NOTE

Thermal Decomposition Kinetics of Azobisnitriles Containing Functional End Groups

INTRODUCTION

Functional groups containing azobisnitriles are frequently used for the synthesis of functionally terminated polymers[1,2] which have wide applications. These initiators generally do not undergo chain transfer reactions[3,4] and give polymers with low polydispersity and good functional group distribution. A number of azobisnitrile initiators containing various functional groups have been synthesized and used for the synthesis of polymers containing functional groups of which 4,4'-azobis(4-cyanopentanol) (ABCP) and 4,4'-azobis(4-cyanopentanoic acid) (ABCA) have been studied extensively.[5-8] However, azobisnitriles containing amide, hydroxyl with amide, ether, and hydroxyl functional groups, which are useful for the preparation of homo and block copolymers, are not reported in the literature.

The present work describes the synthesis (Scheme 1) and kinetics of thermal decomposition of two new azobisnitriles namely 4,4'-azobis(4-cyanopentanoyl)bis 2-aminoethanol (ABCAE) and 4,4'-azobis(4-cyanopentanoyl)bis 2-(2-aminoethoxy)ethanol (ABCAEE) containing amide, hydroxyl with amide, ether, and hydroxyl groups in N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMAC) at 65, 69, and 74°C.

EXPERIMENTAL

Materials

The solvents were purified by conventional drying and distillation procedures. 4,4'-Azobis(4-cyanopentanoic acid) (Fluka AG, Switzerland) was used without further purification. 2-Ethanolamine and 2-(2-aminoethoxy)-ethanol (Aldrich, USA) were purified, dried, and distilled just before use.

Instrumental Methods

The infrared spectra were recorded on a Perkin Elmer 683 spectrophotometer, and proton NMR spectra were re-corded on a Bruker WH90 MHz spectrophotometer with TMS as an internal standard.

Decomposition Rate Measurement

The rates of decomposition of ABCAE and ABCAEE were determined by measuring nitrogen evolution as a function of time. The apparatus used was similar to that of Petersen,[9] and consisted of a jacketed reaction cell connected to a gas burette by a capillary, with provision for purging nitrogen. A levelling bulb was connected to the gas burette to adjust the liquid level in the burette.

A reaction cell containing 50 mL of solvent was immersed in a constant temperature bath controlled to $\pm0.1°C$. The solvent was deoxygenated with a slow stream of nitrogen for half an hour and then allowed to stand for a few minutes to attain thermal equilibrium with the bath. The liquid level in the gas burette was adjusted to zero, and an azo compound of known weight (about 300–400 mg) was added quickly to the reaction cell.

Timing began with the first introduction of azo compound. At specific time intervals (based on the rate of nitrogen evolution) the volume of nitrogen evolved (V_t) was recorded. This procedure was followed until about 75–80% of the theoretical volume of nitrogen had been evolved. The experiment was continued until the evolution of nitrogen ceased and that volume reading was taken as (V_∞). The final readings agreed well with the stoichiometric values. The natural logarithms of the ratios ($V_\infty/V_\infty-V_t$) were calculated and plotted as ordinates versus the time abscissa. The rate constants (k_d) reported are the slopes of the best straight lines which passed through the points so plotted.

Preparations

4,4'-Azobis(4-cyanopentanoyl chloride) (ABCACl). The diacidchloride ABCACl was prepared from the corresponding diacid (ABCA), according to the procedure described in the literature.[10] The structure and purity of ABCACl was confirmed by IR, proton NMR spectra, and microanalytical data.

4,4'-Azobis(4-cyanopentanoyl)bis 2-aminoethanol (ABCAE). A solution of 6.34 g (0.02 mole) of ABCACl in 75 mL of dichloromethane, was added slowly to 10 g of 2-ethanol-
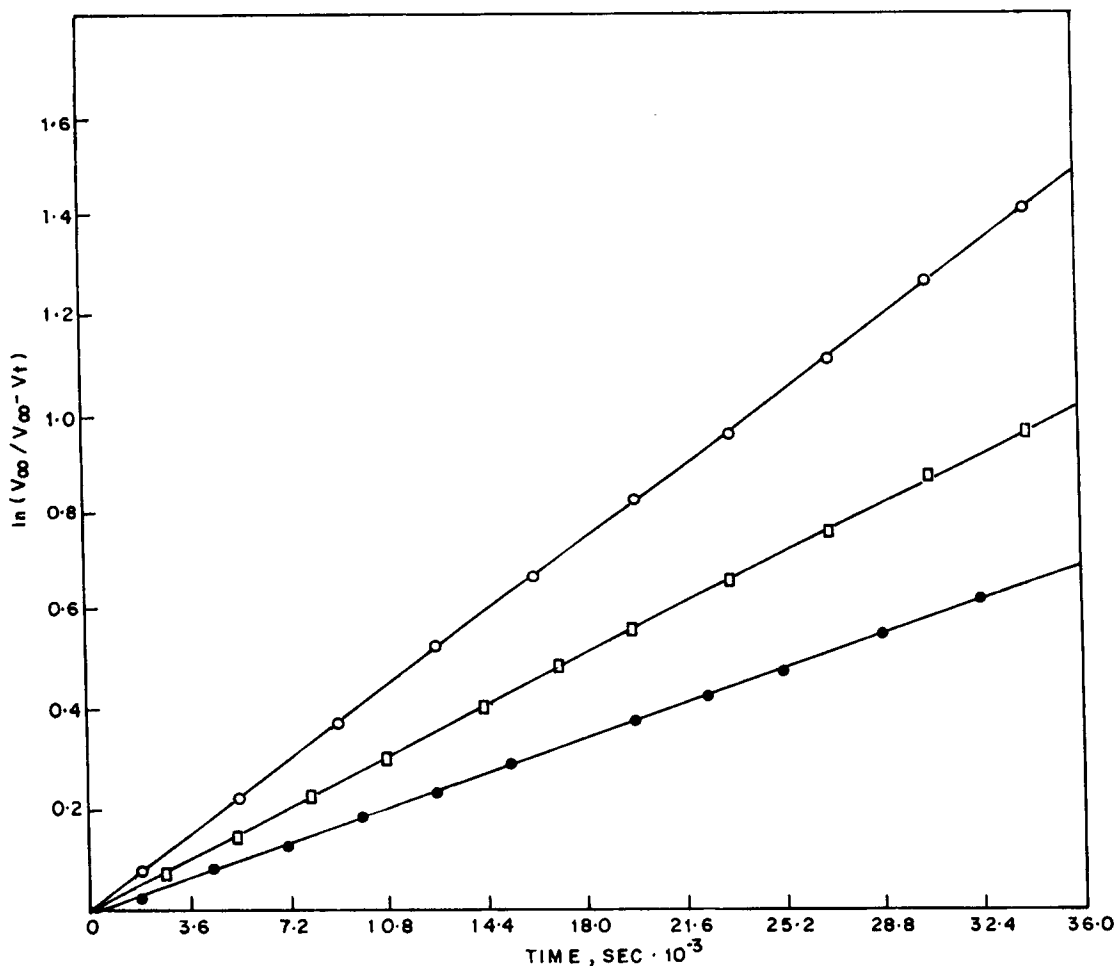
$$\text{ClOC}-\text{H}_2\text{C}-\text{H}_2\text{C}-\overset{\overset{\text{CH}_3}{|}}{\underset{\underset{\text{CN}}{|}}{\text{C}}}-\text{N}{=}\text{N}-\overset{\overset{\text{CH}_3}{|}}{\underset{\underset{\text{CN}}{|}}{\text{C}}}-\text{CH}_2-\text{CH}_2-\text{COCl} \quad + \text{H}_2\text{N}-\text{R}-\text{OH}$$

<u>1</u>   <u>2</u>

DICHLOROMETHANE/
TRIETHYLAMINE
$\xrightarrow{0\,°C}$

$$\text{HO}-\text{R}-\text{HN}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{H}_2\text{C}-\text{H}_2\text{C}-\overset{\overset{\text{CH}_3}{|}}{\underset{\underset{\text{CN}}{|}}{\text{C}}}-\text{N}{=}\text{N}-\overset{\overset{\text{CH}_3}{|}}{\underset{\underset{\text{CN}}{|}}{\text{C}}}-\text{CH}_2-\text{CH}_2-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{NH}-\text{R}-\text{OH}$$

<u>3</u>

WHERE,

R = <u>a</u> ; $-\text{CH}_2-\text{CH}_2-$

<u>b</u> ; $-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$

Scheme 1 Synthesis of azobisnitriles containing functional end groups.

amine containing triethylamine at 0°C under nitrogen. The reaction mixture was then stirred for 5 h at room temperature. At the end of this period, dichloromethane was evaporated and the solid obtained was purified by dissolving it in DMF and precipitating with cold water. Recrystallization of the crude product from DMF and water gave 6.44 g (88%) of ABCAE, mp. 125–127°C.

IR (Nujol, cm^{-1}): 1630 ($\diagdown$C=O), 3250 (—NH), 2220 (—CN), 3450 (—OH), 1570 (—N=N—).

^{1}H NMR (DMSO d$_6$, δ ppm): 1.3 (4H, t, $-\overset{|}{\underset{|}{\text{C}}}-$ CH$_2$—), 1.8 (6H, s, $-\overset{|}{\text{C}}-$CH$_3$), 2.26 (4H, t, —CH$_2$—CO—), 2.85 (4H, t, —HN—CH$_2$—), 3.7 (4H, t, —CH$_2$—OH), 8.0 (2H, s, —CONH—).

ANAL: Calcd. for C$_{16}$H$_{26}$N$_6$O$_4$: C, 52.45%; H, 7.10%; N, 22.95%. Found: C, 52.52%; H, 7.15%; N, 22.88%.

4,4′-Azobis(4-cyanopentanoyl)bis 2-(2-aminoethoxy)ethanol (ABCAEE). The azo compound ABCAEE was prepared by reacting 6.34 g (0.02 mole) of ABCACl with 10 g of 2-(2-aminoethoxy)ethanol, under the same reaction conditions used for ABCAE. The solid product obtained was purified by recrystallization from a mixture of DMF and water to yield 8.17 g (90%) of pure ABCAEE, mp. 94–96°C.

IR (Nujol, cm^{-1}): 1620 ($\diagdown$C=O), 3240 (—NH), 2220 (—CN), 3500 (—OH), 1560 (—N=N—), 1130 (—CH$_2$—O—CH$_2$—).

^{1}H NMR (DMSO d$_6$, δ ppm): 1.37 (4H, t, $-\overset{|}{\text{C}}-$CH$_2$—), 1.66 (6H, s, $-\overset{|}{\text{C}}-$CH$_3$), 2.37 (4H, t, —CH$_2$—CO—), 3.15 (4H, t, —NH—CH$_2$—), 3.48 (8H, m, —CH$_2$—O—CH$_2$—), 3.71 (4H, t, —CH$_2$—OH), 7.04 (2H, s, —CONH—).

ANAL: Calcd. for C$_{20}$H$_{34}$N$_6$O$_6$: C, 52.86%; H, 7.49%; N, 18.50%. Found: C, 52.94%; H, 7.42%; N, 18.32%.

RESULTS AND DISCUSSION

New azobisnitriles containing amide, hydroxyl with amide, ether, and hydroxyl groups namely ABCAE and ABCAEE were prepared by reacting ABCACl with 2-aminoethanol and 2-(2-aminoethoxy)ethanol, according to the reaction scheme.

The azo compounds ABCAE and ABCAEE prepared were characterized by IR, proton NMR spectra, and elemental analysis.

The thermal decomposition studies of azo compounds are very useful for predicting their performance as initiators. The thermal decomposition kinetics of ABCP and ABCA have been studied extensively in various solvents and at different temperatures.[11–15] Generally these initiators follow first order kinetics of decomposition.[16–19] The nature of the solvent does not affect the rate of decomposition of these initiators.

Various techniques such as nitrogen evolution,[18,19] radical scavenging,[20] and direct spectroscopic determination[21] of azo initiator concentration have been employed to study the kinetics of decomposition.

In the present work, the kinetics of thermal decomposition of ABCAE and ABCAEE was studied in DMF

Figure 1   Thermal decomposition of 4,4'-azobis(4-cyanopentanoyl)bis 2-aminoethanol (ABCAE) in N,N-dimethylformamide at (O) 74°C, (□) 69°C, and (●) 65°C.

and DMAC at 65, 69, and 74°C, by measuring nitrogen evolution as a function of time. Figures 1 and 2 show the thermal decomposition behavior of ABCAE and ABCAEE in DMF at 65, 69, and 74°C respectively.

The plots of time versus $\ln(V_\infty/V_\infty - V_t)$ for the decomposition of these two initiators in DMAC look quite similar to that of plots in DMF, hence representative plots of both the initiators are shown only in DMF at three different temperatures. The linear plots of time versus $\ln(V_\infty/V_\infty - V_t)$ indicated that the decomposition of AB-CAE and ABCAEE follow first order kinetics. The decomposition rate constants (k_d) were determined from the slopes of the straight lines for both solvents at three different temperatures. The decomposition rate constants (k_d) for ABCAE and ABCAEE in DMF and DMAC at three different temperatures are listed in Tables I and II.

Values for the half-life, an important parameter of sequential bifunctional initiators, were calculated from the expression, $t_{1/2} = 0.693/k_d$ and are also listed in Tables I and II.

The activation energies were calculated from the slopes

of the plots of $\ln k_d$ versus $1/T.10^3$ by least squares method. The Arrhenius plots for the decomposition of ABCAE and ABCAEE are shown in Figure 3. The activation energy values of these initiators are close to the values usually reported for the azo compounds.

A comparison of the k_d values of ABCAE and ABCAEE at a particular temperature indicated that both the initiators decompose at almost the same rate.

The small change in the rate constants of ABCAE and ABCAEE in going from DMF to DMAC allows the conclusion that the decomposition of azo compounds is independent of solvent. The first order kinetics and the absence of appreciable solvent effects indicate the absence of radical induced secondary decomposition.

The ABCAE and ABCAEE are useful initiators for the free radical polymerization of vinyl monomers yielding polymeric products with one or more functional end groups depending on the kinetic behavior of the particular monomer involved. Detailed studies of these initiators for the synthesis of homo- and block copolymers are now in progress.
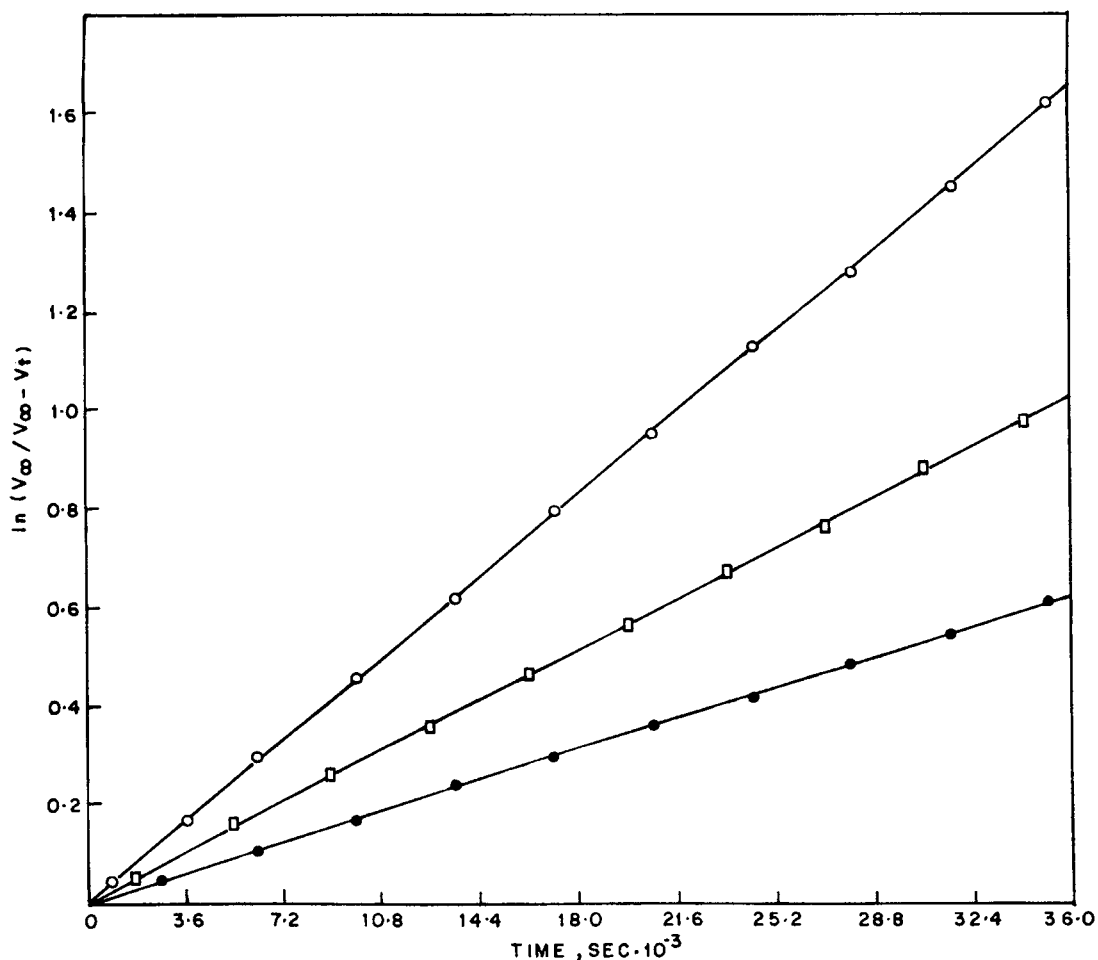
Figure 2   Thermal decomposition of 4,4'-azobis (4-cyanopentanoyl)bis 2-(2-aminoethoxy) ethanol (ABCAEE) in N,N-dimethylformamide at (O) 74°C, (□) 69°C, and (●) 65°C.

CONCLUSIONS

The rates of decomposition of ABCAE and ABCAEE, as measured by nitrogen evolution, follow first order kinetics and the rates are almost identical. The decomposition rate

constants (k_d) of these initiators are not affected by solvents like DMF and DMAC. These initiators are useful for the preparation of functionally terminated polymers and block copolymers.

Table I   Kinetic Data of Thermal Decomposition of ABCAE[a]

Solvent	Temp. (°C)	$k_d \cdot 10^5$ (s^{-1})	Half-life (($t_{1/2}$) s^{-1})	Energy of Activation (kJ · mole^{-1})
DMF	65	1.76	39375.00	103.96
	69	2.85	24315.78	
	74	4.66	14871.24	
DMAC	65	1.73	40290.69	101.86
	69	2.73	25384.60	
	74	4.53	15298.00	

[a] ABCAE—4,4'-azobis(4-cyanopentanoyl)bis 2-aminoethanol.

Table II   Kinetic Data of Thermal Decomposition of ABCAEE[a]

Solvent	Temp. (°C)	$k_d \cdot 10^5$ (s^{-1})	Half-life (($t_{1/2}$) s^{-1})	Energy of Activation (kJ · mole^{-1})
DMF	65	1.77	39375.00	109.15
	69	2.90	23896.55	
	74	4.90	14142.85	
DMAC	65	1.74	40057.80	107.47
	69	2.83	24487.64	
	74	4.65	14903.22	

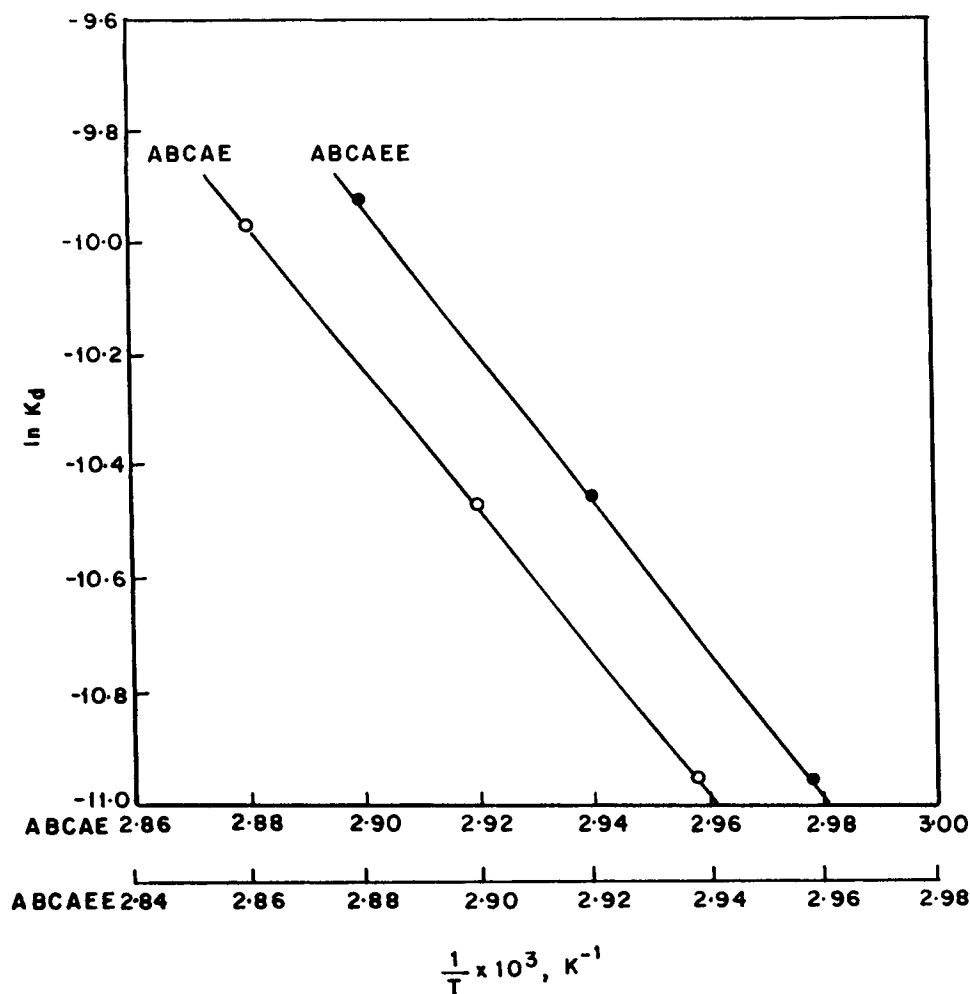[a] ABCAEE—4,4'-azobis(4-cyanopentanoyl)bis   2-(2-aminoethoxy)-ethanol.

Figure 3 Arrhenius plot for the decomposition of 4,4'-azobis(4-cyanopentanoyl)bis 2-amino ethanol (ABCAE) and 4,4'-azobis (4-cyanopentanoyl)bis 2-(2-aminoethoxy)ethanol (ABCAEE).

REFERENCES

1. S. F. Reed, *Polym. Prep.*, **15**, 46 (1974).

2. H. Schnecko, G. Degler, H. Dongowski, R. Caspary, G. Anger, and T. S. Ng, *Angew. Makromol. Chem.*, **70**, 9 (1978).

3. A. B. North, *The Kinetics of Free Radical Polymerization*, Academic Press, London, 1961.

4. B. Baysal and A. V. Tobolsky, *J. Polym. Sci.*, **9**, 471 (1953).

5. S. F. Reed, *J. Polym. Sci. A-1*, **9**, 2029 (1971).

6. S. F. Reed, *J. Polym. Sci. A-1*, **10**, 649 (1972).

7. S. F. Reed, *J. Polym. Sci. Polym. Chem. Ed.*, **11**, 1435 (1973).

8. S. F. Reed, *J. Polym. Sci. A-1*, **19**, 1863 (1981).

9. R. C. Petersen, J. H. Markgraf, and S. D. Rose, *J. Am. Chem. Soc.*, **83**, 3819 (1961).

10. Y. Yagci, *Polym. Commun.*, **26**, 7 (1985).

11. C. G. Overberger and D. A. Labianca, *J. Org. Chem.*, **35**, 1762 (1970).

12. D. Pramanick and B. Chakraborty, *Colloid Polym. Sci.*, **259**, 995 (1981).

13. G. Clouet, M. Knipper, and J. Brossas, *Polym. Bull.*, **11**, 171 (1984).

14. D. C. Blackley and A. C. Haynes, *J. Chem. Soc. Faraday Trans. I*, **75**, 935 (1979).

15. V. P. Kartavykh, V. A. Drach, Y. N. Barantsevich, and Y. L. Abramenko, *Polym. Sci. USSR*, **19**, 1413 (1977).

16. V. P. Kartavykh, V. A. Drach, Y. N. Barantsevich, and Y. L. Abramenko, *Polym. Sci. USSR*, **19**, 1226 (1977).

17. Kwei-Ping Shen Kwei, *J. Polym. Sci. A-3*, 2387 (1965).

18. F. M. Lewis and M. S. Matheson, *J. Am. Chem. Soc.*, **71**, 747 (1949).

19. C. G. Overberger, M. T. O'Shaughnessy, and H. Shalit, *J. Am. Chem. Soc.*, **71**, 2661 (1949).

20. C. E. H. Bawn and S. F. Mellish, *Trans Farady Soc.*, **47**, 1216 (1951).

21. M. T. Erben and S. Bywater, *J. Am. Chem. Soc.*, **77**, 3712 (1955).

Susheela B. Idage
Bhaskar B. Idage
Subhash P. Vernekar*

Division of Polymer Chemistry
National Chemical Laboratory
Pune 411008, India

* To whom correspondence should be addressed.
* NCL Communication No. 4941