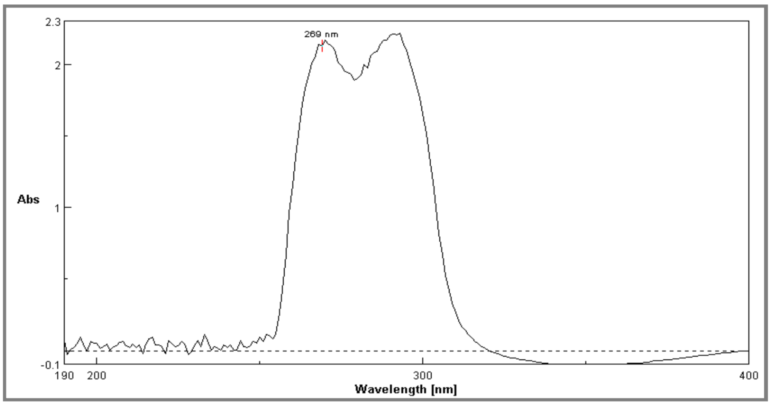


Figure 6 . UV Spectrum of PAN.

FT-IR Spectroscopy: An FT-IR spectrum of the polymer (Figure 7) can be taken along Wave number (cm^{-1}) in X-axis and % Transmittance in Y-axis. A peak at 2920cm^{-1}, which is due to the –CH stretching [27]. The peaks at 1645 cm^{-1} and 2310 cm^{-1} due to the stretching of C═C and cyanide group of the polymer [27]. The peaks at 1340-1700 cm^{-1} are due to the overtones of the combined bands [28]. Out of plane bending of the methylene group is confirmed by the peak at 1110 cm^{-1} Peaks around 2980 cm^{-1} and 2850 cm^{-1} are due to the presence of asymmetric and symmetric stretchings of the methylene group [29].

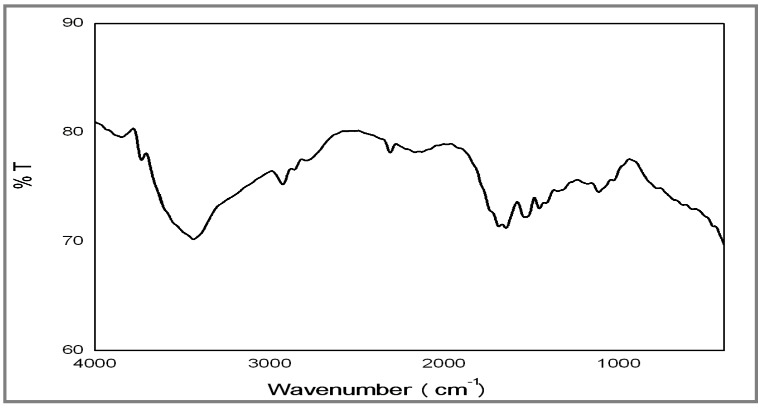


Figure 7. IR Spectrum of PAN.

^{1}H NMR Spectroscopy: A sharp intense peak in figure 8 at 2.5 ppm confirms the presence of methylene proton present in the polymer [27] and also a sharp peak at 3.4 ppm confirms the proton of the –CH group present in the polymer [29] The ^{1}H NMR Spectrum of the polymer indicates the presence of two kinds of protons present in the polymer.(methylene proton and methine proton of the vinylic group).

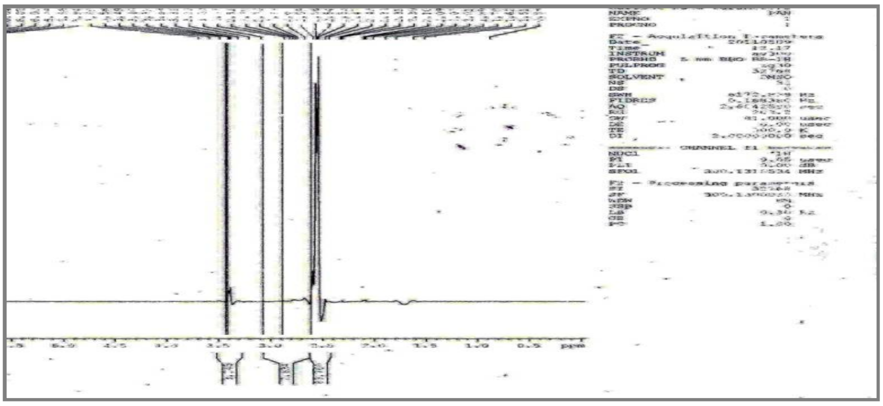


Figure 8. ^{1}H NMR Spectroscopy.

^{13}C NMR Spectroscopy: The ^{13}C NMR spectrum (Figure 9) shows a dominant peak at 40 ppm confirms the presence of methylene carbon (-CH_2) present in the polymer [27]. The peaks at 108 ppm and 118 ppm confirms the presence of methine carbon (-CH) and the carbon of the nitrile group [28]. This ^{13}C NMR spectrum of the polymer reveals the presence of three kinds of carbons present in the polymer (methylene, methine, nitrile carbons of the polymer) [29].

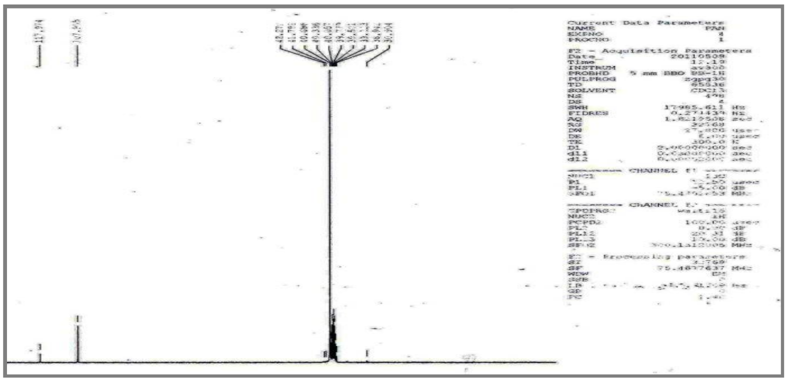


Figure 9. ^{13}C NMR Spectrum of PAN.

Viscosity measurements: The viscosity measurements of the obtained polymers can be done by using BROOKFIELD DV-II PRO-VISCOMETER instrument (Table 7).

Table 7. Viscosity measurements of the polymers

Sample	Viscosity (centipoises)
PAN1 (40°C)	1.95
PAN1 (50°C)	3.66
PAN1 (60°C)	4.23

The above results indicate that the growth as well as the viscosity of the polymers increases with increase of temperature.

APPLICATION

The results indicate that quaternary ammonium salt (TMHDAC) coupled with peroxydiphosphate (PDP) as a very good phase transfer catalyzed free radical initiator for the polymerization of oil-soluble vinyl monomers via, acrylonitrile.

CONCLUSION

Free radical polymerization of acrylonitrile using PDP as an initiator with the phase transfer agent, TMHDAC in aqueous organic diphase system was successfully performed and the studies on the rate of polymerization (Rp) over various concentrations of monomer, initiator, and catalyst and temperature variation were carried out. Rp was found to increase with an increase in concentrations of monomer, catalyst and the initiator. Based upon the kinetic studies, a suitable mechanism has been proposed which was found to explain the experimental results. Thus, with the results obtained from the lively free radical polymerization of AN using $K_4P_2O_8$ as an initiator and ethyl acetate as water insoluble solvent, the efficiency of the phase transfer catalyzed free radical polymerization of AN using PDP as an initiator and ethyl acetate as a solvent in aqueous organic bi phase system was found to be satisfactory and rich in industrial application. The growth and the characteristics of the obtained polymers can be confirmed with various instrumental studies via, UV-Spectroscopy, FT-IR Spectroscopy, ^{1}H NMR Spectroscopy, ^{13}C NMR Spectroscopy and Viscosity measurement studies. From the observed kinetic datas and the obtained results, the rate of polymerization of acrylonitrile in presence of TMHDAC coupled with PDP, the order with respect to [monomer], [PTC], [PDP] over Rp were studied and it was found to be half order dependence for the change in concentration of PTC and PDP and unity for the change in concentration of monomer. In this view, it may be concluded that quaternary ammonium salt (TMHDAC) coupled with peroxydiphosphate (PDP) as a very good phase transfer catalyzed free radical initiator for the polymerization of oil-soluble vinyl monomers via, acrylonitrile.

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