Interaction of Polystyryl Radical with Cu(DMF)$_2$Br$_2$

SHASHI D. BARUAH

Regional Research Laboratory, Jorhat 785 006, Assam, India

SYNOPSIS

The kinetics of 2,2'-azobisisobutyronitrile (AIBN) initiated polymerization of styrene in N,N-dimethylformamide (DMF) at 60°C were investigated in the presence of dibromo(N,N-dimethylformamide)copper(II) complex. The complex was prepared in situ by mixing tetrakis (N,N-dimethylformamide)copper(II) perchlorate with LiBr in the molar ratio of 1 : 2. The equilibrium constant for $[Cu(DMF)_4]^{2+} + 2Br^- \rightleftharpoons Cu(DMF)_2Br_2 + 2DMF$ was calculated by the limiting logarithmic method as 1.80×10^3 L^2 mol^{-2}. The velocity constant at 60°C for the interaction of polystyryl radical with Cu(DMF)$_2$Br$_2$ is 7.46×10^4 L mol^{-1} s^{-1}.

INTRODUCTION

In recent years, the interaction of polystyryl radical with transition metal salts in a nonaqueous media have been extensively studied.[1-8] Bamford et al.[1,2] studied the polymerization of vinyl monomers at 60°C, initiated by 2,2'-azobisisobutyronitrile (AIBN) in the presence of FeCl$_3$ in N,N-dimethylformamide (DMF). Bengough and co-workers later reported that CuCl$_2$ behaved as an ideal retarder for the polymerization of methyl methacrylate,[4] styrene,[6] and methacrylonitrile[7]; but it behaved only as a retarder in the polymerization of acrylonitrile,[5] and they concluded that CuCl$_2$ is a more powerful inhibitor than FeCl$_3$. A similar result was also reported by Billingham et al.[8] The effect of changing the type of organic ligands on the reactivity of the complex with central iron(III) and copper(II) cations towards polystyryl radical attack is of very interesting and recent studies were initiated with different iron(III) and copper(II) cations.[9-11] This communication now reports the kinetic investigations of polymerization of styrene in DMF at 60°C initiated by AIBN in the presence of dibromo (N,N-dimethylformamide)copper(II) complex, Cu(DMF)$_2$Br$_2$.

EXPERIMENTAL

Materials

AIBN, DMF, and styrene were purified and stored as usual. Lithium bromide (BDH) was used without further purification. $[Cu(DMF)_4](ClO_4)_2$, (C) was prepared as previously.[10]

Procedure

Rates of polymerization were measured dilatometrically at 60°C, care being taken to degas the reactants thoroughly before sealing off the dilatometer.

The characterizations of copper(II) complex in DMF by Job's method[12] and the equilibrium constant by the limiting logarithmic method[12] at 595 nm were determined with a SPECORD UV-VIS spectrometer at room temperature.

Gel permeation chromatography was performed at 25°C with distilled THF as eluent using a Waters Associates GPC unit. Elution was conducted with a flow rate of 1 mL/min. Sample concentration was 0.2% w/v, and the injection volume was 50 μL. The GPC column combination was 10^6, 10^5, 10^4, and 500 Å. A universal calibration curve, based on elution volumes of nine narrow-MWD polystyrene samples from Waters Associates, was used to compute the molecular weights of polymer samples.

RESULTS AND DISCUSSION

Characterization of the Complex $Cu(DMF)_2Br_2$

$Cu(DMF)_2Br_2$ was prepared *in situ* by mixing LiBr with the complex C in DMF at the molar ratio of [C] : [LiBr] = 1 : 2. LiBr when mixed with the complex C in DMF produced only one complex, and the complex was spectroscopically identified as $Cu(DMF)_2Br_2$. Ultraviolet-visible spectra of the complex C in DMF containing various ratios of [C] : [LiBr] are shown in Figure 1. The spectra were recorded from 280 nm since the solvent DMF absorbs strongly below 270 nm.[13] In DMF the complex C showed a absorption peak at 290 nm, but it has no absorption maximum in the visible region. This band might be due to the charge-transfer transition from coordinated solvent ligand to metal d-orbital and the molar extinction coefficient at 290 nm for $[Cu(DMF)_4]^{2+}$ was reported to be 2.55×10^4

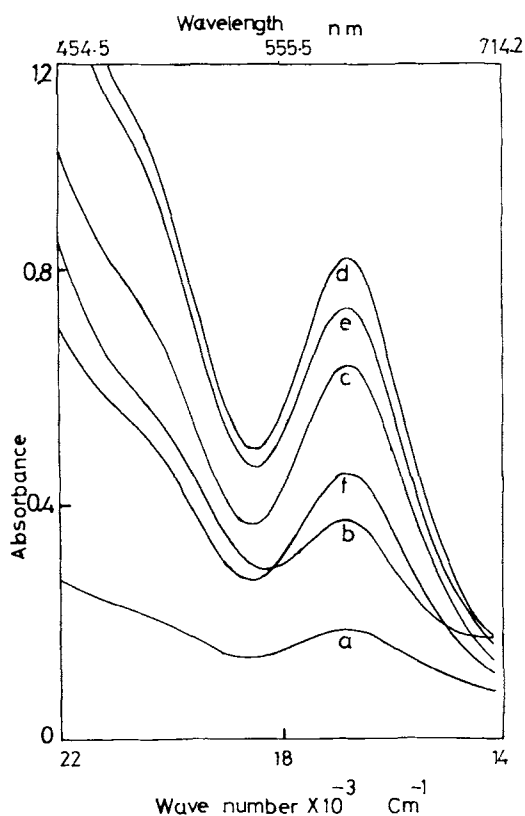**Figure 1** Visible spectra of the complex $[Cu(DMF)_4]$ $(ClO_4)_2$, (C), with added LiBr in DMF at 25°C. 100% of [C] = 7.87×10^{-3} mol L^{-1}; 100% of the ligand, [LiBr] = 7.87×10^{-3} mol L^{-1}. Molar ratio [C] : [LiBr]: (a) = 1 : 9; (b) = 1 : 6.3; (c) = 1 : 4; (d) = 1 : 2; (e) = 1 : 1.5; (f) = 1 : 1.

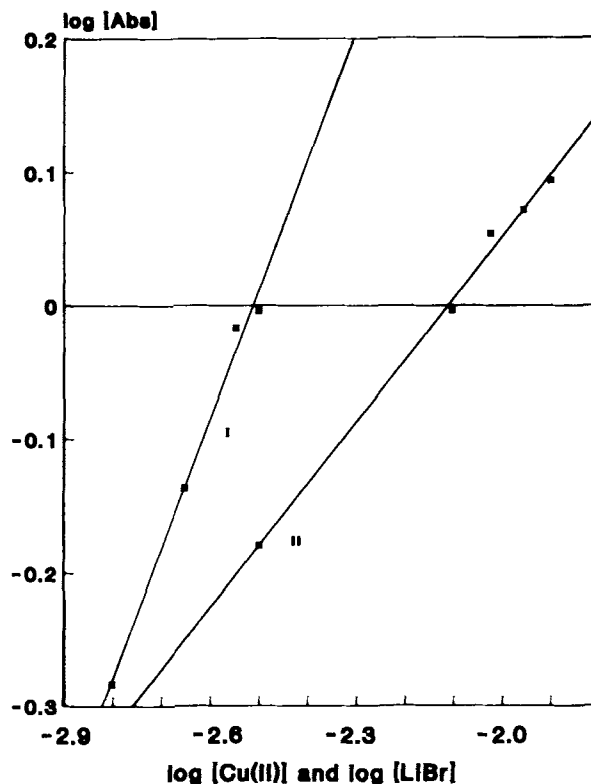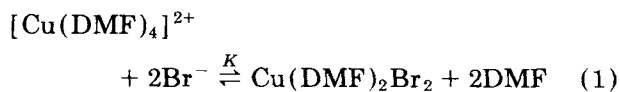**Figure 2** The limiting logarithmic method: (Line I) concentration of the ligand LiBr is kept constant, [LiBr] = 7.87×10^{-3} mol L^{-1}; (Line II) concentration of the complex C is kept constant. [C] = 3.148×10^{-3} mol L^{-1}. Solvent = DMF; experimental wavelength = 595 nm.

L mol^{-1} cm^{-1}.[10] $[Cu(DMF)_4]^{2+}$ with added quantities of LiBr showed two strong absorption peaks at 290 and 595 nm, respectively. It was found that the maximum absorbancy at 595 nm occurred when the molar ratio of [C] : [LiBr] was 1 : 2. From this it may be concluded that, in DMF, added LiBr reacts with C in the molar ratio of [C] : [LiBr] = 1 : 2, forming a dibromo complex of the type $Cu(DMF)_2Br_2$. The peak at 595 nm may be assigned to the d–d transition. Whether the complex formed is an inner or outer sphere or simple salt still remains obscure. For simplicity, it may be assumed to be a simple coordinated complex $Cu(DMF)_2Br_2$. The complex $Cu(DMF)_2Br_2$ could not be isolated in the solid state, but since $Cu(DMF)_2Cl_2$ is reported to be a trans compound,[10,14] $Cu(DMF)_2Br_2$ is therefore likely to be a trans compound. The molar extinction coefficient of $Cu(DMF)_2Br_2$ at 595 nm was found to be 4.15 $\times 10^4$ L mol^{-1} cm^{-1}. The equilibrium for the formation of $Cu(DMF)_2Br_2$ may be represented as

$$[Cu(DMF)_4]^{2+}$$

$$+ 2Br^- \overset{K}{\rightleftharpoons} Cu(DMF)_2Br_2 + 2DMF \quad (1)$$

and the value of K calculated by the limiting logarithmic method at 595 nm was found to be 1.80×10^3 L^2 mol^{-2} (Fig. 2). The ratio of the slopes of curve II and I was 2 : 1, suggesting the formation of the complex Cu(DMF)$_2$Br$_2$.

Effect of Adding LiBr to the Complex C on the Rate of Polymerization

The generally accepted reaction scheme for the interaction of polystyryl radical with CuCl$_2$ may be represented as[6]

$$— CH_2\overset{\cdot}{C}HPh + CuCl_2 \rightarrow$$

$$— CH{=}CHPh + H^+Cl^- + Cu^+Cl^- \quad (2)$$
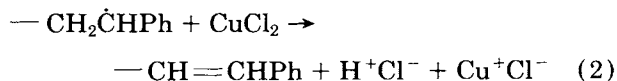
It was found that Cu(DMF)$_2$Br$_2$ in DMF produced well-defined induction periods in the AIBN-initiated polymerization of sytrene. The reaction between polystyryl radical and Cu(DMF)$_2$Br$_2$ may be represented as

$$— CH_2\overset{\cdot}{C}HPh + Cu(DMF)_2Br_2 \rightarrow \ — CH$$

$$={=}CHPh + Cu(DMF)_2Br + H^+Br^- \quad (3)$$
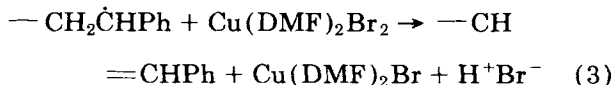
Presumably the copper(I) complex is being rapidly solvated by another DMF molecule.

Like LiCl,[10] LiBr alone, over the concentration range used in the experiments, produced no retardation or inhibition of the polymerization of styrene in DMF initiated by AIBN. Addition of LiBr to a mixture of constant composition of styrene, DMF, AIBN, and complex C at 60°C produced definite induction periods, at the end of which the rate curves always became parallel to the rate curves of poly-
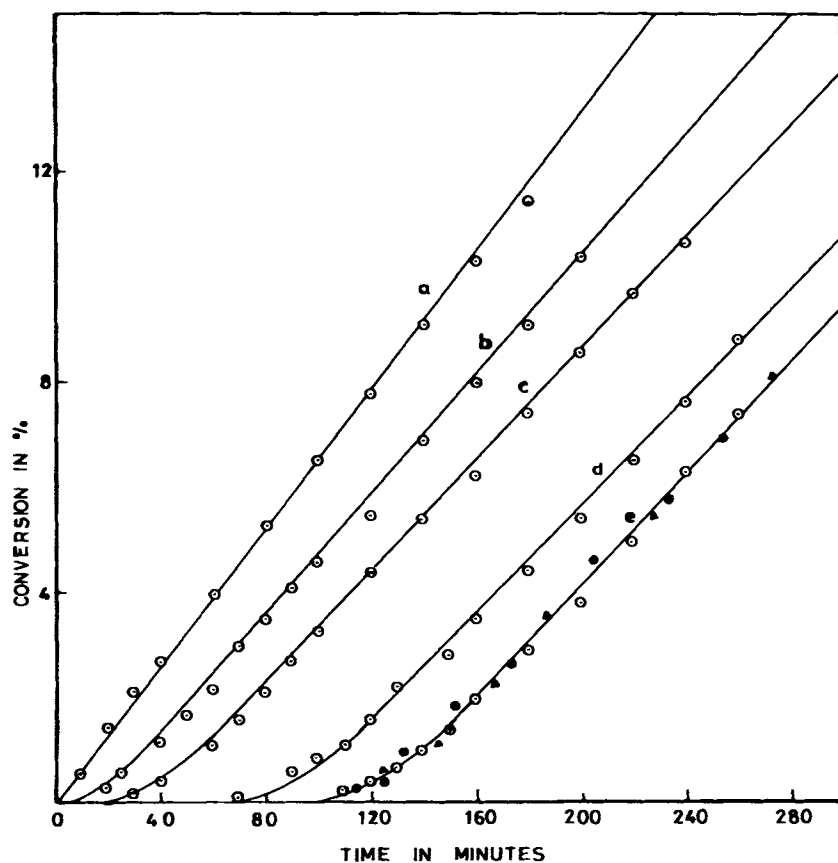

Figure 3   Polymerization of styrene in DMF at 60°C initiated by AIBN and inhibited by various copper(II) species. [Styrene] = 1.673 mol L^{-1}; [DMF] = 10.40 mol L^{-1}; [AIBN] = 7.62 $\times$ 10^{-2} mol L^{-1}; [C] = 7.87 $\times$ 10^{-3} mol L^{-1}. Curve (a) only AIBN. Molar ratios [C] : [LiBr]: (b) = 1 : 0.25; (c) 1 : 0.5; (d) = 1 : 1; (e) (O) = 1 : 2; (●) = 1 : 3; (▲) = 1 : 6.

merization without the addition of C and LiBr (Fig. 3). It was found that at constant [C] the induction periods gradually increased with the increasing molar ratio of [C] : [LiBr] up to 1 : 2. When the ratio exceeded 1 : 2, it became steady. For the ideal retarder $Cu(DMF)_2Br_2$ the initiator efficiency f was evaluated from the induction period τ:

$$\tau = [Cu(DMF)_2Br_2]_0/2k_d f [\bar{In}]$$

$$= [Cu(DMF)_2Br_2]_0/I \quad (4)$$

where τ is defined as the time at which the rate of polymerization is $0.648 \times$ the final maximum rate[1,15] and I, the rate of initiation. $[Cu(DMF)_2Br_2]_0$ represents the initial concentration of the idea retarder, $[\bar{In}]$ is the average concentration of the initiator during the reaction. The experimental value of τ was 128 min, using k_d as[9] 0.95×10^{-5} s^{-1}, f was found to be 0.73, which is in good agreement with the literature values.[1,15,16]

The experiment was repeated with [C] : [LiBr] = 1 : 1, keeping [C] fixed; it was found that the induction period was reduced almost to half. This suggested that for [C] : [LiBr] = 1 : 2, only $Cu(DMF)_2Br_2$ existed in solution and it acted as an ideal retarder.[15] During the induction period, interaction between the polystyryl radical and $Cu(DMF)_2Br_2$ took place, after the induction period, i.e., after complete oxidation of polystyryl radicals, the rate curve became parallel to the polymerization rate curve without the retarder.

Assuming the steady state approximation during the initial stages of polymerization of vinyl monomers retarded by an ideal retarder, z, Bamford et al. showed that[1,15,16]

$$I = k_z[R^\bullet][Z] + 2k_t[R^\bullet]^2 \quad (5)$$

where I is the rate of initiation.

When the inhibitor is completely exhausted, then [Z] is zero, and the concentration of the polymer radical attains a maximum value, $[R^\bullet]_s$, given by

$$I = 2k_t[R^\bullet]_s^2 \quad (6)$$

The fraction of total termination occuring by mutual reactions of polymer radicals during the induction period is sufficiently small to be neglected and a stationary state treatment leads to

$$-(1/\phi_t) + \ln[(1 + \phi_t)/(1 - \phi_t)]$$

$$= k_z[R^\bullet]_s t + A^* \quad (7)$$

where ϕ_t is the ratio of the rate at any time t, R_p, in the presence of the retarder to the final maximum rate, R_{ps}, when the inhibitor has disappeared, i.e., $\phi_t = R_p/R_{ps}$; k_z is the rate constant for the interaction of polystyryl radical with Cu^{2+}, and A^* is the integration constant.

A detailed analysis of the rate curve measured with 1 : 2 molar ratio of [C] : [LiBr] was done by Bamford's method[1,15] and a plot of ϕ_t vs. $k_z[R^\bullet]_s t + A^*$ is shown in Figure 4, where it was assumed that only $Cu(DMF)_2Br_2$ complex was present and k_z refers to eq. (3). Reasonable agreement was found between experimental and theoretical plots when $k_z[R^\bullet]_s$ was 3.30×10^{-3} s^{-1} and A^* was -20. The theoretical curve was obtained by plotting ϕ_t vs.
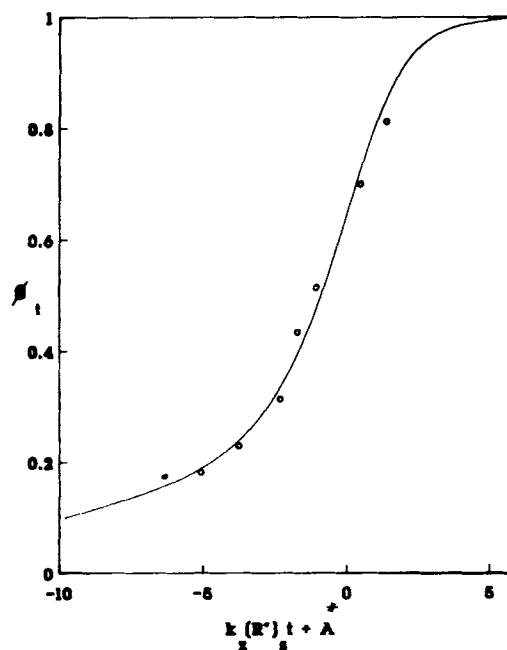

Figure 4 Reduced rate ϕ_t as a function of time t expressed as $k_z[R^\bullet]_s t + A^*$, experimental points (O), calculated curve (– – –); temperature = 60°C. ϕ_t is the ratio of the rate at any time t, R_p, in the presence of the retarder to the final maximum rate, R_{ps}, when the inhibitor has disappeared, i.e., $\phi_t = R_p/R_{ps}$; k_z is the rate constant for the interaction of polystyryl radical with $Cu(DMF)_2Br_2$, prepared *in situ*, and A^* is the integration constant. Molar ratio of [C] : [LiBr] = 1 : 2; [sytrene] = 1.673 mol L^{-1}; [AIBN] = 7.62×10^{-2} mol L^{-1}; [DMF] = 10.40 mol L^{-1}; [C] = 7.87×10^{-3} mol L^{-1}.

$-(1/\phi_t) + \ln[(1 + \phi_t)/(1 - \phi_t)]$ and the experimental one by plotting ϕ_t vs. $k_z[R^\bullet]_s t + A^*$.

Since the final maximum rate of polymerization R_{ps} is given by

$$R_{ps} = -d[M]/dt = k_p[M][R^\bullet]_s \qquad (8)$$

it follows that

$$\frac{k_z[R^\bullet]_s[M]}{R_{ps}} = \frac{k_z}{k_p} \qquad (9)$$

Bengough et al.[4-7] has suggested other methods of analysis for retardation caused by ideal retarding species. For a range of ϕ_t value equal to 0.15–0.8, the plot of the left-hand side of eq. (7) vs. t should produce a straight line of slope $k_z[R^\bullet]_s$ and k_z can be evaluated from eq. (9) with a measured value of R_{ps} at a known monomer concentration [M]. This method is known as Bengough's method I, and analysis of the rate curve by Bengough's method I is shown in Figure 5.
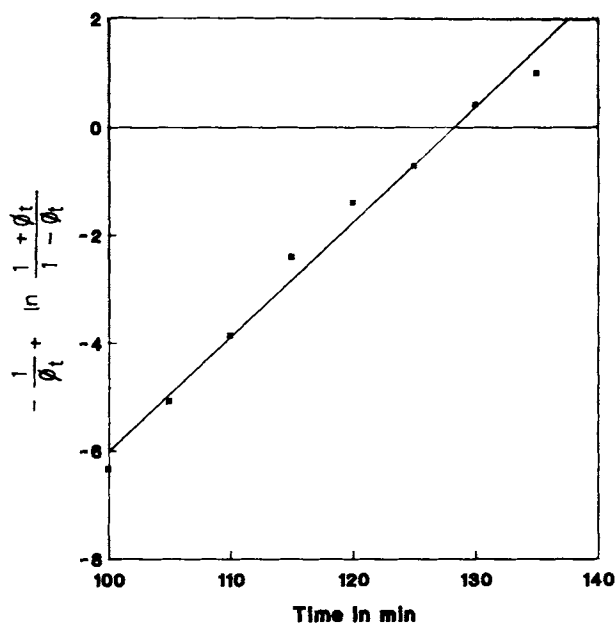

Figure 5 Analysis of the result for the polymerization of styrene initiated by AIBN at 60°C and inhibited by Cu(DMF)₂Br₂, prepared in situ, where $\phi_t = R_p/R_{ps}$ and k_z is the rate constant for the interaction of polystyryl radical with Cu(DMF)₂Br₂. Molar ratio of [C] : [LiBr] = 1.2; [sytrene] = 1.673 mol L⁻¹; [AIBN] = 7.62 × 10⁻² mol L⁻¹; [DMF] = 10.40 mol L⁻¹; [C] = 7.87 × 10⁻³ mol L⁻¹.

Figure 6 Analysis of the result for the polymerization of styrene initiated by AIBN at 60°C and inhibited by Cu(DMF)₂Br₂, prepared in situ, where $\phi_t = R_p/R_{ps}$ and F is the fraction conversion of the monomer to polymer, i.e., $F = ([M]_0 - [M])/[M]_0$ and k_z is the rate constant for the interaction of polystyryl radical with Cu(DMF)₂Br₂. Molar ratio of [C] : [LiBr] = 1.2; [styrene] = 1.673 mol L⁻¹; [AIBN] = 7.62 × 10⁻² mol L⁻¹; [DMF] = 10.40 mol L⁻¹; [C] = 7.87 × 10⁻³ mol L⁻¹.
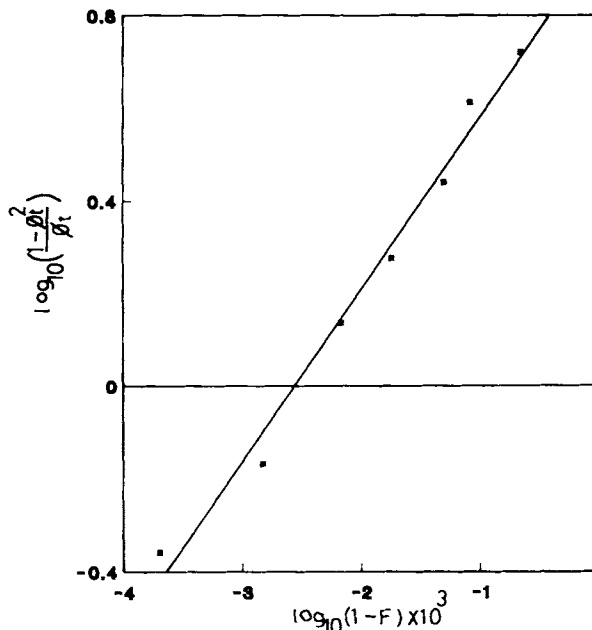
Again rearranging eq. (5) as $2k_t[R^\bullet]_s^2 + k_z[R^\bullet][Z] - I = 0$, Bengough et al.[4-7] showed that for $0.8 > \phi_t > 0.15$

$$k_z = \frac{(1 - \phi_t^2)}{\phi_t} \times \frac{(2Ik_t)^{1/2}}{[Z]} \qquad (10)$$

and deduced the relation

$$\log \frac{(1 - \phi_t^2)}{\phi_t} = \log \frac{k_z[Z]_0}{(2Ik_t)^{1/2}} + \frac{k_z}{k_p} \log(1 - F) \qquad (11)$$

where F is the fraction conversion of monomer to polymer, i.e., $F = ([M]_0 - [M])/[M]_0$. For a fixed value of I and $[Z]_0$, the plot of the left-hand side of eq. (11) vs. $\log(1 - F)$ should produce a straight line with slope k_z/k_p (Bengough's method II). The analysis of the rate curve by Bengough's method II is shown in Figure 6.

Experimental values of maximum rates of polymerization R_{ps} and concentration of monomer [M] were 1.32×10^{-5} mol L^{-1} s^{-1} and 1.673 mol L^{-1}. Assuming k_p^{17} to be 176 L mol^{-1} s^{-1}, k_z calculated by the three methods, viz., Bamford's and Bengough's (I and II) were 7.34×10^4, 7.18×10^4, and 7.89×10^4 L mol^{-1} s^{-1}, respectively. Hence the average value of k_z would be 7.46×10^4 L mol^{-1} s^{-1}.

The effect of varying [C] : [LiBr] molar ratio on the molecular weights of polystyrene are shown in Table I. As expected, the molecular weight of polymer formed were found to decrease with increasing [C] : [LiBr] molar ratio.

The velocity constant k_x for the polystyryl radical attack on $[Cu(DMF)_4]^{2+}$ was 6.64×10^2 L mol^{-1} s^{-1} at 60°C,[11] which was much less than the corresponding value with $Cu(DMF)_2Br_2$, viz., 7.46×10^4 L mol^{-1} s^{-1}.

Electron transfer from copper(II) to copper(I) become easier in the presence of a halide ion because of the very simple structure of the halide ion.[18] The high capacity for formation of complexes may make halide ion a good bridging ligand in electron transfer reaction. Halide bridging in reaction proceeded by two electron changes had been studied by Basolo et al.[19] The presence of halide ion in the copper(II) complex facilitates the electron transfer process in a way that is relatively uneffected by the number of halide ions present, by the net charge carried by the ion or by the geometry of the complex.[10] Coordinated chloride or bromide ion may act as a bridging medium, or it may act as an electron conductor during the electron transfer process; but still the precise mechanism of electron transfer is not conclusive. Copper(II) generally exhibited a d^9 configuration and in this configuration a strong electronic distortion occurs and such distortion probably accounted

for the square plannar arrangements.[20] Due to unusual lability of the copper(II) complexes, the tetragonal copper(II) complexes resembled more closely the square planar complexes than octagonal complexes.[21] In the square plannar complex, π bonds are formed by the interaction of the filled 3p-orbital of the coordinated bromide ion and the partially filled d-orbital of copper(II) by dsp^2 hybridization. Coordinated bromide ion in this complex reacts with polystyryl radical to form extended π bond by the interaction of the d-orbital of copper(II), filled 2p- or empty 3d- or 4p-orbital of the bromide ion and 2p-orbital of polymer radical end carbon atom.[10] In this type of extended π bond system, the electron transfer became easier. Moreover, the coordinated Br^- ion may promote electron transfer by causing d-electron cloud expansion (the "nephelauxelic effect") to a greater extent than the coordinated solvent ligand such as DMF or DMSO.[9] It is noteworthy that, in a reaction where a bridge mechanism is certain, the order of effectiveness of several common anions which act as a bridge for the electron transfer reaction may be represented as $I^- > Br^- > Cl^-$.[21]

Table I   Molecular Weight of Polystyrene Determined by GPC[a]

[C] : [LiBr]	Molecular Weight $(\bar{M}_n)$	Polydispersity Index
Without additive	14,300	2.2
1 : 0.5	10,500	2.3
1 : 1	9630	1.9
1 : 2	8620	2.0
1 : 3	7820	1.9
1 : 4	7540	1.9

[a] [Styrene] = 1.673 mol L^{-1}; [C] = 7.87×10^{-3} mol L^{-1}; [AIBN] = 7.62×10^{-2} mol L^{-1}; temp = 60°C; time = 6 h.

REFERENCES

1. C. H. Bamford, A. D. Jenkins, and R. Johnston, *Proc. Roy. Soc. (London)*, **A239**, 214 (1957).
2. C. H. Bamford, A. D. Jenkins, and R. Johnston, *Trans. Faraday Soc.*, **58**, 1212 (1962).
3. E. R. Entwistle, *Trans. Faraday Soc.*, **56**, 284 (1960).
4. W. I. Bengough and W. H. Fairservice, *Trans. Faraday Soc.*, **61**, 1206 (1965).
5. W. I. Bengough and W. H. Fairservice, *Trans. Faraday Soc.*, **63**, 382 (1967).
6. W. I. Bengough and T. O'Neill, *Trans. Faraday Soc.*, **64**, 1014 (1968).
7. W. I. Bengough and T. O'Neill, *Trans. Faraday Soc.*, **64**, 2415 (1968).
8. N. C. Billingham, A. J. Chapman, and A. D. Jenkins, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 827 (1980).
9. N. N. Dass and M. H. George, *Eur. Polym. J.*, **7**, 1185 (1971).
10. S. D. Baruah and N. N. Dass, *Eur. Polym. J.*, **17**, 513 (1981).
11. S. D. Baruah and N. N. Dass, *Makromol. Chem.*, **182**, 3591 (1981).

12. J. Rose, *Advanced Physico-Chemical Experiments,* Pitman, London, 1964, pp. 54, 67.

13. D. J. Pasto and C. R. Johnson, *Organic Structure Determination,* Prentice-Hall, Englewood Cliffs, NJ, 1969, p. 105.

14. A. G. Massey, in *Comprehensive Inorganic Chemistry,* J. C. Bailar, H. J. Emuleus, Sir R. Nyholm, and A. F. Trofman-Dickens, Eds., Pergamon, Oxford, 1973, Vol. III, p. 75.

15. C. H. Bamford, W. G. Barb, A. D. Jenkins, and P. F. Onyon, *Kinetics of Vinyl Polymerization by Radical Mechanism,* Butterworths, London, 1958, p. 255.

16. J. C. Bevington, *Radical Polymerization,* Academic, London, 1961, p. 34.

17. G. C. Eastmond, in *Comprehensive Chemical Kinetics,* C. H. Bamford and C. F. Tippers, Eds., Elsevier, Amsterdam, 1972, Vol. 14A, pp. 160, 178.

18. H. Taube, *Electron Transfer Reaction of Complex Ions in Solution,* Academic, New York, 1970, p. 51.

19. F. Basolo, M. L. Morris, and R. G. Pearson, *Disc. Faraday Soc.,* **29,** 80 (1960).

20. J. E. Ferguson, *Stereochemistry and Bonding in Inorganic Chemistry,* Prentice-Hall, Englewood Cliffs, NJ, 1974, p. 205.

21. F. Basolo and R. G. Pearson, *Mechanism of Inorganic Reactions,* 2nd ed., Wiley Eastern, New Delhi, 1973.