



Aqueous Polymerization of Vinyl Monomers Initiated by Mn(III)-Amino Acid Chelating Agents

G. SIVA KUMAR¹, N. KRISHNAVENI^{2*}, M. U MAYAVALLI¹, S.P. MANICKAM¹ and S. RATNASABAPATHY¹

¹Post Graduate and Research Department of Chemistry, A.P.A. College of Arts and Culture, Palani-624 601, India

²Velalar College of Engineering and Technology, Erode-638 012, India

*Corresponding author: E-mail: krishnaveninachimuthu@gmail.com

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The polymerization kinetics of acrylamide initiated by the redox pairs *i.e.*, *tris*-acetatomanganese(III)dihydrate-ethylenediaminetetraacetic acid and in dilute sulphuric acid medium was investigated. The rate of polymerization (R_p) was proportional to $[AM]^{1.3}$, $[EDTA]^{0.6}$ and inverse dependence to $[Mn(III)]$ for acrylamide-Mn(III)-EDTA system and $[AM]^{1.2}$, $[EDTA]^{0.3}$ and inverse dependence to $[Mn(III)]$ for acrylamide-Mn(III)-nitrioloacetic acid system. The rate of manganic ion disappearance R_m , was directly proportional to $[Mn(III)]$ and $[NTA]$ but independent of monomer for both the systems. Both R_p and R_m were not affected by the changes in $[H^+]$, ionic strength, added Mn(II) and R_p decreased with the addition of sodium nitrate. The activation energy was evaluated by using Arrhenius plot. Suitable mechanism has been proposed to explain the observed kinetic data.

Key Words: *Tris*-acetatomanganese(III)dihydrate-ethylenediaminetetraacetic acid, Trisacetatomanganese(III)dihydrate-nitrioloacetic acid, Acrylamide, Chelating agent.

INTRODUCTION

The metal ions with high oxidation potentials were found to initiate vinyl polymerization, but the rate of polymerization was found to be very low in these systems¹⁻³. The presence of organic reductants was found to enhance the rate of polymerization and the polymerization takes place even at low concentration of monomer at low temperature.

Many reducing agents were coupled with trivalent manganic ion to initiate the polymerization of vinyl monomer⁴⁻¹². Saha and Chandhuri employed cerium-triethanolamine redox pair in the aqueous polymerization of acrylonitrile¹³. Amino acid type chelating agents have the electron withdrawing carboxyl and amino groups at both sides of methylene group. The chelating agents possess active protons on the carbon to the carboxyl group. Since the structure is similar to triethanolamine, it was suggested that metal ion-amino acid type chelating agent redox pairs may be expected to be effective initiators for aqueous polymerization. Ce(IV)-amino acid chelating agents pairs have been employed in vinyl polymerization¹⁴⁻¹⁶.

Hence in our laboratory, *tris*-acetatomanganese(III)dihydrate has been coupled with the chelating agents, ethylenediaminetetraacetic acid (EDTA) and nitrioloacetic acid (NTA). These redox pairs were employed in the aqueous polymerization of monovinyl monomers, acrylamide, acrylic

acid and a non-conjugated divinyl monomer, N,N'-methylene-bisacrylamide.

The present paper deals with the kinetics of acrylamide initiated by the redox pairs, *tris*-acetatomanganese(III)dihydrate-ethylenediaminetetraacetic acid and trisacetatomanganese(III)dihydrate-nitrioloacetic acid in dilute sulphuric acid medium. From the experimental results, a suitable reaction scheme has been proposed and kinetic parameters were evaluated.

EXPERIMENTAL

The reagents used were purified by standard methods. The polymerization reaction was carried out in nitrogen atmosphere. The rate of monomer disappearance R_p , was determined by bromometry and the rate of manganic ion disappearance R_m , was determined by cerimetry.

RESULTS AND DISCUSSION

Rate of polymerization:

$$R_p = \frac{-d[M]}{dt} \quad (1)$$

In acrylamide-Mn(III)-EDTA system, the rate of polymerization depended on $[M]^{1.3}$ was well indicated by the plots of R_p versus $[M]^{1.3}$ passing through the origin. In the case of acrylamide-Mn(III)-NTA system, similar plots indicated an

order of 1.2 with respect to [M] (Fig. 1). The rate of polymerization R_p , showed an order of 0.6 with respect to [Red] in the case of acrylamide-Mn(III)-EDTA and acrylamide-Mn(III)-NTA systems (Fig. 2). In both the systems, R_p showed an inverse dependence to [Mn(III)] (Fig. 3). R_p was unaffected by the changes in $[H^+]$, ionic strength and added Mn(II) in both the systems in the observed range. In AM-Mn(III)-EDTA system, R_p was found to be increased with increasing temperature, while in AM-Mn(III)-NTA system R_p did not change appreciably up to 25-40 °C then decreased with increasing temperature.

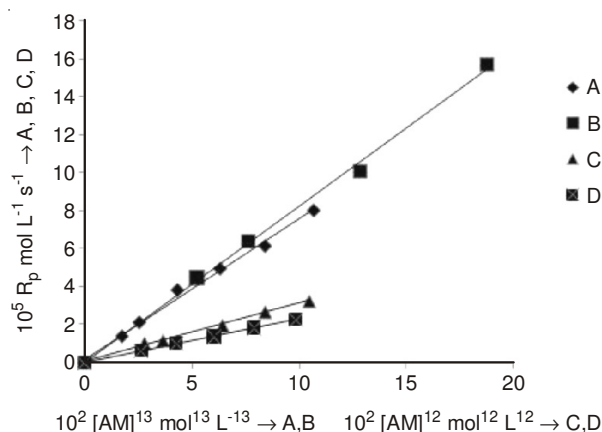


Fig. 1. (A) Dependence of R_p on [MBA]; [EDTA] = $1.00 \times 10^{-3} \text{ mol L}^{-1}$, [Mn(III)] = $8.90 \times 10^{-3} \text{ mol L}^{-1}$ (B) Dependence of R_p on [MBA]; [EDTA] = $2.00 \times \text{mol L}^{-1}$, [Mn(III)] = $1.65 \times 10^{-3} \text{ mol L}^{-1}$ (C) Dependence of R_p on [MBA]; [EDTA] = $2.00 \times \text{mol L}^{-1}$, [Mn(III)] = $1.37 \times 10^{-3} \text{ mol L}^{-1}$ (D) Dependence of R_p on [MBA]; [EDTA] = $2.50 \times \text{mol L}^{-1}$, [Mn(III)] = $1.68 \times 10^{-3} \text{ mol L}^{-1}$

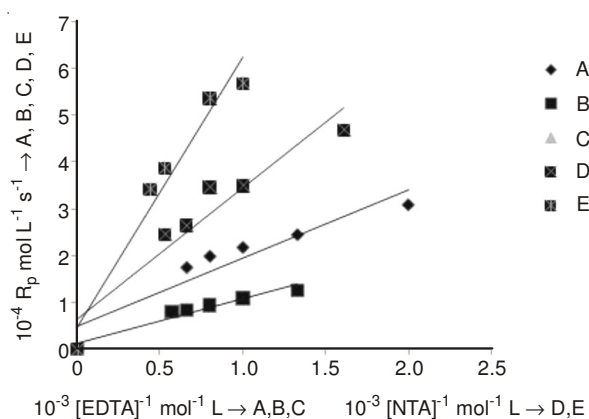


Fig. 2. (A) Dependence of R_p on [EDTA]; [AM] = $13.2 \times 10^{-2} \text{ mol L}^{-1}$, [Mn(III)] = $1.55 \times 10^{-2} \text{ mol L}^{-1}$ (B) Dependence of R_p on [EDTA]; [AM] = $17.6 \times 10^{-2} \text{ mol L}^{-1}$, [Mn(III)] = $1.51 \times 10^{-2} \text{ mol L}^{-1}$ (C) Dependence of R_p on [EDTA]; [AM] = $17.6 \times 10^{-2} \text{ mol L}^{-1}$, [Mn(III)] = $2.80 \times 10^{-2} \text{ mol L}^{-1}$ (D) Dependence of R_p on [NTA]; [AM] = $11.9 \times 10^{-2} \text{ mol L}^{-1}$, [Mn(III)] = $1.00 \times 10^{-2} \text{ mol L}^{-1}$ (E) Dependence of R_p on [NTA]; [AM] = $8.97 \times 10^{-2} \text{ mol L}^{-1}$, [Mn(III)] = $1.25 \times 10^{-2} \text{ mol L}^{-1}$

Effect of added sodium nitrate: R_p decreased with the addition of sodium nitrate in both cases. This may be due to the reason that NO_3^- ion acts as an inhibitor. Increasing the nitrate ion decreased the complex formation constant and lowered the complex concentration, it thus increased the termination rate¹⁷.

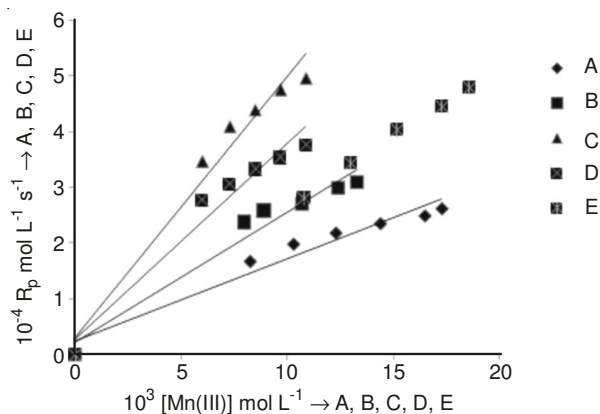


Fig. 3. (A) Dependence of R_p on [Mn(III)]; [AM] = $12.8 \times 10^{-2} \text{ mol L}^{-1}$, [EDTA] = $2.00 \times 10^{-3} \text{ mol L}^{-1}$ (B) Dependence of R_p on [Mn(III)]; [AM] = $8.95 \times 10^{-2} \text{ mol L}^{-1}$, [EDTA] = $1.00 \times 10^{-3} \text{ mol L}^{-1}$ (C) Dependence of R_p on [Mn(III)]; [AM] = $7.15 \times 10^{-2} \text{ mol L}^{-1}$, [NTA] = $1.00 \times 10^{-3} \text{ mol L}^{-1}$ (D) Dependence of R_p on [Mn(III)]; [AM] = $8.95 \times 10^{-2} \text{ mol L}^{-1}$, [NTA] = $1.00 \times 10^{-3} \text{ mol L}^{-1}$ (E) Dependence of R_p on [Mn(III)]; [AM] = $7.65 \times 10^{-2} \text{ mol L}^{-1}$, [EDTA] = $2.00 \times 10^{-3} \text{ mol L}^{-1}$

Rate of manganic ion disappearance:

$$R_m = \frac{-d[\text{Mn(III)}]}{dt} \quad (2)$$

The rate of manganic ion disappearance R_m , was first order with respect to [Mn(III)] but independent of monomer concentration. R_m increased with [Red] and Lineweaver-Burk plots of R_m^{-1} vs. [Red]⁻¹ were produced definite intercepts on the Y axis¹⁷ (Fig. 4). The rate was unaltered by the changes in $[H^+]$, ionic strength and added Mn(II).

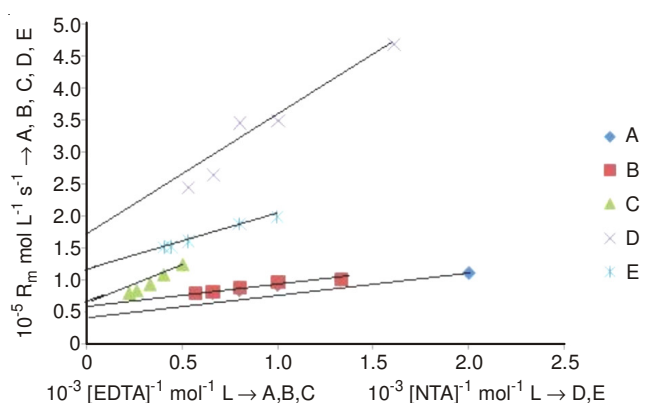


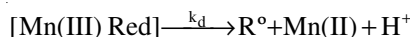
Fig. 4. Lineweaver Burck plots (A) Dependence of R_m on [EDTA]; [AM] = $13.2 \times 10^{-2} \text{ mol L}^{-1}$, [Mn(III)] = $1.55 \times 10^{-2} \text{ mol L}^{-1}$ (B) Dependence of R_m on [EDTA]; [AM] = $17.6 \times 10^{-2} \text{ mol L}^{-1}$, [EDTA] = $1.51 \times 10^{-3} \text{ mol L}^{-1}$ (C) Dependence of R_m on [EDTA]; [AM] = $17.6 \times 10^{-2} \text{ mol L}^{-1}$, [NTA] = $2.80 \times 10^{-3} \text{ mol L}^{-1}$ (D) Dependence of R_m on [NTA]; [AM] = $11.9 \times 10^{-2} \text{ mol L}^{-1}$, [NTA] = $1.00 \times 10^{-3} \text{ mol L}^{-1}$ (E) Dependence of R_m on [NTA]; [AM] = $8.97 \times 10^{-2} \text{ mol L}^{-1}$, [EDTA] = $1.25 \times 10^{-3} \text{ mol L}^{-1}$

Mechanism and rate law: To explain the above observations, the following mechanism which involves initiation by primary radical and termination by metal ion or by metal ion-reductant complex, has been proposed.

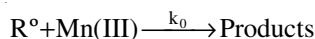
Complex formation



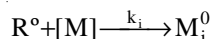
Production of primary radical



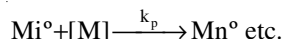
Primary radical oxidation by Mn(III)



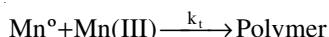
Initiation



Propagation



Termination



Applying steady state approximations, the following rate expressions were arrived at.

$$R_p = \frac{k_p k_i k_d K [\text{Red}] [\text{M}]^2}{k_t (k_i [\text{M}] + k_0 [\text{Mn(III)}]) (1 + K [\text{Red}])} \quad (3)$$

R_m in the presence of monomer is given by the relation,

$$R_m = \frac{2k_d K [\text{Mn(III)}] [\text{Red}]}{1 + K [\text{Red}]} \quad (4)$$

Evaluation of rate parameters: From the plots of R_m^{-1} versus $[\text{Red}]^{-1}$, the unimolecular decomposition constant (k_d) and the formation constant of the complex (K) were evaluated and tabulated. By rearranging eqn. 1, k_p/k_t and k_0/k_i values were calculated and tabulated (Table-1). As indicated earlier the higher value of the formation constant K , indicates the strong complex formation between Mn(III) and the reductants EDTA and NTA. The enhanced stability may be ascribed to the strong coordinating ability of these chelating agents¹⁸. The formation of five membered rings has been shown to be the most stable chelates of aliphatic amino acids¹⁹. EDTA and NTA formed five membered rings with Mn(III). Such ring formation has been reported with Ce(IV)¹⁴. The complex formation constants of these systems are larger than those obtained from other Mn(III)-reducing agent systems (Table-2).

TABLE-1
RATE CONSTANT VALUES FOR THE SYSTEMS
AM-Mn(III)-EDTA AND AM-Mn(III)-NTA

System	K (mol ⁻¹ L)	k_d (s ⁻¹)	k_p/k_t	k_0/k_i
AM-Mn(III)-EDTA	2.41×10^3	4.96×10^{-4}	0.24	5.42
AM-Mn(III)-NTA	1.80×10^3	3.33×10^{-4}	0.14	1.24

R_m was found to be independent of $[\text{M}]$, which indicates that the monomer was not involved in the initiation step. The decrease in concentration of initiating radicals and poor trapping of the initiating radicals by the monomer may be the reason for the decrease in the order with respect to monomer concentration. It may be further attributed to the rapid termination of primary radicals by Mn(III) ion.

Variation of R_m with reductant concentration indicates the complex formation prior to electron transfer. This is further confirmed by Lineweaver-Burck plots. The deviation from the expected first order dependence of R_p with respect to reductant concentration may be due to the above said reason. The inverse dependence of R_p on $[\text{Mn(III)}]$ indicates the involvement

TABLE-2
COMPLEX FORMATION CONSTANT VALUES FOR THE
POLYMERIZATION OF VINYL MONOMERS USING Mn(III)-
ORGANIC SUBSTRATES REDOX SYSTEMS

Monomers	Organic substrates	K (mol ⁻¹ L)
²⁰ Acrylonitrile	Cyclohexanone	16.68
²⁰ Acrylonitrile	DMSO	2.57
²⁰ Methylmethacrylate	Glycerol	10.20
²⁰ Methylmethacrylate	Fructose	80.00
²¹ N,N'-Methylene bisacrylamide	Cyanoacetic acid	34.70
²¹ N,N'-Methylene bisacrylamide	Ethylene glycol	6.20
²¹ N,N'-Methylene bisacrylamide	Thiomalic acid	210.00
Acrylamide	EDTA	2410.00
Acrylamide	NTA	1800.00

of Mn(III) ion in the termination step. Increase of ionic strength and $[\text{H}^+]$ showed negligible effect on R_p and R_m which is common in free radical polymerization.

Effect of temperature: The normal increase in the rate of polymerization with increasing temperature was observed in the system AM-Mn(III)-EDTA. This may be the result of (i) the increase in the steady state concentration of the initiating radicals and (ii) the increase in the rate of propagation. But in AM-Mn(III)-NTA system a decrease in R_p was observed in the temperature range of 45-60 °C. Destruction of good portion of initiating species at the reaction temperature by side reactions and also at higher temperature the chain terminating reaction may be faster than the free radical generation reaction. By using Arrhenius plot, the activation energy of the two systems was calculated. They were 2.69 and 14.7 kJ mol⁻¹ for the AM-Mn(III)-EDTA and AM-Mn(III)-NTA systems respectively, which is close to the usual redox systems^{14,15}.

Reactivity of redox pairs: To compare the efficiency of the redox pairs Mn(III)-EDTA and Mn(III) NTA, they have been employed on the same monomer and the rates of polymerization were calculated. The reactivity of the redox pairs followed the order Mn(III)-EDTA > Mn(III)-NTA (Table-3).

TABLE-3
REACTIVITY OF REDOX PAIR. $[\text{Mn(III)}] = 1.06 \times 10^{-2}$
mol L⁻¹, $[\text{H}^+] = 0.05$ mol L⁻¹, $[\text{EDTA}]$, $[\text{NTA}] = 1.00 \times 10^{-3}$
mol L⁻¹, $I = 0.30$ mol L⁻³, $t = 50$ °C

10 ² [AM] (mol L ⁻¹)	Mn(III)-NTA		Mn(III)-EDTA	
	10 ⁵ R _p (mol L ⁻¹ s ⁻¹)	10 ⁶ R _m (mol L ⁻¹ s ⁻¹)	10 ⁵ R _p (mol L ⁻¹ s ⁻¹)	10 ⁶ R _m (mol L ⁻¹ s ⁻¹)
8.75	1.96	7.49	3.12	8.58
12.2	3.04	7.49	5.04	8.58
15.7	3.79	7.49	6.54	8.58

Reactivity of monomers and polymer radicals: The reactivity of the monomers, acrylamide and acrylic acid can be compared since both the monomers follow the same reaction mechanism.

$$R_p = \frac{k_p k_i k_d K [\text{Red}] [\text{M}]^2}{k_t (k_i [\text{M}] + k_0 [\text{Mn(III)}]) (1 + K [\text{Red}])} \quad (5)$$

$$R_p = \frac{k_p R_i [M]}{k_t [Mn(III)]} \quad (6)$$

where the rate of initiation is given by,

$$R_i = \frac{k_d K [Red] [Mn(III)] [M]}{([M] + (k_0 / k_i) [Mn(III)] (1 + K [Red]))} \quad (7)$$

From eqn. 4, it follows that at a given rate of initiation and a given [M] and [Mn(III)], the rate of polymerization of a single monomer will be directly proportional to the ratio k_p/k_t might be regarded as a measure of reactivity²².

Q, the resonance stabilization of the reacting monomer and e, polar character associated with the monomer can be used to measure the reactivity of the monomers^{23,24}. The Q values of AA and AM are 1.15 and 1.12 when the Q values of the two monomers are nearly the same then values may account for the difference in reactivities.

Gergely and Seaman²⁵ observed that the highly reactive monomer yields less reactive polymer radicals and *vice versa*. Therefore considering the e values of AM (1.20) and AA (0.74), the poly (acrylamide) radical should be less reactive compared with the poly(acrylic acid) radical. This is in agreement with present observation that the k_p/k_t for acrylic acid is greater than for acrylamide. Hence the order of reactivity of the monomers is AM > AA. This is supported by the kinetic results given (Table-4).

TABLE-4

REACTIVITY OF ACRYLAMIDE AND ACRYLIC ACID
[Mn(III)] = 1.78×10^{-3} mol L⁻¹ [EDTA], [NTA] = 2.00×10^{-3} mol L⁻¹

$10^2 [AA]/[AM]$ (mol L ⁻¹)	$10^5 R_p$ (mol L ⁻¹ s ⁻¹) (AA)	$10^5 R_p$ (mol L ⁻¹ s ⁻¹) (AM)
10.2	3.52	4.48
13.6	5.06	6.41
20.4	8.76	10.1

Conclusion

The kinetics of acrylamide initiated by the redox pairs, *tris*-acetatomanganese(III) dihydrate-ethylenediaminetetracetic acid and *tris*acetatomanganese(III)dehydrate-nitrilotriacetic

acid in dilute sulphuric acid medium was studied. From the experimental results, a suitable reaction scheme which involves initiation by primary radical and termination by metal ion or metal ion-reductant complex has been proposed.

REFERENCES

1. J. Sadlick, *J. Polym. Sci.*, **19**, 73 (1956).
2. V.S. Ananthanarayanan and M. Santappa, *J. Appl. Polym. Sci.*, **9**, 2437 (1965).
3. D. Pramanick and S.K. Sarkar, *Colloid. Polym. Sci.*, **254**, 989 (1976).
4. N.G. Devi and V. Mahadevan, *Makromol. Chem.*, **166**, 209 (1973).
5. P. Elayaperumal, T. Balakrishnan, M. Santappa and R.W. Lenz, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 2471 (1980).
6. M. Haragopal, A. Jayakrishnan and V. Mahadevan, *Makromol. Chem.*, **183**, 657 (1982).
7. S. Ratnasabapathy, N. Marisami and S.P. Manickam, K. Venkatarao and N.R. Subbaratnam, *J. Macromol. Sci.-Chem.*, **A25**, 83 (1988).
8. S.N. Sudakar and K. Srinivasan, *Colloid Polym. Sci.*, **272**, 777 (1994).
9. S. Rai and J. Q-Chambers, *Transition Met. Chem.*, **20**, 61 (1995).
10. S.K. Rai, B.S. Sherigara and N.M. Madegowda, *Eur. Polym. J.*, **34**, 1031 (1998).
11. S.K. Rai, K. Shivakumar and B.S. Sherigara, *Eur. Polym. J.*, **36**, 1339 (2000).
12. A.A. Mizali, H.R. Shaterio and S.M. Habibi, *J. Appl. Polym. Sci.*, **89**, 3918 (2003).
13. S.K. Saha and A.K. Chaudhuri, *J. Polym. Sci. A-L.*, **10**, 797 (1972).
14. Wen-Cheng Hsu, Jen-Feng Kuo and Chuh-Yung Chen, *J. Polym. Sci. A, Polym. Chem.*, **31**, 267 (1993).
15. Wen-Cheng Hsu, Jen-Feng Kuo and Chuh-Yung Chen, *J. Polym. Sci. A: Polym. Chem.*, **30**, 2459 (1992).
16. T.D. Mahadevaiah, *J. Appl. Polym. Sci.*, **103**, 3498 (2006).
17. H. Lineweaver and D. Burk, *J. Am. Chem. Soc.*, **56**, 658 (1934).
18. J. Dziejgiec, *Polym. J. Chem.*, **55**, 495 (1981).
19. A.E. Martell and M. Galvin, *Chemistry of the Metal Chelate Compounds*, Prentice Hall, Englewood Cliffs, N.Y., edn. 3, p. 21 (1956).
20. S.P. Rout, A. Rout, N. Mallick, B.C. Singh and M. Santappa, *Makromol. Chem.*, **178**, 1971 (1977).
21. P.L. Nayak and S. Lenka, *J. Macromol. Sci. Rev-Macromol. Chem.*, **C19**, 83 (1980).
22. S. Ratnasabapathy, Ph.D. Thesis, Madurai Kamaraj University, India (1989).
23. A.D. Jenkins and A. Ledwith, *Reactivity Mechanisms and Structure in Polymer Chemistry*, Wiley, New York, p. 117 (1974).
24. T. Otsu, *Progr. Polym. Sci. (Japan)*, **1**, 1 (1971).
25. E.M.G. Gergely and E.C. Seaman, *J. Polym. Sci.*, **3**, 866 (1948).