

Phase Transfer Agent-Aided Free Radical Polymerization of Butylacrylate

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ABSTRACT

Polymerization of butylacrylate under phase transfer conditions in different organic solvent/water mixtures is studied. The kinetic approach points to the influence of the nature of the organic solvent as well as that of the volume ratio between aqueous and organic phase. The overall activation energy of the polymerization is calculated to be 70.3 kJ/mol and transfer constants C_M and C_I are found to be 3.98×10^{-5} and 2.036×10^{-4} , respectively.

Key Words: phase transfer, catalysis, polymerization, kinetics, onium salts

INTRODUCTION

The interest in polymerization of vinylic monomers under the phase transfer conditions initiated by peroxidisulphates has increased due to the possibility of extended use of lipophilic peroxidisulphate dianions to conduct free radical polymerization reactions in organic media under mild conditions [1-6].

Reports on the mechanistic aspects of the polymerization in the presence of phase transfer catalysts reveal that the initiating species is the sulphate anion radical appearing in the monomer containing the organic phase by decomposition of the peroxidisulphate transferred from the aqueous phase by the ammonium salts used as the PT agent. It might be that the decomposition of peroxidisulphate occurs in the aqueous phase and the sulphate anion radicals are transferred into organic phase by PT [7].

One should expect also that the formation of

sulphate anion-radicals occurs in both media but their concentration in the two phases will depend on the reaction conditions (volume ratio between aqueous and organic phases, nature of the organic solvent, nature of monomer, stirring of the system). All these aspects will generate a complex kinetics of the process.

The paper is concerned with kinetic studies on phase transfer agent aided free radical polymerization of butylacrylate (BuA) with $K_2S_2O_8$ as initiator and cetylpyridylammonium bromide as (Cetazol) phase transfer agent in various unstirred water/organic solvent mixtures.

EXPERIMENTAL

Materials

Commercial butylacrylate (BuA) was purified by conventional methods. Solvents (Merck and Reactivul Bucuresti) and Cetazol (Aldrich) p.a.

were used as supplied.

The polymerization was carried out in closed glass vials under nitrogen and pre-established conditions. The reaction mixtures were equilibrated at room temperature prior to polymerization. The $K_2S_2O_8$ aqueous solution containing Cetazol was mixed with organic solvent and monomer and finally purged with nitrogen. All reaction mixtures were two phase systems except that containing benzene in which, at the interface, an insoluble solid phase was formed.

The interface between the organic and aqueous phases was constant in all polymerization experiments.

Finally, the vials were immersed in a water bath thermostated at a pre-established temperature (± 0.02 °C) for a predetermined period of time.

The polymer was isolated by precipitating in a large amount of acidified (HCl) methanol and its yield calculated gravimetrically after washing and drying to constant weight.

Viscosimetry was used to determine the viscometric molecular weights by applying the relation [8]:

$$[\eta] = 6.85 \times 10^{-5} \bar{M}_v^{0.75}$$

RESULTS AND DISCUSSION

Table 1 summarizes data concerning polymerization of butylacrylate under the phase transfer conditions indicating the efficiency of Cetazol when used as the phase transfer agent

Since the reaction proceeds in a two phase system, influence by the organic solvent might be expected. By comparing the polymeric yields obtained with different solvent it may be concluded that:

-The nature of the organic solvent influences the conversion of the monomer to polymer. While water immiscible can be ordered by their dielectric

Table 1. The Influence of the Organic Solvent on Polymerization of BuA under transfer Conditions.

| Solvent | Dielectric constant ϵ | Polymer Yield | | Volume of the aqueous phase | Volume of the organic phase |
|------------------------------|--------------------------------|---------------|------------------|-----------------------------|-----------------------------|
| | | $K_2S_2O_8$ | $K_2S_2O_8 + QX$ | | |
| A) Water miscible solvent | | | | | |
| Dioxane | 2.2 | 3.35 | 77.96 | 6.0 | 11.5 |
| Acetone | 20.7 | 1.31 | 78.06 | 6.5 | 11.0 |
| Dimethyl-formamide | 38.0 | 22.71 | 49.82 | 11.5 | 6.0 |
| Tetrahydrofurane | | 3.07 | 73.96 | 6.0 | 11.5 |
| B) Water immiscible solvents | | | | | |
| Benzene | 2.28 | 0 | 5.91 | 3.5 | 14.0 |
| Ethylacetate | 6.02 | 0 | 13.58 | 3.5 | 14.0 |
| Methylene-chloride | 9.08 | 0.69 | 68.31 | 3.5 | 14.0 |
| Cyclohexanone | 18.3 | 0.28 | 84.50 | 3.5 | 14.0 |
| Methylethyl-ketone | 18.5 | 0.64 | 83.59 | 3.8 | 13.7 |

Reaction condition: [BuA] = 2.395 mol/L; $[K_2S_2O_8] = 1.42 \times 10^{-2}$ mol/L;

$[K_2S_2O_8]/[QX] = 1/2$ mol/mol; $V_w/V_o = 0.25$;

time = 70 min., T = 50 C.

QX = quaternary ammonium salt (Cetazol)

constant and polymer in the case of water miscible organic liquids. It might be that the solubility parameter of the resultant and mixtures has a more important role.

-Volume ratio between aqueous and organic phases modifies in function with the organic solvent used. If one starts with constant volume ratios of water/organic solvent/monomer (3.5:8:6), after phase transfer catalyst is added, mixtures of different phase ratios and polymer yields are obtained. Thus, in the case of DMF, the DMF-water mixture does not dissolve the monomer and separates as a dense aqueous phase. In case of the other organic solvents, part of them form the organic layer together with BuA and part forms the aqueous phase by mixing with water.

Figure 1 represents a correlation between reaction rate and the volume of the two phases. It can be seen that the variation is not the same over the entire domain of the studied values. In the absence of water, dissociation of $K_2S_2O_8$ is not possible and thus the polymerization yield is zero. For $V_w/V_o = 0.1$ to 0.3 good polymer yields are obtained, but it decreases when V_w/V_o is $0.3 \dots 0.7$.

This suggests two different mechanisms of initiation [9]. For $V_w/V_o < 0.3$ the $\log R_p - \log(V_w/V_o)$, Figure 2 gives the following dependence:

$$R_p \sim (V_w/V_o)^{0.66}$$

with the optimum results for $(V_w/V_o) = 0.25$. This ratio was further used in our syntheses.

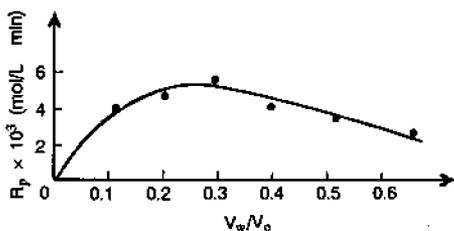


Figure 1. Polymerization rate vs volume ratio of water phase and organic phase. Reaction conditions: [BuA] = 2.395 mol/L; $[K_2S_2O_8] = 1.42 \times 10^{-2}$ mol/L; $[K_2S_2O_8]/[QX] = 1/2$ (mol/mol); $T = 50^\circ C$; time = 50 min; Ac/water = 0.25.

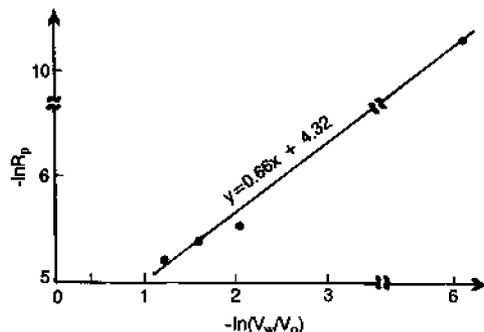


Figure 2. Dependence of $\ln R_p$ on $\ln V_w/V_o$.

These data point to the complex influence of organic solvents in such polymerization systems. Thus, the possible modification of catalysts reactivity due to molecular aggregations or change of distribution coefficients of the onium salts caused by organic solvents should not be ignored. The aggregation of the onium salts in anhydrous polar solvents is relatively high so their transfer capacity is reduced. While the water gets into organic phase, it stops formation of the aggregates so the activity of the quaternary salt improves [10]. In this way, the differences in polymer yields can be explained when reaction is carried out in dioxane and benzene, which are solvents with nearly the same dielectric constant, but with different water miscibility.

The overall activation energy was calculated from data referring dependence of the conversion on reaction time at different temperatures (Figure 3). The computed value (70.3 kJ/mol) is comparable to the values usually found in common free radical polymerizations.

Reaction orders with respect to monomer, initiator and phase transfer catalyst were obtained from data plotted in Figures 4 and 5 and verified by the intercept of line B in Figure 4.

According to experimental data, the expression for the polymerization rate, can be written as:

$$R_p = k[K_2S_2O_8]^{0.311} [QX]^{0.311} [BuA]^{1.263} (V_w/V_o)^{0.66} \quad (1)$$

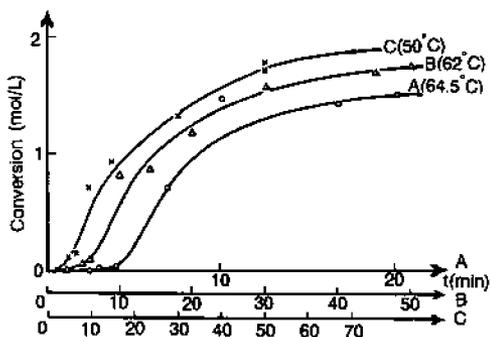


Figure 3. Conversion-time plot for polymerization of BuA under the phase transfer conditions: reaction conditions: $[BuA] = 2.395 \text{ mol/L}$; $[K_2S_2O_8] = 1.42 \times 10^{-2} \text{ mol/L}$; $[K_2S_2O_8]/[QX] = 1/2 \text{ mol/mol}$; $Ac/water = 0.25$.

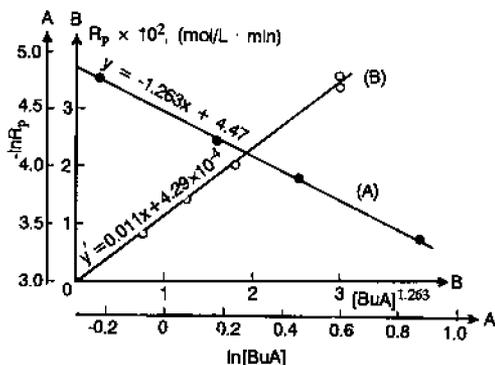


Figure 4. Dependence of polymerization rate on monomer concentration; reaction conditions: $[K_2S_2O_8] = 1.42 \times 10^{-2} \text{ mol/L}$; $[K_2S_2O_8]/[QX] = 1/2 \text{ mol/mol}$; $Ac/water = 0.25$; $T = 50^\circ\text{C}$; time = 50 min.

The influence of the chain transfer upon polymerization degree is given by:

$$DP = \frac{V_p}{V_t + \sum V_{tr}} \quad (2)$$

or:

$$\frac{1}{DP} = \frac{k_t V_p}{k_p^2 [M]^2} + C_M + C_I \frac{[I]}{[M]} + C_S \frac{[S]}{[M]} + C_P \frac{[P]}{[M]} \quad (3)$$

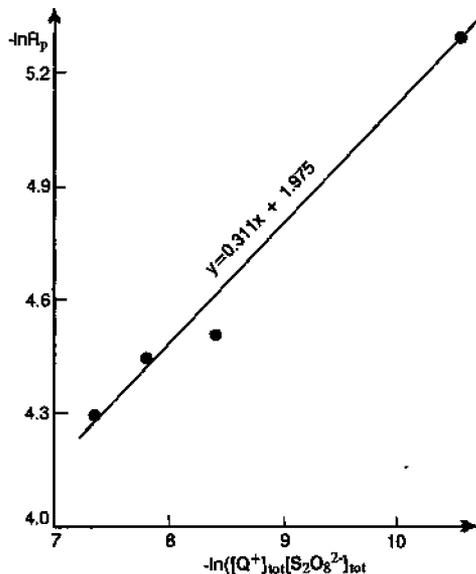
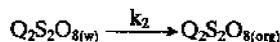
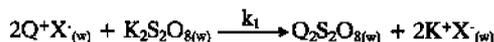


Figure 5. Dependence of polymerization rate on initiator concentration; reaction conditions: $[BuA] = 2.395 \text{ mol/L}$; $T = 50^\circ\text{C}$; time = 50 min.; $Ac/water = 0.25$.

where $[M]$, $[I]$, $[S]$ and $[P]$ denote concentrations of the monomer, initiator, solvent and polymer, respectively; C_M , C_I , C_S and C_P represent the chain transfer constants.

From dependence $(1/DP - \lambda k_t R_p / k_p^2 [M]^2 \times 10^5 \text{ vs } [I]/[M])$ (Figure 6), C_I and C_M were determined to be 2.036×10^{-4} and 3.98×10^{-5} , respectively. These values show that the chain transfer to initiator is more important [3] while the chain transfer reactions to solvent and polymer are negligible. They also do not influence significantly the termination of the process.

Concerning the initiation process, it might be expected that it starts in the organic phase where the cetylpyridylammonium persulfate is soluble, so the following mechanism can be proposed:



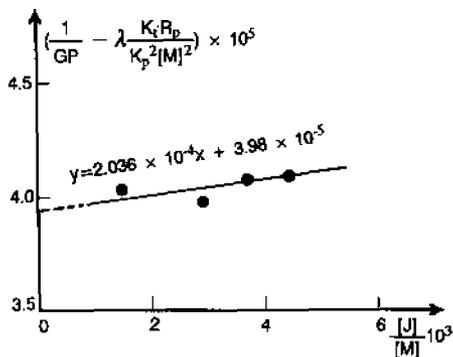
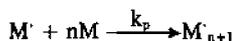
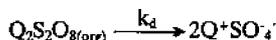


Figure 6. Evaluation of the chain transfer constants to initiator and monomer; reaction conditions: [BuA] = (2.395...0.79) mol/L; $[K_2S_2O_8] = 1.42 \times 10^{-2}$ mol/L; $[K_2S_2O_8]/[QX] = 1/2$ mol/mol; $T = 50^\circ C$; time = 50 min; Ac/water = 0.25.



The initiation rate is:

$$R_i = 2k_d[Q_2S_2O_8]_{(\text{org})} \quad (4)$$

The total amount of ammonium ions is given by:

$$[Q^+]_{\text{tot}} = [QX]_w + 2[Q_2S_2O_8]_w + 2[Q_2S_2O_8]_{(\text{org})} \quad (5)$$

and that of peroxodisulfate ions by:

$$[S_2O_8^{2-}]_{\text{tot}} = [K_2S_2O_8]_w + [Q_2S_2O_8]_w + [Q_2S_2O_8]_{(\text{org})} \quad (6)$$

From (5) and (6):

$$[Q_2S_2O_8]_{(\text{org})} = K_1K_2([Q^+]_{\text{tot}} - [KX]_w)^2(2[S_2O_8^{2-}]_{\text{tot}} -$$

$$[KX]_w)/2[KX]_w^2 \quad (7)$$

where K_1 and K_2 are equilibrium constants. Since:

$$[KX]_w = 2([Q_2S_2O_8]_w + [Q_2S_2O_8]_{(\text{org})}) \quad (8)$$

Equation (7) becomes:

$$[Q_2S_2O_8]_{(\text{org})} = K_1^{1/3}K_2[Q^+]_{\text{tot}}^{1/2} [S_2O_8^{2-}]_{\text{tot}}^{1/2}/K^* \quad (9)$$

where $K^* = V \bar{Z}(K_2 + 1)^{2/3} [1 + K_1^{1/3}(K_2 + 1)^{1/3}]$

After substitution of $[Q_2S_2O_8]_{(\text{org})}$ the rate of initiation is:

$$R_i = k_dK_1^{1/3}K_2[Q^+]_{\text{tot}}^{1/2} [S_2O_8^{2-}]_{\text{tot}}^{1/2}/K^* \quad (10)$$

Based on the above considerations the rate of polymerization becomes the expression:

$$R_p = (k_dK_1^{1/3}K_2)^{1/2}/(k_tK^*)^{1/2} \times k_p[Q^+]_{\text{tot}} [S_2O_8^{2-}]^{1/4}$$

$$[M] \quad (11)$$

from which it results that polymerization depends on both equilibrium constants in a very complex manner.

CONCLUSION

The polymerization of BuA under phase transfer conditions denotes the efficiency of Cetazol as phase transfer agent and that the reaction obeys a particular mechanism in the initiation step.

The polymerization rate is dependent on volume ratio of water and organic phases and is first order with respect to monomer.

The proposed mechanism is supported by kinetical data.

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