INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN CHEMISTRY AND PHARMACEUTICAL SCIENCES

(p-ISSN: 2348-5213: e-ISSN: 2348-5221)
www.ijcrcps.com

Research Article

KINETICS AND MECHANISM OF POLYMERIZATION OF N-BUTYL METHACRYLATE INITIATED BY POTASSIUM PEROXYDISULFATE –CETYL PYRIDINIUM CHLORIDE SYSTEM

DR.K. MOHAN

[2*]Professor and Head, Department of Chemistry, Thirukkoilur College of Arts and Science, Thirukkoilur -653 766
Corresponding Author: kmohan.acm@gmail.com/kmohan.acm1@gmail.com

Abstract

This paper reports the polymerization mechanism of n-Butyl Methacrylate by using Potassium Peroxydisulfate –Cetyl Pyridinium Chloride Phase transfer catalysis . This Polymerizations to be carried out at substantially lower temperatures and/or in much shorter reaction times than those previously possible with common initiators like AIBN. It was proposed to study the effect of variation in monomer concentration, Peroxydisulfate concentration, Quaternary salt concentration, hydrogen ion concentration, ionic strength and temperature on the rate of polymerization. Based on the kinetic results, suitable mechanism for the polymerization would be proposed. It was also proposed to evaluate the overall energy of activation and other thermodynamic parameters. The findings of this investigation may help in the selection of phase transfer catalysts for industrial processes and also the optimum conditions for the execution of laboratory synthesis.

Keywords: polymerization, Potassium Peroxydisulfate –Cetyl Pyridinium Chloride, Peroxydisulfate concentration.

Introduction

phase transfer catalysis is a method which allows to carry out a reaction between a substrate soluble in an organic solvent and an ionic reagent insoluble in this solvent, by using a phase transfer agent. The key factor in phase transfer catalyzed reaction is the choice of a suitable catalyst.

These factors contribute to overall process efficiency in terms of process simplification, equipment size, product and solvent purity and ease of their recovery, as well as cost saving by the elimination of the need for the expensive solvents, anhydrous strong base and oxidants needed as the alternative to PTC.

In general, all phase transfer catalyzed reactions involve at least two steps:

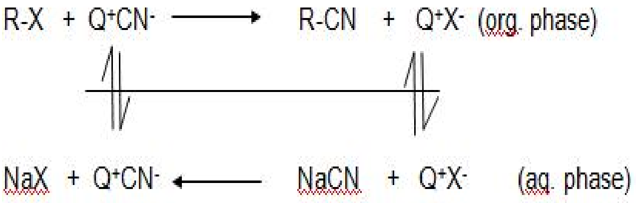
a) Transfer of one reagent from its normal phase into the second phase and

b) Reaction of the transferred reagent with the non-transferred reagent.

The following two mechanisms were proposed to explain the behavior of most of the phase transfer catalyzed reactions :

1.The Extraction Mechanism

This mechanism was proposed by Starks[27-28]. The scheme given below illustrates this mechanism :



Where, QX represents a quaternary ammonium or phosphonium salt or a crown ether alkali metal ion complex. The Q^+ is said to extract the cyanide ion from the aqueous phase into the organic phase in the form of an ion-pair (Q^+CN), via an equilibrium process. Once in the organic phase, the nucleophilic anion reacts with the substrate, RX (e.g., 1-chlorooctane) to form RCN and X^- ion.

The leaving group X^- pairs with Q^+ to form an ion pair (Q^+X^-), which may equilibrate between the two phases. If the aqueous phase is charged with an excess of the reacting anion CN^-, the Q^+ may preferentially combine with CN^- to form Q^+ CN^- which is dragged into the organic phase and another cycle is initiated.

2. The Interfacial Mechanism

This mechanism was proposed by Makosza[29-30]. According to this mechanism, a molecule of an organic substrate (R-H) in the organic phase located near the interphase but within the aqueous phase. An ion-pair, (R^-Na^+) thus formed at the boundary is insoluble in both the phases and hence remains at the interphase until the catalyst cation, Q^+draws the organic anion deep into the bulk organic phase in the form of a new ion-pair(Q^+ R^-) The original counter anion of Q^+ namely X^- is simultaneously liberated into the aqueous phase. Finally, Q^+ R^- reacts with the second reactant R'-Y to form the product R-R' and the Q^+Y^- thus formed may initiate a new catalytic cycle.

Whatever be the mechanistic scheme, the activation of the anion is due to the exchange of the paired counter cation and to the consequent solubilization of a more reactive loose ion-pair in a solvent of low polarity.

EXPERIMENTAL METHODS

REACTION VESSELS

Reaction Tubes

Polymerization studies were carried out in long Pyrex tubes (4 cm x 20 cm) of about 80 ml capacity with B-24 quick fit socket fitted with B-24 cone with a provision for inlet and outlet terminals in order to isolate the reaction mixture from the atmospheric oxygen.

Thermostat

All the experiments were conducted in a thermostat bath of 20 litre capacity. The temperature of the bath was controlled by a hot wire vacuum switch relay to an accuracy of ± 0.1°C using a toluene regulator. Water in the bath was heated electrically and stirred well by a mechanical stirrer for maintaining constant temperature throughout the bath. Experiments were carried out in the temperature range 50 – 60°C.

De-aeration Technique

Nitrogen gas used for de-aeration was freed from the traces of oxygen and other impurities by passing through four vertical glass tubes containing separately) Fieser's solution ii) Lead acetate solution iii)Potassium hydroxide solution and iv) Distilled water. Fieser's solution was prepared by dissolving 18 g of sodium hydroxide in one litre of water and then adding 150 g of sodium dithionate to the warm solution, followed by 5 g of sodium anthraquinone –β- sulphonate. It was stirred vigorously to get a clear, blood red coloured solution. The Fieser's solution was covered with a black cloth and whenever needed it was renewed as indicated by a change in colour from blood red to brown. The gas after passing through the Fieser's solution was then passed through a saturated solution of lead acetate to remove hydrogen sulphide, sulphur dioxide etc., and then through potassium hydroxide and distilled water to remove CO_2 and other water solution gaseous impurities .Before passing the purified nitrogen gas through the reaction tube, it was passed through a similar reaction tube containing monomer solution to avoid the possibility of the loss of monomer during deaeration. A constant deaeration time was used for all the experiments.

REAGENTS

Water

Double distilled water was used throughout the experiment for the preparation of reagents and solutions. Double distilled water is obtained by distilling deionized distilled water with alkaline permanganate in an all quickfit Pyrex apparatus.

Monomer

The monomer n-butyl methacrylate (Loba Chemie) was first washed with a 5% solution of sodium hydroxide to remove the phenolic inhibitor and then with a 3% solution of orthophosphoric acid to remove the basic impurities. It is then washed with water, dried over anhydrous calcium chloride and then distilled under reduced pressure under nitrogen atmosphere. The middle fraction of the distillate was used in all the polymerization experiments. The purified, distilled monomer was stored in a dark colored bottle at 5°C in a refrigerator.

Other Reagents

Cetylpyridinium chloride (Loba Chemie), potassium persulfate, potassium sulfate and sulfuric acid (SD fine) were used as received.

POLYMERIZATION TECHNIQUE

Polymerization reactions were carried out in the reaction vessels thermostated at the desired temperature (60^o C). A known amount of monomer, cetylpyridinium chloride, sulfuric acid and potassium sulfate were taken in the reaction tube and flushed with purified nitrogen gas for about 30 minutes to ensure an inert atmosphere. A calculated amount of deaerated peroxydisulfate solution thermostated at the experimental temperature was added to the reaction mixture and simultaneously a stop watch was started. The reaction tubes were then carefully sealed by rubber gaskets to ensure an inert atmosphere. The reaction was arrested by blowing air inside the tube and keeping the reaction vessel in ice cold water for some time.

The polymer was filtered out quantitatively through a crucible (G-3), washed several times with double distilled water and dried at 50 – 60°C in a vacuum oven to constant weight. The rate of polymerization was computed from the weight of the polymer formed, using the following relation.

$$R_p = 1000\ W / V\ t\ M$$

Where, W = weight of the polymer

V = total volume of the reaction mixture
t = reaction time in seconds
M = molecular weight of the monomer

By separate experiments it was confirmed that neither PDS nor CPC alone initiated polymerization under the experimental conditions employed.

ANALYSIS OF THE RESULTS

In order to estimate the limits of consistency in the results, duplicate experiments were carried out under identical conditions and it was found that the R_p values were subjected to the error limits of ± 5 %. The accuracy of the results was tested by the method of least squares.

STEADY STATE RATE OF POLYMERIZATION

Polymerization reactions were carried out at different time intervals at fixed concentrations of n-BMA, CPC, PDS, H^+ and ionic strength to arrive at the steady rate of polymerization. It has been found that at first the polymerization rate increased sharply with time, then decreases and finally attains a constant value. Steady sate rate of polymerization was found to be attained at about 3 hours (Table-1, Fig-1). To study the effects of various reaction parameters on the rate of polymerization, the polymerization was conducted for a duration of 3 hours.

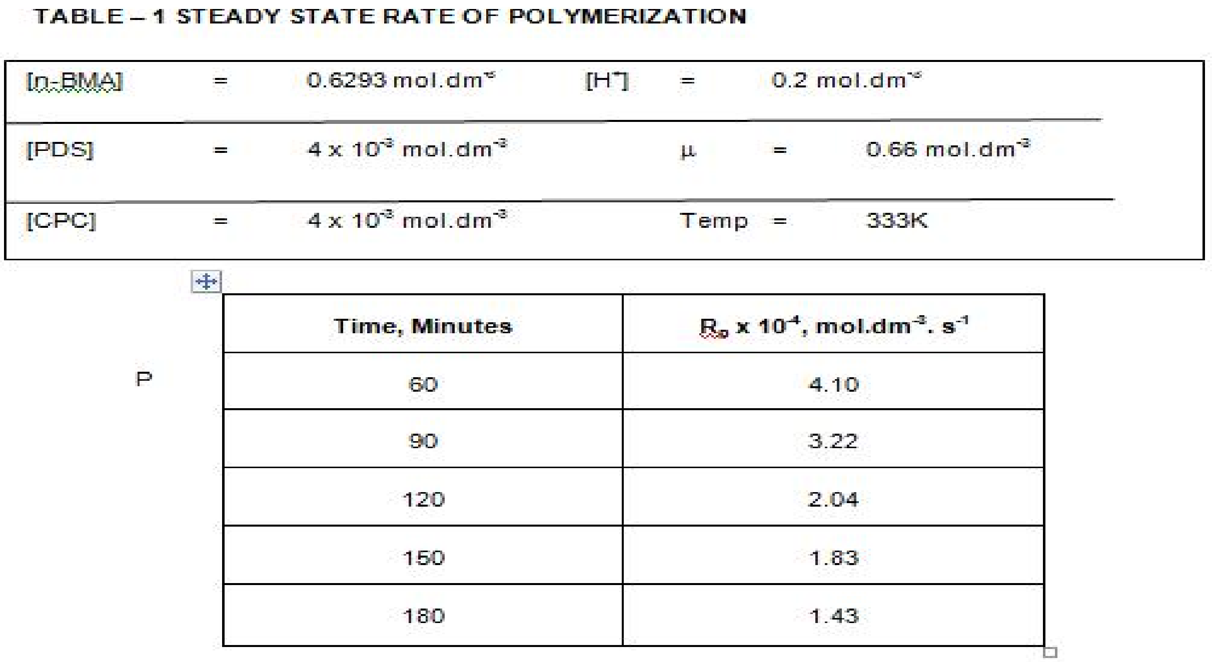


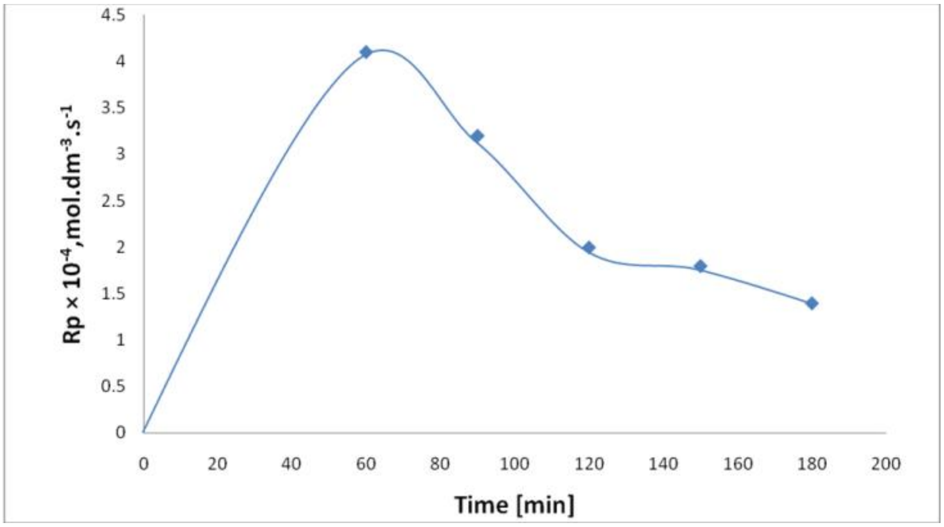
TABLE – 1 STEADY STATE RATE OF POLYMERIZATION

[n-BMA] = 0.6293 $mol.dm^{-3}$ [H^+] = 0.2 $mol.dm^{-3}$
[PDS] = 4 x 10^{-3} $mol.dm^{-3}$ μ = 0.66 $mol.dm^{-3}$
[CPC] = 4 x 10^{-3} $mol.dm^{-3}$ Temp = 333K

P

Time, Minutes	R_p x 10^{-4}, $mol.dm^{-3}$. s^{-1}
60	4.10
90	3.22
120	2.04
150	1.83
180	1.43

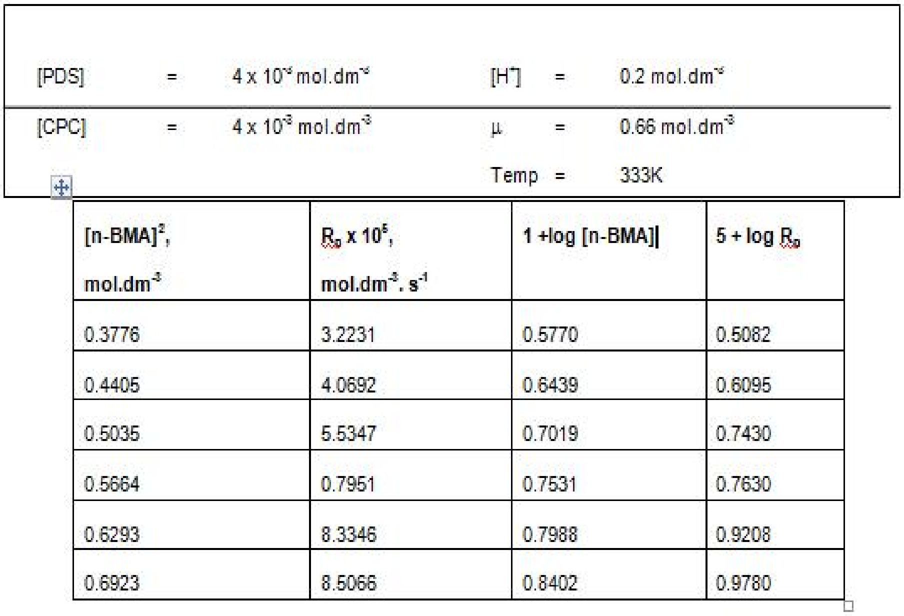
Fig.1 – Plot : $R_p \times 10^{-4}$, mol.dm^{-3}. s^{-1} Vs Time, min.



EFFECT OF [n-MBA] on R_P

To find the effect of [n-BMA] on R_p the concentration of n-BMA was varied in the range of 0.3776 – 0.6923 mol.dm^{-3} at fixed concentration of other components. R_p was found to increase with increase of [n-BMA] [Table-2]. The slope of the straight line obtained in the plot of log R_p Vs log [n-BMA] is equal to 2.0 [Fig-2]. The reaction order of 2.0 with respect to n-butyl methacrylate is further confirmed from the straight line passing through origin in the plot of R_p Vs [n-BMA] [Fig-3].

TABLE – 2 EFFECT OF VARIATION OF [n-BMA] ON R_P



[PDS] = 4×10^{-3} mol.dm^{-3} [H$^+$] = 0.2 mol.dm^{-3}

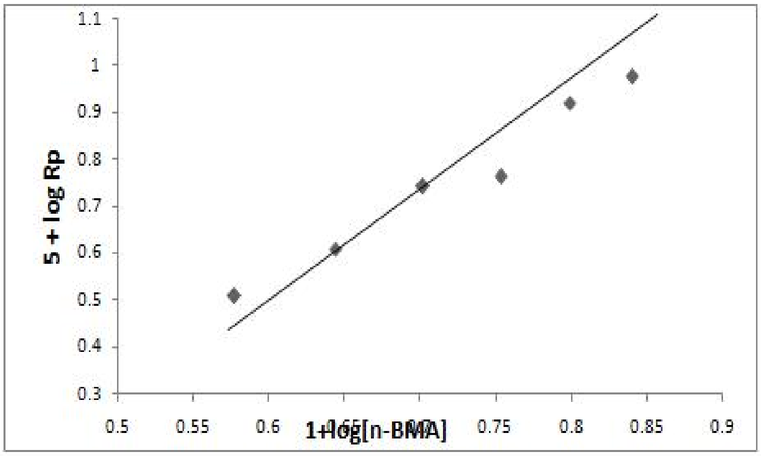
[CPC] = 4×10^{-3} mol.dm^{-3} μ = 0.66 mol.dm^{-3}

Temp = 333K

[n-BMA]^2, mol.dm^{-3}	$R_p \times 10^5$, mol.dm^{-3}. s^{-1}	1 +log [n-BMA]	5 + log R_p
0.3776	3.2231	0.5770	0.5082
0.4405	4.0692	0.6439	0.6095
0.5035	5.5347	0.7019	0.7430
0.5664	0.7951	0.7531	0.7630
0.6293	8.3346	0.7988	0.9208
0.6923	8.5066	0.8402	0.9780

Fig.2 – Plot : $5 + \log R_p$ Vs $1 + \log [\text{n-BMA}]$

Fig.3 – Plot : $R_p \times 10^5$, $\text{mol.dm}^{-3}.\ \text{s}^{-1}$ Vs [n-BMA], mol.dm^{-3}



EFFECT OF VARIATION OF [n-BMA] ON R_P

EFFECT OF [PDS] on R_P

The effect of varying the [PDS] on R_p was examined by varying [PDS] in the rage of $2.5 \times 10^3 - 5 \times 10^3$ mol.dm^{-3} at fixed [n-BMA], [CPC], $[H^+]$ and ionic strength. R_p increases with increase in the [PDS] [Table-3]. A plot of log R_p Vs log [PDS] is linear with a slope of 0.5 indicating the half order dependence of R_p on [PDS] [Fig-4]. This is supported by a straight line passing through origin in the plot of R_p Vs $[\text{PDS}]^{0.5}$ [Fig-5]. The half order dependence of R_p on initiator concentration indicates that the termination is bimolecular[78]. An important characteristic of polymerization of n-BMA is auto-acceleration or the gel-effect[79,80]. It is the autogenous increase in the rate of polymerization and molecular weight observed in media of high viscosity. This effect is more often seen in bulk and high concentration solution polymerization[81]. It is also observed in polymerization reactions involving high conversions[82].

In such cases, the reaction order with respect to initiator was reported to be greater than 0.5. An initiator rate exponent of 0.5 in the present study shows that the gel-effect is not observed in this case.

TABLE – 3
EFFECT OF VARIATION OF [PDS] ON R_P

[n-BMA] = 0.6293 mol.dm^{-3} $[H^+]$ = 0.02 mol.dm^{-3}
[PDS] = 4×10^{-3} mol.dm^{-3} μ = 0.66 mol.dm^{-3}
Temp = 333K

$[\text{PDS}] \times 10^3$, mol.dm^{-3}	$[\text{PDS}]^{0.5} \times 10^2$, $(\text{mol.dm}^{-3})^{0.5}$	$R_p \times 10^5$, $\text{mol.dm}^{-3}.\ \text{s}^{-1}$	3+log[PDS]	5+ log R_p
2.5	5.00	7.7486	0.3979	0.8891
3.0	5.48	8.1392	0.4771	0.9105
3.5	5.92	9.1811	0.5440	0.9628
4.0	6.32	9.6043	0.6020	0.9824
4.5	6.71	10.3201	0.6532	1.0136
5.0	7.07	10.8089	0.6989	1.0337

Fig.4 – Plot: 5 + log R_p Vs 3 + log [PDS]

Fig.5 – Plot: $R_p \times 10^5$, $mol.dm^{-3}.s^{-1}$ Vs $[PDS]^{0.5} \times 10^2$, $(mol.dm^{-3})^{0.5}$

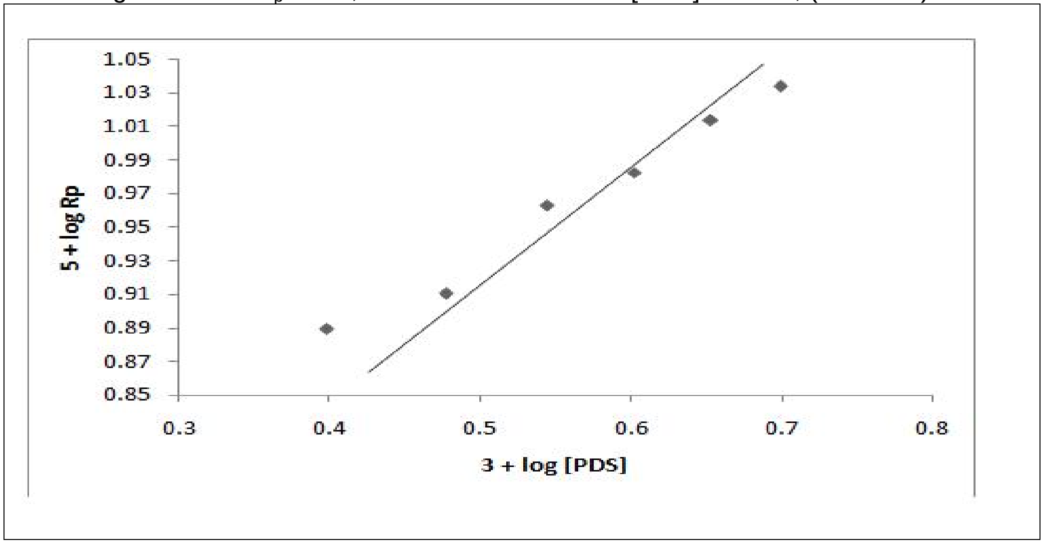


Fig.4 DEPENDENCE OF [PDS] ON R_p

This has tremendous advantages, especially in bulk or solution polymerization, in minimizing problems associated with heat dissipation. Shorter reaction times also have their obvious economic advantages. It was also observed that polymers prepared by phase transfer catalyzed free radical polymerization showed improved properties such as ten-fold increase in shear strength of copolymers derived from acrylic acid and isooctyl acrylate[73].

DISCUSSION

Reaction Mechanism and Rate Law

The kinetic features observed in the polymerization n-butyl methacrylate initiated by $K_2S_2O_8$ – CPC catalyst systems are as follows: The rate of polymerization displays,

i. a – 2nd order dependence on [n-BMA]

ii. a – 1/2 order dependence on [PDS]

iii. R_p is found to be independent of $[H^+]$ and ionic strength under the given experimental conditions.

As already explained, the monomer order greater then unity is traceable to the dependence of initiation rate on monomer concentration and also to the gel effect. For polymerizations involving primary radical terminations, the monomer and initiator exponents approach two and zero respectively. Primary radical termination being in anyway responsible for the monomer order of 2 can be a priori ruled out, since the order with respect to initiator is as high as 0.9 and not zero. The increase in initiator exponent from the classical value of 0.5 to -1.0 may be due to the operation of the gel effect, which is common in polymerization of n-butyl methacrylate in heterogeneous conditions.

The introductory chapter deals with the general aspects of phase transfer catalysis and presents a survey of the available work on phase transfer catalyzed vinyl polymerization.

The second chapter outlines the scope and object of the present investigation. It was proposed to study the kinetics of aqueous polymerization of n-butyl methacrylate with the view of finding out the dependence of rate of polymerization, R_p on variables such as [n-BMA], [PDS], [CPC], acid strength, ionic strength and temperature.

The experimental methods adopted, reaction vessels employed etc., are described in the third chapter. The descriptions of deaeration procedure and polymerization methods are also given. The kinetic data obtained are presented in the fourth chapter in the form of figures and tables.

Discussion on the experimental results and possible conclusions made are covered in the subsequent chapter. From the results obtained, it is found that in the free radical polymerization of n-butyl methacrylate using peroxydisulfate – CPC – system, the R_p depends on $[n\text{-}BMA]^{2.0}$ AND $[PDS]^{0.5}$, The activation energy E_a and other thermodynamic parameters such as $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ are calculated. A suitable mechanism is proposed to explain the experimental results.

References

1. M.Makosza, B.Serafinowa and T.Urbanski, *Chemie et Industric* (Paris), **93**, 537 (1965).
2. M.Makosza and B.Serafinowa, *Rocz.chem*., **39**, 1223 (1965).
3. N.A.Gibson and J.W.Hosking, *Aust.J.Chem*., **18**, 123 (1965).
4. M.Makosza and W.Wawrzyniewicz, *Tetrahedron Lett*., 4659 (1969).
5. M.Makosza, *Tetrahedron Lett*., 673 & 677 (1969).
6. A.Brandstron and U.Junggren, *Acta Chem. Scand*., **23**, 2204 (1969).
7. W.P.Weber and G.W. Gokel, "*Phase Transfer Catalysis in Organic Synthesis*", Springer-Verlag, Berlin (1978).
8. C.M.Starks and C.Liotta, "*Phase Transfer Catalysis : Principles and Techniques*", Academic Press, New York (1978).
9. W.E.Keller, "*Compendium of Phase Transfer Reactions and Related Synthetic Methods*", Fluka, Switzerland (1979).
10. E.V.Dehmlow and S.S. Dehmlow, "*Phase Transfer Catalysis*" ,Springer-Verlag, Weinheim (1980).
11. P.Cocange, J.Elguero and R.Gallo, *Heterocycles*, **20**, 1379 (1983).
12. H.H.Freedman, *Pure & Appl. Chem*., **58**, 857 (1986). Ref. 25, Chapter 3.
13. G.W.Gokel, P.M.Goli and R.A.Schultz, *J. Org. Chem*. **48**, 2837 (1983).
14. J.Hradil and F.Svec, *Polym. Bull*., **10**, 14 (1983).