(9) Thermolysis of the Polycarbonates. The thermolysis reactions were monitored by both TGA and GC–MS techniques. All of the products of the thermolysis were volatile and no solid residue was observed. In the case of the GC–MS experiments, the thermolysis products were separated on appropriate capillary columns prior to mass spectral analysis. Direct MS analysis without prior separation afforded composite spectra with identical features.

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Registry No. III, 98716-64-4; (III)·(*m*-benzenedimethanol) (copolymer), 99214-22-9; (III)·(2,5-dimethyl-2,5-hexanediol) (copolymer), 99214-23-0; (III)·(*p*-benzenedimethanol) (copolymer), 99214-21-8; (III)·(1,4-butynediol) (copolymer), 99214-24-1; (III)·(*m*-benzenedimethanol)·(*p*-benzenedimethanol) (copolymer), 99214-25-2; (III)·(1,4-bis(1-hydroxyethyl)benzene) (copolymer), 99214-26-3; (III)·(*p*-benzenedimethanol)·(1,4-butynediol) (copolymer), 99214-27-4; VIa (SRU), 99214-35-4; VIb (SRU), 98716-42-8; VIc (SRU), 99214-34-3; VId (SRU), 99214-36-5; VIe (SRU), 99214-37-6; VIf (SRU), 99280-54-3; 2,5-dimethyl-2,5-hexanediol, 110-03-2; 1,1′-carbonyldiimidazole, 530-62-1; *p*-diacetylbenzene, 1009-61-6; 1,4-bis(1-hydroxyethyl)benzene, 6781-43-7.

References and Notes

(1) Taken in part from the Ph.D. thesis of F. M. Houlihan, University of Ottawa, 1984.

(2) Fréchet, J. M. J.; Eichler, E.; Ito, H.; Wilson, C. G. *Polymer* **1983**, *24*, 995.

(3) Ito, H.; Willson, C. G.; Fréchet, J. M. J.; Farrall, M. J.; Eichler, E. *Macromolecules* **1983**, *16*, 510.

(4) Bodansky, M.; Klausner, Y. S.; Ondetti, M. A. "Peptide Synthesis", 2nd ed.; Wiley: New York, 1976.

(5) Houlihan, F. M.; Bouchard, F.; Fréchet, J. M. J.; Willson, C. G. *Can. J. Chem.* **1985**, *63*, 153.

(6) Carpino, L. A. *J. Am. Chem. Soc.* **1957**, *79*, 98. Gutte, B.; Merrifield, R. B. *J. Am. Chem. Soc.* **1969**, *91*, 501.

(7) Bailey, W. J.; Griffith, J. R. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1964**, *5*, 279.

(8) Overberger, C. G.; Daly, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 3402. Daly, W. H.; Lee, C. S. "Reactions on Polymers"; Moore, J. A., Ed.; Reidel Press: Boston, 1973.

(9) Choppin, A. R.; Rogers, J. W. *J. Am. Chem. Soc.* **1948**, *70*, 2967.

(10) Woodward, R. B.; Heusler, K.; Gosteli, H.; Naegeli, P.; Oppolzer, W.; Ramage, R.; Ranganathan, S.; Vorbrugen, H. *J. Am. Chem. Soc.* **1966**, *88*, 852.

(11) Staab, H. A.; Mannschreck, A. *Chem. Ber.* **1962**, *95*, 1284. Staab, H. A. *Justus Liebigs Ann. Chem.* **1951**, *609*, 75.

(12) Corey, E. J.; Winters, R. A. E. *J. Am. Chem. Soc.* **1963**, *85*, 2677. Nagabhuschan, T. L. *Can. J. Chem.* **1970**, *48*, 383.

(13) Under a variety of reaction conditions such as phase-transfer catalysis or base catalysis with alkoxide generated from sodium and the diol, pinacol reacts with the carbonylimidazolide of benzyl alcohol to afford the cyclic carbonate, imidazole, and benzyl alcohol.

Mechanism of Phase-Transfer-Agent-Aided Free Radical Polymerization Using Potassium Peroxydisulfate Initiator and Tetrabutylammonium Bromide Phase-Transfer Agent

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ABSTRACT: The kinetics of the phase-transfer-agent-aided free radical polymerization of styrene has been investigated at 60 °C by using $K_2S_2O_8$ initiator, tetrabutylammonium bromide (Bu_4NBr) phase-transfer agent, and o-dichlorobenzene solvent. The rate of polymerization was found to be proportional to $[K_2S_2O_8]^{1/2}\cdot[Bu_4NBr]^{1/2}$ and to (volume of the aqueous phase)$^{1/2}$ at constant volume of the organic phase. Analysis of the organic phase showed that the extent of phase transfer of the divalent $S_2O_8^{2-}$ is greater than that of the monovalent bromide ion, although the amount transferred is very small. The kinetic results fit in a polymerization mechanism that considers the phase-transferred $SO_4^{-}\cdot$ ion radical as the predominant initiating species instead of the phase-transferred $S_2O_8^{2-}$ acting as the principal initiator. The end-group analysis by dye extraction test indicated the presence of $SO_4^{-}Bu_4N^{+}$ end groups in the polymers.

Introduction

There has been considerable interest in recent years in phase-transfer-agent-aided free radical polymerization of vinyl monomers using water-soluble peroxydisulfates as initiators and crown ethers or quaternary ammonium salts (QX) as phase-transfer (PT) agents.[1-6] The mechanism for the rapid polymerization in the presence of PT agents that seems obvious involves the transfer of the peroxydisulfate anion from the aqueous phase to the monomer-containing organic phase by PT agents (eq 1), where the former initiates polymerization following its decomposition to sulfate anion radical (eq 2).[1-3] For the quaternary PT agent this mechanism may be symbolically written as follows:

$$Q^{+}{}_{w} + X^{-}{}_{w} \overset{K_x}{\rightleftharpoons} Q^{+}X^{-}{}_{o} \tag{1}$$

$$2Q^{+}{}_{w} + S_2O_8{}^{2-}{}_{w} \overset{K_p}{\rightleftharpoons} Q_2{}^{+}S_2O_8{}^{2-}{}_{o} \tag{2}$$

$$Q_2{}^{+}S_2O_8{}^{2-}{}_{o} \xrightarrow{k_d} 2Q^{+}SO_4{}^{-}\cdot{}_{o} \tag{3}$$

$$Q^{+}SO_4{}^{-}\cdot{}_{o} + \text{monomer }(M)_{o} \rightarrow Q^{+}\ {}^{-}O_3SO\text{-}\dot{M}_{o} \text{ etc.} \tag{4}$$

where X^- is Cl^-, Br^-, HSO_4^-, etc. and the subscripts o and w refer to the organic phase and aqueous phase, respectively. In the reaction scheme the quaternary salts are assumed to be present as ion pairs in the organic phase. This mechanism has been proposed even though it was recognized that the phase transfer of divalent anions, in general, is notoriously difficult.[3,7]

A kinetic study of the polymerization reaction would help unravel the mechanism. This work was undertaken with this end in view. Styrene has been used as the monomer and Bu_4NBr as the PT agent.

While this work was in progress a kinetic study with much the same objective as the present work was reported by Jayakrishnan and Shah.[5] However, in their work the pH and ionic strength of the reaction media were not kept constant in the series of experiments designed to study the dependence of rate of polymerization (R_p) on the concentration of the initiator or the PT agents. These are essential requirements for a kinetic study using peroxydisulfate, as the rate of decomposition of the latter depends on the pH of the media.[8] The equilibrium concentration of the species involved in the various equilibria (eq 1 and 2) would also be sensitive to ionic strength variation. Furthermore, although these workers provided evidence against phase transfer of $Q_2S_2O_8$, the mechanism proposed by them involved the phase-transfer step (eq 2) and thus considered whatever little $Q_2S_2O_8$ transferred to the organic phase (either in the bulk phase or in water solubilized in the oil phase) as the sole initiator.

Experimental Section

Styrene was washed three times with 5% NaOH solution and then with water, dried over $CaCl_2$, and distilled under reduced pressure. The middle fraction of the distillate was used.

Potassium peroxydisulfate (E. Merck) was purified by crystallization thrice from water. The crystals were dried at room temperature in a vacuum desiccator. Bu_4NBr and Aliquat 336 (tricaprylylmethylammonium chloride) are Aldrich products and used as received. Potassium bicarbonate, potassium sulfate, potassium bromide, and other chemicals were analytical reagent-grade materials. The solvents *o*-dichlorobenzene (DCB) and 1,2-dichloroethane were washed with water, dried over $CaCl_2$, and distilled. Aliquat peroxydisulfate ($AQ_2S_2O_8$) was prepared following the method of Rasmussen and Smith[3] with a minor modification. A solution of Aliquat 336 (2×10^{-2} M) in petroleum ether (boiling range 40–60 °C) was shaken with a saturated aqueous solution of excess $K_2S_2O_8$, whereby $AQ_2S_2O_8$ separated as an intermediate layer. The aqueous layer was drawn off. The process was repeated two more times. The $AQ_2S_2O_8$ layer was then drawn off and diluted with CH_2Cl_2. The solution was washed with water three times to remove any entrapped $K_2S_2O_8$. It was then dried over molecular sieves (Linde 3A) and CH_2Cl_2 removed under reduced pressure. An estimation of peroxydisulfate in the material showed it to be 99% pure.

Polymerization was carried out with stirring in three-necked flasks under a nitrogen atmosphere at 60 °C. The stirring rate was approximately the same (ca. 800 rpm) in all experiments. At the desired time samples were withdrawn under nitrogen pressure, and the polymer was precipitated into methanol to which a few drops of concentrated HCl were added in order to coagulate the colloidal polymer completely. Acid was avoided when polymers were needed for sulfate end-group analysis to eliminate the possibility of the hydrolysis of sulfate group under acidic condition.[9] The polymer yield was determined gravimetrically.

Solution polymerization using $AQ_2S_2O_8$ initiator was carried out in sealed ampules. Before the solutions were sealed, they were degassed through three freeze–thaw cycles in a high-vacuum line. $AQ_2S_2O_8$ is highly soluble in CH_2Cl_2 but sparingly in DCB. For the preparation of a stock solution of $AQ_2S_2O_8$ a 1:10 (v/v) mixture of CH_2Cl_2/DCB was therefore used.

Viscosity-average molecular weights ($\bar{M}_v$) were determined with solutions of polymers in a solvent mixture of toluene (90% by volume) and methanol at 25 °C using K and α values of 10.4×10^{-3} mL/g and 0.715, respectively.[10] It was expected that methanol would eliminate any aggregation of polymer molecules through sulfate end groups.[11,12] It was later found that, unlike potassium polystyrene sulfate, the tetrabutylammonium polystyrene sulfate prepared in this work is not prone to association in hydrocarbon solvents such as toluene.[13]

Number-average molecular weights ($\bar{M}_n$) were determined in THF with an HP 501 high-speed membrane osmometer using 0–8 membranes.

End-Group Analysis

For end-group analysis the polymers were purified by dissolution in benzene, filtration, and precipitation into methanol. The procedure was repeated three times.

The dye extraction and extrapolation method of end-group analysis was used in which methylene blue (MB) dye was extracted from its solution in 0.01 N H_2SO_4 into an organic diluent containing the polymer sulfate as extractant. The extraction process may be represented by the equilibrium

$$\sim OSO_3^- M^+_o + MB^+_w \overset{K_E}{\rightleftharpoons} \sim OSO_3^- MB^+_o + M^+_w \quad (5)$$

where the subscripts o and w refer to the organic and aqueous phases, respectively. The diluent was chloroform containing 2% ethanol. The method has been previously described.[14,15] This method requires that the concentration of monomeric MB in the aqueous phase that is in equilibrium with the dye extracted into the organic phase be determined (eq 5). To this end, an approach different from that previously used was adopted. Equation 6 quantitatively describes dye extraction[14]

$$\frac{1}{A_o} = \frac{1}{\epsilon_{RD} Cl} + \frac{[M^+]_w}{\epsilon_{RD} Cl K_E [MB^+]_w} \quad (6)$$

where M^+ may be H^+ or any other univalent cation, A_o is the absorbance of the organic phase in a cell of optical path length l at λ_{max} = 655 nm, C is the sulfate group concentration, and ϵ_{RD} is the molar absorbancy index of the dye–polymer ion pair, which has a value of 9.07×10^4 L mol^{-1} cm^{-1}. A fixed concentration of polymer solution is equilibrated with varying concentrations of MB in 0.01 N H_2SO_4. The plot of $1/A_o$ vs. $1/[MB^+]_w$ yielded a straight line. From the intercept of the line at $1/A_o$ axis C was determined. The average number of sulfate end groups per polymer molecule ($\bar{n}$) was calculated with eq 7

$$\bar{n} = C\bar{M}_n / W_p \quad (7)$$

where W_p is the weight of the polymer used in the estimation in g/L units.

In this plot monomeric $[MB^+]_w$ is used. However, MB undergoes aggregation in aqueous solutions even at low concentration levels. An indirect method was therefore used to determine the monomeric $[MB^+]_w$. MB exists as a monomer in ethanol–water mixtures that contain at least 80% (by volume) of the former.[16] The total concentration of MB in the aqueous phase was therefore estimated by diluting an aliquot with absolute ethanol and measuring the absorbance of the solution ($\epsilon_{MB} = 9.08 \times 10^4$ L mol^{-1} cm^{-1}). The monomeric $[MB^+]_w$ was then calculated from this total value by using a dimerization constant value 5.9×10^3 L mol^{-1} given by Bergman et al.[17]

Estimation of Phase-Transferred Quaternary Salts

Bu_4NBr_o and $(Bu_4N)_2S_2O_{8\,o}$. The total amount of phase-transferred quaternary ammonium salts was estimated by volumetric titration using $NaBPh_4$ as titrant.[18] The phase-transferred peroxydisulfate was determined separately in the following way using an iodometric method. Control experiments showed that both Bu_4NBr and $(Bu_4N)_2S_2O_8$ could be quantitatively back-extracted from

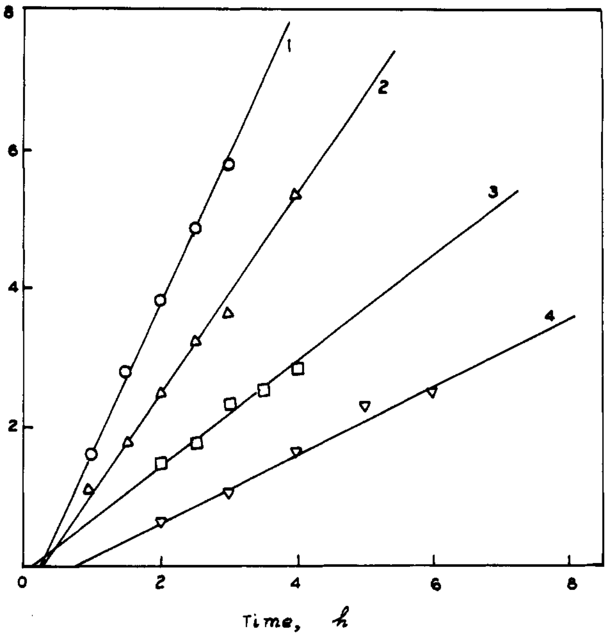

Figure 1. Plot of percent conversion against time at 60 °C. Recipe: [styrene] = 4.31 M in o-dichlorobenzene; [Bu_4NBr] = 0.0185 M; $KHCO_3$ = 2% (w/v); ionic strength = 0.274 maintained by K_2SO_4; V_o/V_w = 1; [$K_2S_2O_8$] are 0.0185, 0.0093, 0.0037, and 0.0019 M for curves 1–4, respectively.

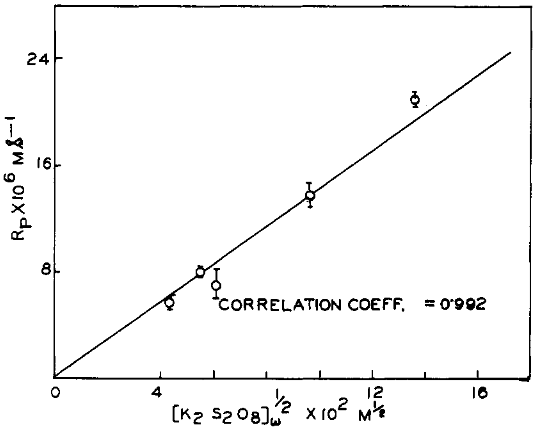

Figure 2. Dependence of R_p on $K_2S_2O_8$ concentration. Recipe as in Table I.

the organic phase (1:1 mixture of o-dichlorobenzene and toluene) into water. Accordingly, an aliquot (10 mL) was back-extracted with three 20-mL portions of water. The extracts were quantitatively transferred into an Erlenmeyer flask. The standard iodometric method for persulfate estimation cannot be used in presence of Q^+ ion because it precipitates as QI_3, which reacts only sluggishly with thiosulfate ion. The Q^+ ions were therefore precipitated with $NaBPh_4$ in a stoichimetric quantity as determined from the estimation of the total Q salts in the organic phase described above. The precipitated $QBPh_4$ was removed by filtration and washed. The $S_2O_8^{2-}$ ion in the combined filtrate and washings was then titrated iodometrically by following the standard method.[19] Control experiments show that the method gives results with a relative error of 2%.

Results and Discussion

When a suspension of styrene in water is heated in the presence of $K_2S_2O_8$ initiator, polymerization of styrene takes place (ca. soapless emulsion polymerization). However, polymerization proceeds at enhanced rates in the organic phase when a PT agent is added in the medium.

Table I

Rates and Degrees of Polymerization at Fixed [Bu_4NBr] and Varying [$K_2S_2O_8$][a]

[$K_2S_2O_8$], M	$R_p \times 10^5$,[b] M s^{-1}	$\bar{P}_v \times 10^{-3}$
0.0185	2.10 ± 0.05	1.46
0.0093	1.37 ± 0.09	1.53
0.0037	0.70 ± 0.11	2.42
0.0030	0.80 ± 0.02	
0.0019	0.57 ± 0.05	2.81

[a] Solvent is o-dichlorobenzene, [styrene] = 4.31 M, [Bu_4NBr] = 0.0185 M, aqueous phase buffered by $KHCO_3$ (2% w/v), ionic strength = 0.274 maintained by adding K_2SO_4, V_o/V_w = 1, temperature is 60 °C. [b] Values corrected for R_p due to $K_2S_2O_8$ alone.

Table II

Rates and Degrees of Polymerization at Fixed [$K_2S_2O_8$] and Varying [Bu_4NBr][a]

[Bu_4NBr], M	overall[b] R_p × 10^5, M s^{-1}	$\bar{P}_v$ × 10^{-3}	R_p' × 10^5,[c] M s^{-1}	excess[d] R_p × 10^5, M s^{-1}
0.025	2.69 ± 0.17	1.03	0.92	1.77 ± 0.17
0.015	2.07 ± 0.05	1.07	0.58	1.49 ± 0.05
0.010	1.77 ± 0.06	1.54	0.39	1.38 ± 0.06
0.0075	1.39 ± 0.07	1.38	0.29	1.10 ± 0.07
0	0.48 ± 0.03			

[a] Solvent is o-dichlorobenzene, [styrene] = 4.31 M, [$K_2S_2O_8$] = 0.037 M, aqueous phase buffered by $KHCO_3$ (2% w/v), ionic strength = 0.348 maintained by adding KBr, V_o/V_w = 1, temperature is 60 °C [b] Actually observed values. [c] Estimated R_p due to phase-transferred $Q_2S_2O_8$. [d] Column 2 − column 4.

Table III

Amount of Peroxydisulfate and Quaternary Ion Transported to the Organic Phase[a]

[$K_2S_2O_8$]$_{w,init}$ × 10^3, M	[Bu_4NBr]$_{w,init}$ × 10^3, M	[$(Bu_4N)_2S_2O_8$]$_o$ × 10^3, M	[$(Bu_4N)_2S_2O_8$]$_o$ % of total $S_2O_8^{2-}$	K_p, M^{-2}	[Bu_4NBr]$_o$ × 10^3, M
37	37.0	0.910	2.45	20.37	0.21
37	25.0	0.440	1.19	20.69	0.11
37	12.5	0.127	0.34	22.97	
37	7.5	0.039	0.11	19.16	

[a] Recipe: 75 mL organic phase consisting of 1:1 (v/v) mixture of o-dichlorobenzene and toluene; 75 mL aqueous phase buffered by $KHCO_3$ 2% (w/v), ionic strength = 0.348 maintained by KBr at a temperature of 60 °C.

Figure 1 shows some representative plots of percent conversion vs. time for the polymerization of styrene. The polymerization was preceded by an induction period, which presumably occurs due to the incomplete removal of oxygen from the polymerizing system by nitrogen purge. The plots yield straight lines, and from their slopes values of R_p were obtained. Figure 2 shows that at a fixed concentration of Bu_4NBr, viz. 0.0185 M, R_p was proportional to the square root of the $S_2O_8^{2-}$ concentration over the range 0.0019–0.0185 M. It should be noted that in these experiments the ionic strength of the aqueous phase was maintained constant at 0.274 with the help of K_2SO_4, and the medium was buffered by $KHCO_3$ (2% w/v). The rate data are given in Table I. From Figure 3 it is evident that at the fixed concentration of $K_2S_2O_8$, 0.037 M, R_p (corrected for the value in absence of Bu_4NBr) was proportional also to the square root of the Bu_4NBr concentration over the range 0.0075–0.025 M. The dotted line in Figure 3 refers to the actually observed R_p. The full line in the same figure refers to the R_p data obtained by subtracting the R_p contributed by phase-transferred $Q_2S_2O_8$ from the actually observed R_p (see later). The rate data are given in Table II.

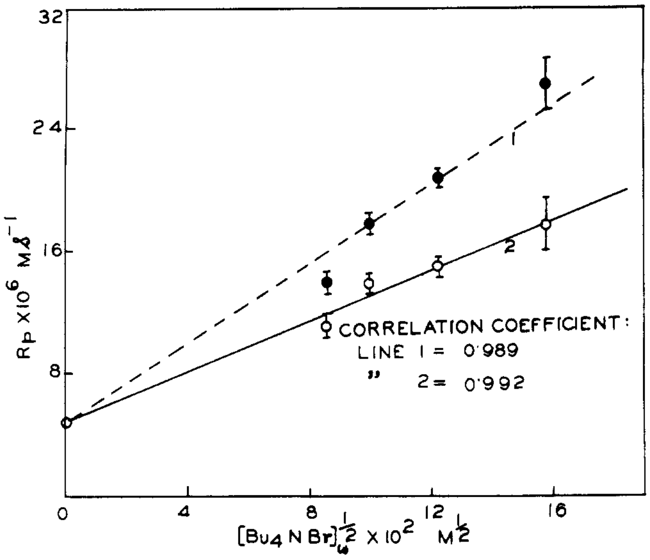

Figure 3. Dependence of R_p on Bu_4NBr concentration. Recipe as in Table II. Dotted line refers to the actually measured R_p data, full line refers to R_p data corrected for contribution due to phase-transferred $Q_2S_2O_8$.

The amount of quaternary salts extracted into the organic phase is reported in Table III for control experiments simulating that used in polymerization experiments (quaternary variation series) described above (Table II). In these control experiments styrene was replaced by toluene and 1:1 (v/v) mixtures of *o*-dichlorobenzene and toluene were stirred for 2 h at 60 °C with equal volumes of aqueous solutions having the same recipes used for the polymerizations reported in Table II and Figure 3. The organic phases were then analysed for $(Bu_4N)_2S_2O_{8\,o}$ and Bu_4NBr_o. The data in Table III lead to some important conclusions: (i) The phase transfer of peroxydisulfate (a divalent anion) is more facile than the transfer of the monovalent bromide ion. The higher the charge and smaller the size of an anion, the greater is its degree of hydration and the less its tendency to be phase transferred.[7] The charge-to-volume ratio of the persulfate anion must therefore be less than that of bromide ion. However, the amount of phase-transferred $S_2O_8^{2-}$ is, at most, 2.5% of the total $S_2O_8^{2-}$ anion available in the system under the experimental conditions reported in Table III. (ii) The amount of $S_2O_8^{2-}$ phase transferred is proportional to the square of the initial aqueous phase concentration of Bu_4NBr, as shown in Figure 4.

From a treatment of equilibria (1) and (2) on the basis of a material balance approach[14] it may be easily shown that

$$K_p = \frac{C(1 + K_x[X^-]_w)^2}{(C_i - 2C)^2[S_2O_8^{2-}]_w} \tag{8}$$

where $C_i = [Q^+]_{w,init}$ and $C = [Q_2S_2O_8]_o$. The activity coefficients of the various species were assumed constant because the ionic strength has been maintained constant. Therefore, replacement of activity by concentration in eq 8 would yield a constant K_p value valid for the particular ionic strength used. The K_p values so measured are indeed constant (Table III). Furthermore, since C is much less than C_i (vide Table III), we may write

$$C = \frac{K_p C_i^2[S_2O_8^{2-}]_w}{(1 + K_x[X^-]_w)^2} \tag{9}$$

In eq 9 $[X^-]_w$ may be considered constant because $[QX]_o$ is negligibly small compared to the total QX used and $[X^-]$ was maintained constant in all the experiments reported in Table III by using KBr. From eq 9 it follows that at constant $[X^-]_w$, C would be proportional to the peroxydisulfate concentration and to the square of the quaternary ammonium ion concentration. The latter is substantiated by the data plotted in Figure 4. These results support the premise that the quaternary salts exist as ion pairs in the organic phase (vide eq 2).

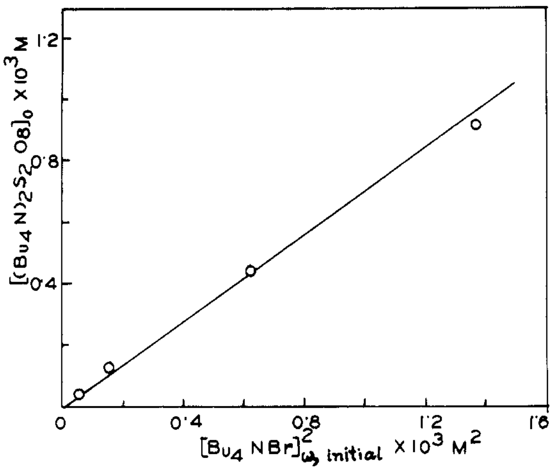

Figure 4. Phase-transferred $(Bu_4N)_2S_2O_8$ as a function of Bu_4NBr concentration. Recipe as in Table III.

For a free radical polymerization involving mutual bimolecular termination of polymer radicals, R_p is proportional to the square root of the initiator concentration. If the mechanism (eq 1–4) is operative the initial R_p should be proportional to the initial $[Bu_4NBr]_w$ and to the initial $[K_2S_2O_8]_w^{1/2}$. But the present work found the rate law to be

$$R_p \propto [K_2S_2O_8]_w^{1/2}[Bu_4NBr]_w^{1/2} \tag{10}$$

Contribution of the Phase-Transferred $Q_2S_2O_8$ to R_p. A direct check of the mechanism (eq 1–4) would be to verify if the phase-transferred $Q_2S_2O_8$ could account for the observed R_p. Rasmussen and Smith[3] reported that in organic solvents $Q_2S_2O_8$ decomposes at a very fast rate, which could be as high as 20 times the rate in aqueous medium at 60 °C, and that the rate of decomposition (R_d) is little influenced by the structure of the Q^+ ion. It should be noted however that the increased R_d in organic solvents may be due to induced decomposition of $Q_2S_2O_8$ caused by the solvent radicals which are produced by the abstraction of the H atom from the solvent molecule by $SO_4^{-}\cdot$. This latter reaction may be prevented in the presence of a monomer that reacts with $SO_4^{-}\cdot$ at much faster rates, and the resulting polymer radical may not cause induced decomposition.[20]

Figure 5 shows that by using $AQ_2S_2O_8$ initiator in *o*-dichlorobenzene the square root law $R_p \propto [\text{initator}]^{1/2}$ is obeyed, proving the absence of any induced decomposition of $Q_2S_2O_8$. R_p may be expressed as

$$R_p = (2k_d[Q_2S_2O_8])^{1/2}k_p[M]/(2k_t)^{1/2} \tag{11}$$

For styrene polymerization $(2k_t)^{1/2}/k_p = 40\ M^{1/2}s^{1/2}$ at 60 °C.[21] The data in Figure 5 coupled with eq 11 yields $k_d = 0.81 \times 10^{-5}\ s^{-1}$, which is only 1.7 times as large as the k_d value in aqueous medium viz., $0.48 \times 10^{-5}\ s^{-1}$ (calculated from the data given in ref 8).

Estimated R_p due to the phase-transferred $Q_2S_2O_8$ for the quaternary variation series experiments is shown in column 4 of Table II. The amount of phase-transferred $Q_2S_2O_8$ needed for this estimate was available from Figure 4. A comparison of R_p data given in column 4 with that

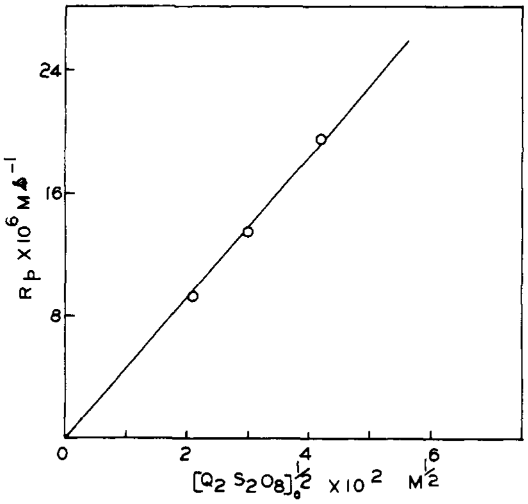

Figure 5. Solution polymerization of styrene in *o*-dichlorobenzene using $AQ_2S_2O_8$ initiator at 60 °C. [Styrene] = 4.31 M.

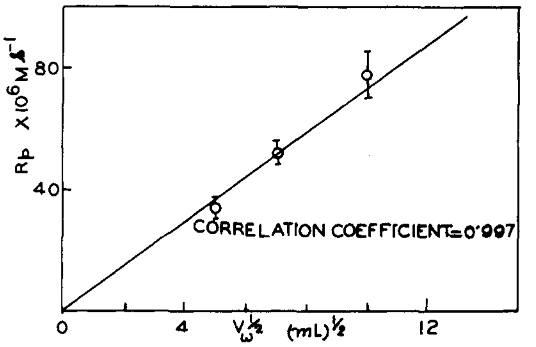

Figure 6. Dependence of R_p on the volume of the aqueous phase at fixed volume of the organic phase. Recipe: [styrene] = 4.31 M in 1,2-dichloroethane; $[K_2S_2O_8]$ = 0.037 M; $[Bu_4NBr]$ = 0.037 M; $KHCO_3$ = 2% (w/v); V_o = 75 mL; temperature = 60 °C.

in column 2 of Table II reveals that the R_p effected by the phase transferred $Q_2S_2O_8$ falls far short of the R_p actually observed.

Effect of the Variation of the Volume of the Aqueous Phase (V_w) on R_p. Since very small amounts of $S_2O_8^{2-}$ were phase-transferred (Table III), its concentration in the organic phase should be approximately the same independent of V_w at a fixed volume of the organic phase (V_o) for a given $[K_2S_2O_8]$ and $[Bu_4NBr]$ provided V_w is not too small compared to V_o. Thus were the phase-transferred $S_2O_8^{2-}$ the chief initiator, R_p would have been independent of V_w other conditions remaining same. Figure 6 on the other hand, shows that at fixed $[K_2S_2O_8]$, $[Bu_4NBr]$ and V_o, R_p is proportional to the square root of V_w when V_w/V_o was varied from 1.33 to 0.33. This result indicates that R_i should be directly proportional to V_w. The solvent used in this series of experiments was 1,2-dichloroethane. Although the extraction results (Table III) referred to *o*-dichlorobenzene, it is expected that the general conclusions will be applicable for both solvents.

Molecular Weight. For a free radical polymerization DP is usually expressed by the following relation

$$\frac{1}{\bar{P}_n} = C_M + C_S\frac{[S]}{[M]} + C_I\frac{[I]}{[M]} + \frac{1+X}{2}\,\frac{2k_tR_p}{k_p^2[M]^2} \qquad (12)$$

where the C_j terms stand for the chain-transfer constants to monomer (M) solvent (S) and initiator (I) and X represents the fraction of total termination events occurring by the disproportionation mode. Thus a plot of $1/\bar{P}_n$ vs. $R_p/[M]^2$ should be linear at a constant [S] and [M] but varying [I], provided C_I is small. For the series of experiments reported in Tables I and II the viscosity-average degrees of polymerization ($\bar{P}_v$) of the polymers are also included. A plot of $1/\bar{P}_v$ against $R_p/[M]^2$ is shown in Figure 7. The plot is essentially linear with an intercept due to transfer to solvent (C_S is reported to be 3.4×10^{-4} at 60 °C in the literature[22]). Some of the points in this figure refer to the series of experiments where $[K_2S_2O_8]$ was held constant while $[Bu_4NBr]$ was varied; for others the opposite was true. The fact that $\bar{P}_v$'s for both cases fall in the same line in Figure 7 indicates that contribution of chain transfer by the $S_2O_8^{2-}$ or Bu_4NBr to $\bar{P}_v$ is indeed small. This is not unexpected in view of the low values of $[(Bu_4N)_2S_2O_8]_o$ and $[Bu_4NBr]_o$ (Table III).

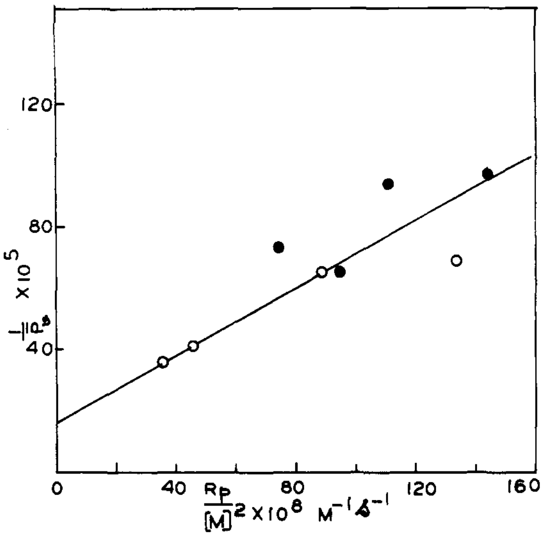

Figure 7. Dependence of DP on R_p: open and filled symbols represent polymers obtained under conditions as shown in Tables I and II, respectively.

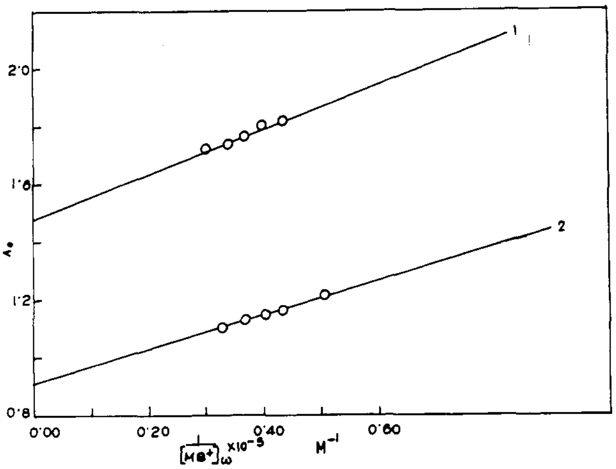

Figure 8. Dye extraction test, plot according to eq 6: lines 1 and 2 refer to same polymer but at different concentrations, 0.224 and 0.390 g/L, respectively.

End Group. The dye partition test suggests the presence of sulfate end groups in the polymers. Plots of $1/A_o$ vs. $1/[MB^+]_w$ according to eq 6 are shown in Figure 8 for two different concentrations of the polymer. In this analysis a low molecular weight polymer ($\bar{M}_n$ = 41 500) prepared by using $K_2S_2O_8$ (0.037 M) and Bu_4NBr (0.037 M) was used. The low molecular weight helped reduce the contribution of solvent chain transfer. Calculations using eq 12 and a C_s value of 3.4×10^{-4} reveal that under the above experimental conditions, 14% of the chain ends would be formed by chain transfer to solvent. The number of sulfate end groups ($\bar{n}$) per polymer molecule turned out to be 1.35. If the solvent transfer could have been avoided altogether, calculation showed that the value of $\bar{n}$ would have risen to above 1.6. This value may be compared to the expected value of about 1.8 for $\bar{n}$.[23-27] In view of the possible inaccuracy in C_S and in the determination of $\bar{M}_n$ for the polymer, the agreement is fair. The value of $\bar{n}$ supports our premise that initiation involves addition of $SO_4^{-}\cdot$ to styrene and termination occurs mainly by mutual bimolecular reactions.

As pointed out by a referee, there is a disagreement between this work and an earlier work from this laboratory regarding the mode of reaction of $SO_4^{-}\cdot$ with styrene. The earlier study on emulsion polystyrene reported very few sulfate end groups per polymer molecule, following which an initiation mechanism involving electron transfer between $SO_4^{-}\cdot$ and styrene originally proposed by Ledwith et al.[28] was supported by us. On the other hand, our subsequent work showed that under conditions where the solubility of styrene was increased in the polymerization medium polystyrene with 1.8 ± 0.1 sulfate end groups per molecule is obtained. This latter result discards Ledwith's mechanism. The reason for the low sulfate content of emulsion polystyrene is still under investigation. It may possibly be a consequence of the low solubility of styrene in the aqueous phase, which favors the participation of secondary radicals such as $\dot{O}H$ in the initiation process.[9]

A feature of the straight lines in Figure 8 is noteworthy. Results of dye partition tests for sulfate and/or sulfonate group in polystyrene prepared in the absence of phase-transfer agents have been reported to yield straight lines with very low slopes.[14,15] In fact, the lines were almost parallel to the $1/[MB^+]_w$ axis. On the other hand, the straight lines in Figure 8 are characterized by rather high slopes. A high slope in a dye extraction test arises in the presence of some interferring ions that compete with the dye ion for extraction into the organic phase (vide eq 5).[14,29] Bu_4N^+ is probably the interferring ion in the present case. The dye partition test thus indirectly suggests that the polymers have a $SO_4^{-}Bu_4N^+$ end group.

Proposed Mechanism. From the results presented so far it is evident that the mechanism of eq 1–4 is not applicable for the present system.

Jayakrishnan and Shah considered essentially the same mechanism with the exception that they ignored eq 1. They arrived at the following rate expression:[5]

$$R_p = \frac{k_p(2k_dK_p)^{1/2}[S_2O_8{}^{2-}]_w{}^{1/2}[M]}{k_t{}^{1/2}}\left\{\frac{[Q^+]_{tot}}{1 + 2K_p[Q^+]_w[S_2O_8{}^{2-}]_w}\right\} \tag{13}$$

where k_d, k_p, and k_t are the rate constants for the decomposition of the phase-transferred peroxydisulfate and the propagation of and the termination of polymer radicals, respectively. This equation results following some approximations that are valid only if the extent of phase transfer is small and the volumes of the two phases are equal. But under such conditions $2K_p[Q^+]_w[S_2O_8{}^{2-}]_w \ll 1$. For example, using our K_p data (Table III) the value of this term turns out to be only 0.037 for the polymerization reported in Table II at the highest $[Bu_4NBr]$. This term in the denominator of eq 13 may therefore be neglected, and R_p should be proportional to $[S_2O_8{}^{2-}]_w{}^{1/2}$ and to $[Q^+]_{tot}$. But, as has been discussed earlier in this paper, R_p is not found to be proportional to $[Q^+]_{tot}$. Nevertheless, we examined the complete equation (13) and found it to be inappropriate, as was expected. For example, when the R_p values for the quaternary variation series (vide column 2 of Table II) are plotted against the term in the braces in eq 13, a straight line with a correlation coefficient 0.944 results. On the other hand, a plot of R_p against $[Bu_4NBr]^{1/2}$ yields a straight line with a much better correlation coefficient, viz. 0.989 as discussed earlier (Figure 2). Furthermore, eq 13 cannot explain the effect of the change in the volume ratio of the two phases on R_p. Also, as has been discussed earlier, direct experimentation showed that the observed R_p cannot be accounted for by the phase-transferred $Q_2S_2O_8$. An alternative mechanism is therefore called for.

The data in Table III show that at least 97.5% of the total $S_2O_8{}^{2-}$ remained in the aqueous phase. The $SO_4^{-}\cdot$ generated in copious quantity in the aqueous phase could be a major initiating species. $SO_4^{-}\cdot$ being one half of $S_2O_8{}^{2-}$ symmetrically divided, its charge-to-volume ratio is expected to be about the same as that of $S_2O_8{}^{2-}$. There is a good chance of some of the transient $SO_4^{-}\cdot$ generated in the aqueous phase being transported to the organic phase and thus effecting initiation there. On the basis of these considerations we propose the following alternative mechanism:

$$S_2O_8{}^{2-}{}_w \xrightarrow{k_d} 2SO_4^{-}\cdot_w \tag{14}$$

$$SO_4^{-}\cdot_w + H_2O \xrightarrow{k_w} \text{products} \tag{15}$$

$$SO_4^{-}\cdot_w + Q^+{}_w \xrightarrow{k_{p,t}} Q^+\ SO_4^{-}\cdot_o \tag{16}$$

followed by reaction 4, etc. With the $SO_4^{-}\cdot$ the back process for the phase-transfer (eq 16) would be absent unlike the situation with $S_2O_8{}^{2-}$ (eq 2) because of the rapid consumption of $Q^+SO_4^{-}\cdot_o$ in reaction 4. Thus, transported $SO_4^{-}\cdot$ is likely to be a greater contributing factor to initiation compared to $S_2O_8{}^{2-}$.

Considering reactions 14–16 we may write for the steady-state concentration of $[SO_4^{-}\cdot]_w$

$$2k_d[S_2O_8{}^{2-}]_w = k_w[SO_4^{-}\cdot]_w + k_{p,t}[SO_4^{-}\cdot]_w[Q^+]_w \tag{17}$$

or

$$[SO_4^{-}\cdot]_w = \frac{2k_d[S_2O_8{}^{2-}]_w}{k_w + k_{p,t}[Q^+]_w} \tag{18}$$

where k_w is the pseudo-first-order rate constant for reaction 15. Thus the rate of phase transfer of $SO_4^{-}\cdot$ would be equal to

$$R_{p,t} = 2k_dk_{p,t}[Q^+]_w[S_2O_8{}^{2-}]_w/(k_w + k_{p,t}[Q^+]_w) \tag{19}$$

Since the rate of initiation (R_i) would be equal to $R_{p,t}$, with due correction for any difference between V_w and V_o[30]

$$R_i = R_{p,t}V_w/V_o \tag{20}$$

Inasmuch as only very small percentages of Q^+ or of $S_2O_8{}^{2-}$ are transported to the organic phase (vide Table III) eq 20 may be written as

$$R_i = 2k_dk_{p,t}[Q^+]_w[S_2O_8{}^{2-}]_wV_w/\{(k_w + k_{p,t}[Q^+]_w)V_o\} \tag{21}$$

The concentration terms in eq 21 refer to the total value of the respective species. Since for a free radical polymerization involving mutual bimolecular termination of polymer radicals $R_p \propto R_i{}^{1/2}$ it follows from eq 21 that R_p would be proportional to $[S_2O_8{}^{2-}]^{1/2}$ and $(V_w/V_o)^{1/2}$. As regards the dependence of R_p on $[Q^+]$, the following further approximations may be considered. If all the $SO_4^{-}\cdot$ generated in the aqueous phase were transported to the organic phase, R_p would have been much greater. For example, for the series of experiments reported in Table II and Figure 3 for 0.037 $M[K_2S_2O_8]$, R_p would have been 6.40 × 10^{-5} M s^{-1} as calculated from the relation

$$R_p = (2k_d[S_2O_8^{2-}])^{1/2}k_p[M]/(2k_t)^{1/2}$$

where $k_d = 0.478 \times 10^{-5}$ s^{-1},[8] $(2k_t)^{1/2}/k_p = 40$ M$^{1/2}$ s$^{1/2}$,[21] and [M] = 4.31 M. This value of R_p is 3.6 times as high as the largest value of excess R_p achieved for 0.037 M $K_2S_2O_8$ under the experimental conditions reported in Table II (column 5). Inasmuch as $R_p \propto R_i^{1/2}$ only $1/3.6^2$ fraction, i.e., about $^1/_{13}$, of the total $SO_4^{-}\cdot$ generated is transported to the organic phase for the most favorable case, i.e., at the highest [Bu_4NBr] used, viz., 0.025 M. From these considerations it follows that for [Bu_4NBr] at 0.025 M, k_w is 12 times as high as $k_{p,t}[Q^+]_w$. Similarly, it can be shown that for the lowest [Bu_4NBr] used in the series of experiments reported in Table II, viz., 0.0075 M, k_w is 33 times as high as $k_{p,t}[Q^+]_w$. These considerations allow us to approximate eq 21 as

$$R_i \simeq 2k_dk_{p,t}[Q^+]_w[S_2O_8^{2-}]_wV_w/(k_wV_o) \qquad (22)$$

and thus R_p should be proportional to the square root of the quaternary ammonium salt concentration also.

Conclusion

This study suggests that in phase-transfer polymerization using $K_2S_2O_8$ and QX a significant part of initiation could be effected also by phase-transferred $SO_4^{-}\cdot$ generated in the aqueous phase. With Bu_4NBr as the phase-transfer agent, initiation is predominantly effected by this process. It further shows that the extent of phase transfer of $S_2O_8^{2-}$, a divalent anion, is greater than that of the monovalent Br^-. However, the amount transferred is a very small percentage of the total [$S_2O_8^{2-}$] when Bu_4NBr is used as the phase-transfer agent.

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Registry No. $K_2S_2O_8$, 7727-21-1; Bu_4NBr, 1643-19-2; styrene, 100-42-5.

References and Notes

(1) Rasmussen, J. K.; Smith, H. K., II *J. Am. Chem. Soc.* **1981**, *103*, 730.
(2) Rasmussen, J. K.; Smith, H. K., II *Makromol. Chem.* **1981**, *182*, 701.
(3) Rasmussen, J. K.; Smith, H. K., II "Crown Ethers and Phase Transfer Catalysis in Polymer Science"; Mathias, L. J., Carraher, C. E., Jr.; Ed.; Plenum: New York, 1984; p 105.
(4) Takeishi, M.; Ohkawa, H.; Hayama, S. *Makromol. Chem. Rapid Commun.* **1981**, *2*, 457.
(5) Jayakrishnan, A.; Shah, D. O. *J. Polym. Sci. Polym. Chem. Ed.* **1983**, *21*, 3201.
(6) Łukasik, L.; Kuran, W.; Łaguna, B.; Gosk, J. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 3333.
(7) Starks, C. M.; Liotta, C. "Phase Transfer Catalysis—Principles and Techniques"; Academic Press: New York, 1978; Chapter 2.
(8) Kolthoff, I. M.; Miller, I. K. *J. Am. Chem. Soc.* **1951**, *73*, 3057.
(9) Misra, M.; Mandal, B. M. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *13*, 63.
(10) Oth, J.; Desreux, V. *Bull. Soc. Chim. Belg.* **1954**, *63*, 285.
(11) Misra, N.; Banthia, A. K.; Mandal, B. M. *Eur. Polym. J.* **1979**, *15*, 943.
(12) Misra, N.; Mandal, B. M. *Macromolecules* **1984**, *17*, 497.
(13) Ghosh, N.; Mandal, B. M. to be published.
(14) Mandal, B. M.; Palit, S. R. *J. Polym. Sci., Part A-1* **1971**, *9*, 3301.
(15) Banthia, A. K.; Mandal, B. M.; Palit, S. R. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 945.
(16) Mukerjee, P.; Ghosh, A. K. *J. Phys. Chem.* **1963**, *67*, 193.
(17) Bergman, K.; O'Konski, C. T. *J. Phys. Chem.* **1963**, *67*, 2169.
(18) Cross, J. T. *Analyst* **1965**, *90*, 318.
(19) Bartlett, P. D.; Cotman, J. D., Jr. *J. Am. Chem. Soc.* **1949**, *71*, 1419.
(20) Kolthoff, I. M.; Meehan, E. J.; Carr, E. M. *J. Am. Chem. Soc.* **1953**, *75*, 1439.
(21) Bevington, J. C. *Proc. R. Soc. London* **1957**, *A239*, 420.
(22) Kapur, S. L. *J. Polym. Sci.* **1953**, *11*, 399.
(23) Olaj, O. F.; Breitenbach, J. W.; Wolf, B. *Monatsh, Chem.* **1964**, *95*, 1646.
(24) Barger, K. C.; Meyerhoff, G. *Makromol. Chem.* **1975**, *176*, 1983.
(25) Gleixner, G.; Olaj, O. F.; Breitenbach, J. W. *Makromol. Chem.* **1979**, *180*, 2581.
(26) Moad, G.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Macromolecules* **1982**, *15*, 1188.
(27) Moad, G.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Macromolecules* **1984**, *17*, 1094.
(28) Ledwith, A.; Russell, P. J. *J. Polym. Sci., Polym. Lett. Ed.* **1976**, *13*, 109.
(29) Biswas, H. K.; Mandal, B. M. *Anal. Chem.* **1972**, *44*, 1636.
(30) $R_{p,t}$ is based on the aqueous phase volume, while R_i is based on the organic phase volume. One referee points out that the dependence of R_p on V_w may be a surface area effect. This view is also compatible with the mechanism of initiation by $SO_4^{-}\cdot$ transported from the aqueous phase since the latter process is rate-controlling.

Preparation of 3,6-Bis(hydroxymethyl)pyridazine and Poly(3,6-pyridazinediylbis(methylene) terephthalate)

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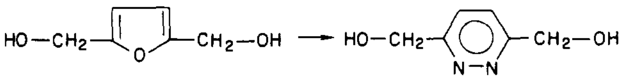
ABSTRACT: 3,6-Bis(hydroxymethyl)pyridazine (II) was prepared from 2,5-bis(acetoxymethyl)furan (VII) by way of 1,6-diacetoxy-3-hexene-2,5-dione (VIII) without the use of electrolytic methoxylation of 2,5-bis(hydroxymethyl)furan (I). This new synthetic method avoids the tedious electrolytic methoxylation step and is suitable for scaled-up operations. A new polymer, poly(3,6-pyridazinediylbis(methylene) terephthalate) (X), was synthesized from II and terephthaloyl chloride. A comparison of the thermal properties of X with those of analogous poly(*p*-xylylene terephthalate) (XI) shows that X is subject to thermal decomposition at about 310 °C, attributed to the resonance stabilization of the benzylic-like 3,6-pyridazinedimethyl radicals.

The objective of this study was the development of a process for the conversion of 2,5-bis(hydroxymethyl)furan (I) to 3,6-bis(hydroxymethyl)pyridazine (II) (eq 1) and the use of the latter as a difunctional monomer. The work was motivated by the expectation that the strong intermolecular forces exhibited by pyridazine would affect favorably the mechanical and thermal properties of polymers con-



I

II

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