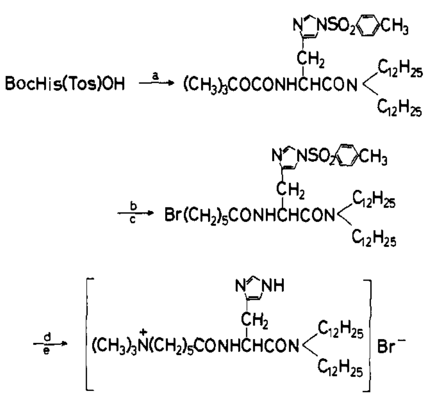
Scheme I[a]



1

[a] Reagents: (a) $(C_{12}H_{25})_2NH$-DCC/CH_2Cl_2; (b) CF_3COOH/CH_2Cl_2; (c) $Br(CH_2)_5COCl$/CH_2Cl_2; (d) $(CH_3)_3N/C_6H_6$; (e) $(CH_3)_3N/\{H_2O, (CH_3)_2CO, C_6H_6\}$.

lowered and reaches 4.4 below the phase-transition temperature.[10] A stereoselectivity as large as 4.4 is the largest one ever encountered for the hydrolysis or degradation of *simple* enantiomeric esters as catalyzed by chiral molecular assemblies composed of a single molecular species.[11]

An Arrhenius plot for the hydrolysis of L-(*Z*)-Phe-PNP as catalyzed by **2** provides only a single straight line for the whole temperature range studied, while such a plot for the catalytic hydrolysis of the same ester by **1** is not correlated with a single line, and a break is observed in the 5–10 °C range as shown in Figure 3; this is referred to the kinetic T_c value. The thermodynamic parameters evaluated for the hydrolysis of L-(*Z*)-Phe-PNP as catalyzed by both micelle and membrane are listed in Table II. These parameters suggest that the mobility of both vesicular assembly of **1** and incorporated substrate (L-(*Z*)-Phe-PNP) is effectively restricted in a temperature range below T_c at the ground state, as reflected on the activation entropy change. This is primarily due to the tight structure of vesicular assembly in the crystalline state provided by efficient hydrogen bonding and hydrophobic interactions.

The vesicular assembly formed with amphiphile **1** in aqueous media can be called *functionalized membrane* since active imidazolyl groups are located in an interface region between the hydrophobic region with aliphatic double-chained moieties and the hydrophilic layer involving charged head groups. It should be noted for the present work that not only the catalytic activity but also the enantioselectivity were exercised by the functionalized membrane in the hydrolysis reaction, both effects being largely controlled by the phase-transition temperature.

---

[10] The phase-transition temperature for vesicular assembly of $N^+C_5His2C_{12}$ in aqueous media containing 1.6% (v/v) ethanol was estimated by using pyrene excimer fluorescence according to the method developed by Smith et al.: pyrene, 5.15×10^{-6} M; $N^+C_5His2C_{12}$, 1.31×10^{-3} M. The ratio of fluorescence intensities, I_e/I_m, was correlated with temperature, where I_e and I_m stand for fluorescence intensities of excimer and monomer at 470 and 393 nm, respectively. The correlation indicated that the phase transition must occur below 15 °C, consistent with the value obtained by the kinetic method (Arrhenius plot). Refer to: Soutar, A. K.; Pownall, H. J.; Hu, A. S.; Smith, L. C. *Biochemistry* **1974**, *13*, 2828–2836.

[11] (a) Moss et al.[1f] observed stereoselectivity as high as 4.33 for the hydrolysis of diastereomeric substrates, LL- and DL-*N*-carbobenzyloxyalanylproline *p*-nitrophenyl esters. They claim that the stereoselectivity was provided by the conformational difference between the LL and DL species when incorporated into micelles. However, the enantiomeric recognition exercised by the vesicular assembly must be a sole origin of the selectivity in the present study. (b) Recently, high enantioselectivity (5.5–5.7) has been reported for the deacylation of *p*-nitrophenyl esters possessing a long alkyl chain by comicelles of *N*-(*N*-dodecanoyl-L-histidyl)-L-leucine and (*R*)-(+)-*N*-(α-methylbenzyl)-*N*,*N*-(dimethyloctadecyl)ammonium bromide: Ohkubo, K.; Sugahara, K.; Yoshinaga, K.; Ueoka, R. *J. Chem. Soc., Chem. Commun.* **1980**, 637–639. However, their substrates are somewhat more specific since these molecules involve a highly hydrophobic segment besides an enantiomeric center.

Phase-Transfer Free-Radical Reactions: The Crown Ether Potassium Peroxydisulfate Initiator System[1]

Jerald K. Rasmussen* and Howell K. Smith, II

Central Research Laboratories, 3M Company
St. Paul, Minnesota 55133

Received September 25, 1980

The use of phase-transfer agents to accelerate the rate of two-phase reactions by bringing together chemical reagents which generally do not have a common solvent has become common practice in recent years.[2] Whereas this technique has been concerned for the most part with the transfer of anionic reagents for the purpose of carrying out ionic reactions, and has even been extended into the realm of anionic polymerizations,[3] the concept is believed to be much more general. We wish to report the first examples of the phase-transfer-initiated free-radical polymerization of olefinic monomers.

Recently, we discovered[4] that the presence of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6, **1**) accelerates the rate of disappearance of aqueous potassium peroxydisulfate. This result suggested, among other things, that it might be possible to conduct free-radical polymerization reactions in organic media under much milder conditions than is possible with typical free-radical initiators such as azobis(isobutyronitrile) (AIBN) or benzoyl peroxide. The only question at the outset seemed to be whether peroxydisulfate could be effectively phase transferred, a notoriously difficult process with divalent anions.[5] Voronkov and co-workers, in an independent study, have recently reported[6] the preparation of a 1:2 $K_2S_2O_8$/18-crown-6 complex characterized as being soluble in methanol, dimethyl sulfoxide, and dimethylformamide and that this complex was useful for initiating polymerizations in methanol solvent. By contrast, we have found that peroxydisulfate may be phase transferred into a variety of solvents, *including hydrocarbon solvents*,[7] with surprising facility and as such can be utilized for the rapid polymerization of acrylic and methacrylic monomers, even at temperatures approaching ambient. In this report we will concentrate on the phase-transfer free-radical polymerization of butyl acrylate mediated by various crown ethers. Results obtained by using quaternary ammonium salts and other phase-transfer agents will be reported elsewhere.

Experimentally, reaction vessels were charged with butyl acrylate as supplied commercially (45 g), acetone (90 mL), potassium peroxydisulfate (0.135 g, 0.5 mmol), and crown ether (1 mmol). The mixtures were sparged for 5 min with argon, and the vessels were sealed and then tumbled in a constant temperature bath maintained at 55 °C for a period of 24 h. Following reaction, the conversion of monomer to polymer was determined by a simple gravimetric technique. Initial results obtained under these conditions seemed to indicate that there was a direct relationship between conversion and the complexing ability of the various crowns for the potassium cation. In fact, when percent conversion was plotted vs. the log of the binding constant in methanol, log *K*, an apparently linear correlation was obtained.[8]

---

[1] Chemistry of Naked Persulfate. 2.

[2] Starks, C. M.; Liotta, C. "Phase Transfer Catalysis: Principles and Techniques"; Academic Press: New York, 1978.

[3] Weber, W. P.; Gokel, G. W. "Phase Transfer Catalysis in Organic Synthesis"; Springer-Verlag: New York, 1977; pp 130–132.

[4] Rasmussen, J. K.; Heilmann, S. M.; Toren, P. E.; Pocius, A. V.; Kotnour, T. A., submitted for publication.

[5] Reference 2, p 162.

[6] Rakhmatulina, T. N.; Baiborodina, E. N.; Rzhepka, A. V.; Lopyrev, V. A.; Voronkov, M. G. *Vysokomol. Soedin., Ser. B* **1979**, *21*, 229–230. *Chem. Abstr.* **1979**, *90*, 187436v.

[7] Using phase-transfer techniques, we have been able to conduct free-radical polymerizations in acetone, ethyl acetate, *tert*-butyl alcohol, tetrahydrofuran, toluene, heptane, and methanol, as well as mixtures of two or more of these solvents. Additional details will be reported at a later date.

[8] Log *K* for methanol solutions were used in the comparisons due to the ready availability of these values in the literature. Although a linear correlation of log *K* values has not been established in going from one solvent to another, it is generally believed that the correlation is reasonably good: Lamb, J. D.; Christensen, J. J.; Oscarson, J. L.; Nielsen, B. L.; Asay, B. W.; Izatt, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 6820–6824.

0002-7863/81/1503-730$01.00/0

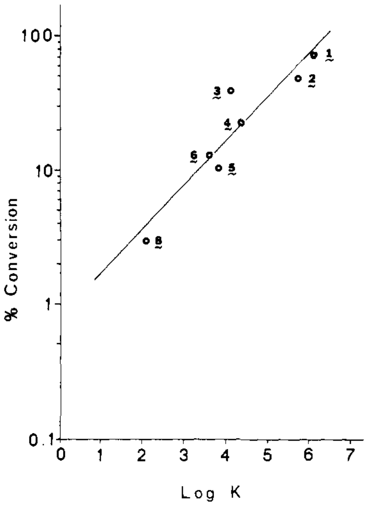


Figure 1. Dependence of butyl acrylate percent conversion to polymer on the stability constants for potassium ion complexation in methanol of the various crown ethers (Table I). Line calculated by regression analysis; O, experimental values.

According to free-radical addition polymerization theory, the rate of polymerization of monomer (M) is proportional to the square root of the initiator (I) concentration (eq 1)[9] when termination is bimolecular. Under our conditions, the absence of

$$\frac{-d[M]}{dt} = k_p[I]^{1/2}[M] \qquad (1)$$

an appreciable induction period and a fairly linear correlation to ca. 80% conversion between conversion of monomer to polymer and reaction time allowed us to use conversion as a measure of the rate. Equations 2–6 derive the relationship between rate of polymerization and the stability constant K.

$$K_2S_2O_8(S) \overset{K_{sp}}{\rightleftharpoons} 2K^+ + S_2O_8^{2-} \qquad (2)$$

$$K^+ + \text{crown} \overset{K}{\rightleftharpoons} \text{crown}{\cdot}K^+ \qquad (3)$$

By substitution

$$[S_2O_8^{2-}] = \frac{K^2K_{sp}[\text{crown}]^2}{[\text{crown}{\cdot}K^+]^2} \qquad (4)$$

If now $S_2O_8^{2-}$ is initiator as usual, then

$$\frac{-d[M]}{dt} = k_p[M][S_2O_8^{2-}]^{1/2} \qquad (5)$$

and

$$\frac{-d[M]}{dt} = \frac{k_pKK_{sp}^{1/2}[\text{crown}][M]}{[\text{crown}{\cdot}K^+]} \qquad (6)$$

In other words, conversion should correlate with K rather than with log K.

In repeating our initial work in an attempt to resolve this apparent anomaly, we soon discovered that the correlation of conversion with log K apparently still held but notably the slope of this correlation depended upon the particular commercial lot of butyl acrylate used in this study. We now believe these results to be the consequence of differing levels of inhibitor and/or impurities in the various monomer lots which may have been retarding polymerization.

Table I. Polymerization of Butyl Acrylate by $K_2S_2O_8$/Crown Ethers

crown	conversion, %	log K_{CH_3OH}
18-crown-6 (1)	73.4 ± 0.6[a]	6.06[b]
dicyclohexyl-18-crown-6 (2)	49.2	5.70[c,d]
21-crown-7 (3)	41.1	4.22[b]
dibenzo-18-crown-6 (4)	23.6	4.36[c]
15-crown-5 (5)	10.7	3.77[b]
cyclohexyl-15-crown-5 (6)	13.7	3.58[c]
dibenzo-24-crown-8 (7)	1.04	3.49[c]
1,10-diaza-18-crown-6 (8)	3.10	2.04[c]
1,10-dithia-18-crown-6 (9)	0.25	1.15[c]
12-crown-4 (10)	0.16	e
none (control)	0.10	

[a] Average of two trials. [b] Lamb, J. D.; Izatt, R. M.; Swain, C. S.; Christensen, J. J. *J. Am. Chem. Soc.* 1980, *102*, 475–479. [c] Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* 1974, *74*, 351–384. [d] The crown used was a mixture of isomers: isomer A (log K = 6.01) and isomer B (log K = 5.38). [e] Not available.

To circumvent these problems, polymerizations were conducted using butyl acrylate which had been purified by passing it successively through silica gel and alumina. Reactions were conducted as before except that the reaction time was limited to a total of 3 h. The results are collected in Table I. This time a plot of conversion vs. log K showed curvature. Dibenzo-24-crown-8 (7) is seen to deviate quite markedly in its behavior, probably due in part to its incomplete solubility in the polymerization medium. The results obtained for crown ethers **9** and **10** are indications of no polymerization, since they are essentially identical, within experimental error, with that of the control. A log–log plot of the remaining data (Figure 1) is linear as theory predicts, with a good correlation coefficient (R = 0.948), considering the assumptions made in deriving the relationship.

To put the results into better perspective, a polymerization was carried out by using AIBN, which has a similar activation energy for decomposition (E_a = 31 kcal/mol[10]) to that of potassium peroxydisulfate (E_a = 33.5 kcal/mol in 0.1 N aqueous base[11]), as the initiator. Under conditions identical with those used with the crown/peroxydisulfate reactions, less than 1% conversion to polymer was observed. Thus, the efficiency of the new initiator system is quite remarkable, and the results indicate that the activation energy for peroxydisulfate decomposition in organic media must be markedly different from that in aqueous solution. Additional studies in this regard and studies concerning the general area of phase-transfer free-radical reactions are ongoing in our laboratories.[12]

Acknowledgment. We acknowledge the helpful discussions held with our colleagues, Dr. Steven M. Heilmann, Dr. Alphonsus V. Pocius, and Dr. Thomas A. Kotnour, during the course of this work.

---

(9) Priest, W. J. *Tech. Org. Chem.* **1953**, *8*, 441–534.

(10) Pryor, W. A. "Introduction to Free Radical Chemistry"; Prentice-Hall: Englewood Cliffs, NJ, 1966.

(11) Kolthoff, I. M.; Miller, I. K. *J. Am. Chem. Soc.* **1951**, *73*, 3055–3059.

(12) A referee has pointed out the fact that the slope of the line in the figure deviates markedly from the expected 1.0, suggesting that the mechanistic picture may be overly simple. Answers to this question and to predictions inherent in eq 2–6 are the subject of further investigations.