

Catalase-like activity of triethyleneglycol dimethacrylate-crosslinked polyacrylamide supported metal complexes

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The catalase-like activity of complexes resulting from the interaction between triethyleneglycol dimethacrylate crosslinked polyacrylamide amine and metal ions such as Cu(II), Cr(III), Fe(III), Mn(II) and Pb(II) has been investigated. The decomposition of H₂O₂ was chosen as a model reaction for this purpose. The percentage conversion of H₂O₂ was found to be in the order Mn(II) > Cu(II) > Fe(III) > Cr(III) > Pb(II) complexes. The catalytic activity was found to depend upon the initial concentration of H₂O₂, amount of the complex, temperature and pH of the solution. The activation energy of H₂O₂ decomposition was calculated to be 10.26 kJ mol⁻¹. The polymeric metal complex catalysts could be reused four times without any reduction in activity. © 1997 Elsevier Science Ltd.

(Keywords: polyacrylamide; triethyleneglycol dimethacrylate; metal complex)

INTRODUCTION

The polymer-supported analogues of transition metal complexes are currently being vigorously investigated in various fields such as metal ions' separation, catalysis and hydrometallurgy^{1–3}. The resin binding will provide typical homogeneous catalytic chemistry plus the convenience and economy of heterogeneous catalysts^{4–7}. The three-dimensional structure without a support gives rise to extra steric demands and hence enhances selectivity^{8,9}. Resin binding can change the steric environment and consequently the substrate specificity found in homogeneous systems^{10–12}. The support can itself influence the selectivity of a reaction at a given site¹³. When a metal complex is supported on what is effectively a polydentate ligand, the position of equilibrium between the metal ion and its surrounding ligands is significantly different to that of a metal ion in homogeneous solution which enhances selectivity^{8,14}. The present paper describes the preparation of triethyleneglycol dimethacrylate (TEGDMA)-crosslinked polyacrylamides with 2–20 mol% TEGDMA crosslinks, their functionalization with ethylenediamine to afford the amino resins, complexation with Cu(II), Cr(III), Fe(III), Mn(II) and Pb(II) ions and the results of catalytic decomposition of H₂O₂ by these supported metal complexes.

EXPERIMENTAL

All the reagents used were of certified ACS reagent grade. The purest available metal salts were used to prepare metal ion solutions.

Synthesis of TEGDMA-crosslinked polyacrylamides

For the preparation of 2 mol% TEGDMA-crosslinked

polyacrylamide, acrylamide (20.87 g in 20 ml water) and TEGDMA (1.716 g or 1.572 ml) were added, with stirring, to ethanol (100 ml) containing K₂S₂O₈ (100 mg) at 70°C¹⁵. Heating and stirring were continued until the polymer was precipitated. Water (100 ml) was added and heating was continued for 1 h to complete the polymerization. The polymer was filtered, washed with water and methanol and dried at 70°C. Polyacrylamides with 4, 8, 12 and 20 mol% of TEGDMA crosslinks were prepared by varying the molar percentage of the monomers in the feed (Table 1).

Preparation of poly(N-2-aminoethylacrylamides)

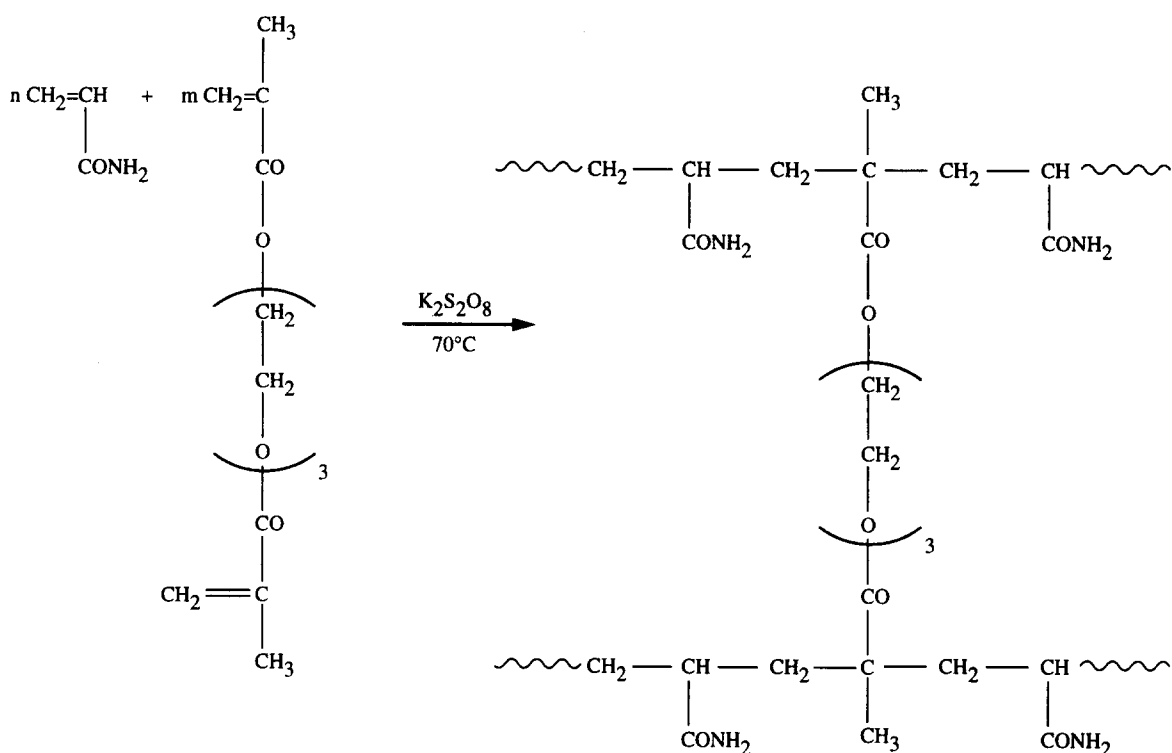
Polyacrylamide (10 g) was added in small portions to well-stirred ethylenediamine (100 ml). The mixture was refluxed at 100–110°C for 9 h. The reaction mixture after transamidation was poured into water (1 l) containing crushed ice. The resin was filtered off and washed with NaCl solution (1 M) until the filtrate was free from ethylenediamine as indicated by the absence of any blue colouration with ninhydrin reagent. The gel was washed with distilled water to remove chloride ions. The resin was washed with methanol and dried *in vacuo*.

The amino resin (100 mg) was neutralized by equilibration with HCl (0.2 N, 10 ml) for 9 h under stirring. The resin samples were filtered and washed. The filtrate

Table 1 Preparation of TEGDMA-crosslinked polyacrylamides

TEGDMA (mol%)	Wt of acrylamide (g)	Wt of TEGDMA (g)	Yield (g)
2	20.87	1.62	20.00
4	20.43	3.24	21.47
8	19.59	6.48	24.95
12	18.74	9.72	26.20
20	17.04	16.20	22.24

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Scheme 1 Preparation of TEGDMA-crosslinked polyacrylamides

together with washings were titrated against NaOH (0.2 N) to a phenolphthalein end point.

Complexation of amino resin with metal ions

The complexation of the resin, with varying extents of TEGDMA crosslinks, was carried out with Cr(III), Mn(II), Fe(III), Cu(II) and Pb(II) ions by a batch equilibration method. Each resin sample (100 mg) was stirred with a definite concentration of excess metal salt solution (5×10^{-3} M, 80 ml) for 9 h. The concentrations of the metal ions before and after complexations were estimated; Pb(II) was estimated by complexometry using xylenol orange as indicator, and Cu(II), Cr(III), Mn(II) and Fe(III) by spectrophotometry at 814.6, 575, 544 and 299 nm, respectively^{16,17}.

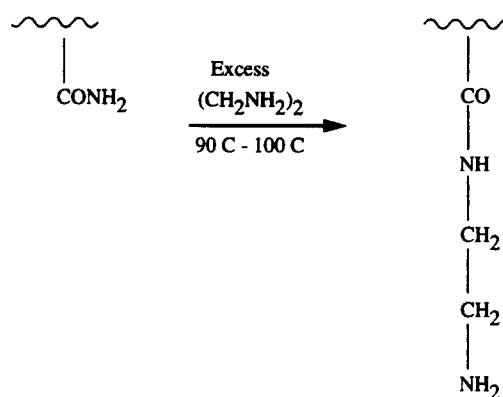
Catalytic activity of the metal complexes

The metal complex (50 mg) was mixed with H₂O₂ (0.01–0.1 N, 20 ml) and stirred for 2 h. The polymer metal complex catalysed the decomposition of H₂O₂, and O₂ was evolved. After 2 h the reaction was arrested by cooling in ice and the supernatant liquid was pipetted and titrated with 0.02 N KMnO₄ solution. The difference in titre values of the KMnO₄ solution before and after the catalysed decomposition was followed. The experiment was similarly conducted with the various metal complexes. The catalytic decomposition of H₂O₂ was studied at various pH values, temperatures, H₂O₂ concentrations and complex concentrations. A blank experiment was also simultaneously conducted with uncomplexed resin (50 mg) under the same conditions.

The time course and kinetics of catalytic decomposition of H₂O₂ were followed at equal intervals of time by titrating with standard KMnO₄.

RESULTS AND DISCUSSION

Polyacrylamides with 2–20 mol% of TEGDMA



Scheme 2 Functionalization of crosslinked polyacrylamide with ethylenediamine

crosslinks were prepared by solution polymerization of the monomers in ethanol at 70°C using K₂S₂O₈ as the initiator (Scheme 1). The compositions of the monomers and crosslinking agent used for polymerization are given in Table 1.

Preparation of poly(N-2-aminoethylacrylamides)

Amino functions were incorporated into TEGDMA-crosslinked polyacrylamides by transamidation with excess ethylenediamine at 100°C (Scheme 2).

The amino functions were detected by the semi-quantitative ninhydrin reaction, the resins developing a deep blue colour with ninhydrin reagent¹⁸. The amino functions were estimated by equilibrating a definite amount of the resin with a known concentration of excess hydrochloric acid and estimating the unreacted acid. The variation of amino capacity with crosslinking in the case of the different resins is represented in Figure 1. With increasing crosslinking the amino capacity decreases. Thus the 2% crosslinked resin has the maximum capacity of 5.06 mmol g⁻¹, and the 20%

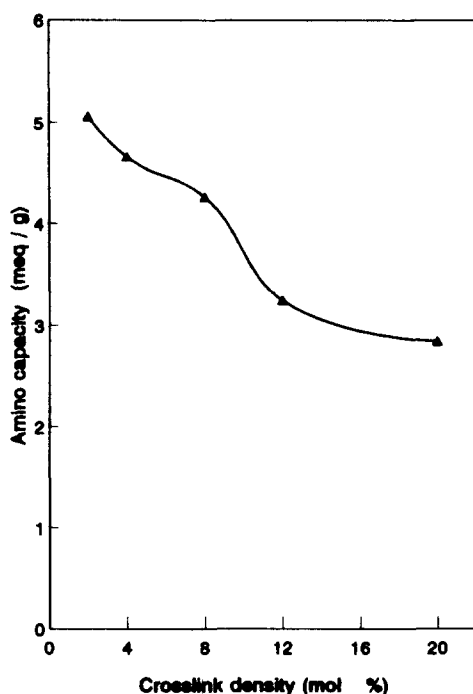


Figure 1 Amino capacity versus extent of TEGDMA crosslinking

Table 2 Metal ion intake by TEGDMA-crosslinked aminopolyacrylamides

TEGDMA (mol%)	Metal ion intake (meq g ⁻¹)				
	Cu(II)	Cr(III)	Mn(II)	Fe(III)	Pb(II)
2	2.43	1.34	1.38	0.82	0.79
4	2.39	1.18	1.11	0.73	0.67
8	2.39	0.94	0.71	0.72	0.50
12	1.79	0.80	0.58	0.64	0.45
20	1.56	0.63	0.40	0.60	0.34

crosslinked system has the minimum (2.84 mmol g⁻¹). The reduction in capacity with increase in crosslinking is expected because of the reduced availability of the reactive sites buried within the crosslinks for transamidation¹⁹.

Polymeric systems with oligoethyleneglycol crosslinking units show a higher capacity²⁰. This could arise from the favourable microenvironment created by the polar and flexible oligoethyleneglycol units in the crosslinking agent for the polar transamidation reaction. The reduction in capacity with increasing crosslinking is also less in this case.

Complexation of aminopolyacrylamides

The complexation of aminopolyacrylamides with amino functions in different structural environments was investigated with Cr(III), Mn(II), Fe(III), Cu(II) and Pb(II) by a batch equilibration method. The metal ion intake by the different resins are given in Table 2.

The metal ion intake decreases with increasing crosslinking. As in the case of amino capacity, the metal ion intake is maximum for the 2% crosslinked system and minimum for the 20% (Figure 2).

Catalytic effect of various metal complexes on the decomposition of H₂O₂

The decomposition of H₂O₂ was followed in the presence of Cu(II), Cr(III), Fe(III), Mn(II) and Pb(II)

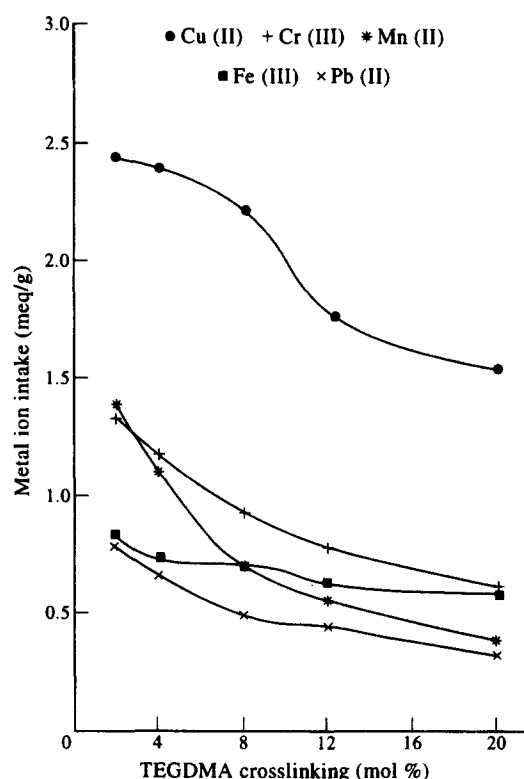


Figure 2 Metal ion intake versus extent of TEGDMA crosslinking

Table 3 Catalytic decomposition of H₂O₂ using various metal complexes

Crosslinking	Metals	Metal content (meq g ⁻¹)	[H ₂ O ₂] decomposed (mol g ⁻¹)
8% TEGDMA	Cu(II)	2.39	31.52
	Cr(III)	0.94	7.58
	Fe(III)	0.72	12.58
	Mn(II)	0.71	36.25
	Pb(II)	0.50	5.02

[H₂O₂]: 0.1 M; complex: 50 mg; time: 2 h; temperature: 28°C

Table 4 Catalytic decomposition of H₂O₂ using 2–20 mol% TEGDMA-crosslinked polyacrylamide–Cu(II) complexes

Crosslinking	Metal content (meq g ⁻¹)	[H ₂ O ₂] decomposed (mol g ⁻¹)
2% TEGDMA	2.43	35.75
4% TEGDMA	2.39	32.25
8% TEGDMA	2.39	31.52
12% TEGDMA	1.79	25.46
20% TEGDMA	1.56	22.65

[H₂O₂]: 0.1 M; complex: 50 mg; time: 2 h; temperature: 28°C

complexes of TEGDMA-crosslinked polyacrylamide amines (Table 3). The catalytic efficiency is found to decrease in the order Mn(II) > Cu(II) > Fe(III) > Cr(III) > Pb(II) complexes.

The decomposition of H₂O₂ using crosslinked polyacrylamide amine–Cu(II) complexes of 2–20 mol% TEGDMA crosslinks was studied (Table 4). The catalytic efficiency decreases as the crosslinking increases. As the crosslinked density increases the

Table 5 Catalytic decomposition of H₂O₂ at various H₂O₂ concentration

Concentration of H ₂ O ₂ (mol)	[H ₂ O ₂] decomposed (mol g ⁻¹)
0.1576	34.82
0.0780	28.65
0.0157	15.20
0.0078	8.15
0.0038	5.63

Complex: 50 mg; time: 2 h; temperature: 28°C

Table 6 Catalytic decomposition of H₂O₂ at various complex concentrations

Complex concentrations (mg)	[H ₂ O ₂] decomposed (mol g ⁻¹)
50	31.52
100	38.65
150	40.25
200	48.90

[H₂O₂]: 1 M; time: 2 h; temperature: 28°C

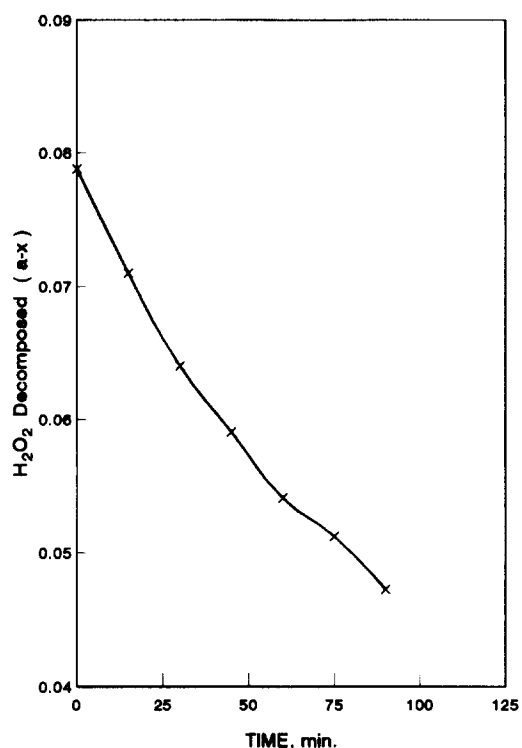


Figure 3 Catalytic decomposition of H₂O₂ by 8 mol% TEGDMA-crosslinked polyacrylamide amine-Cu(II) complex versus time

hydrophobicity and density of the polymer support increases. Diffusion and accessibility of catalytic sites decrease due to the crosslink networks. The variation in catalytic efficiency is in line with the hydrophilic/hydrophobic nature of the polymer support.

Phenomenological aspects of catalytic decomposition of H₂O₂

The catalytic properties of an 8 mol% TEGDMA-crosslinked polyacrylamide amine-Cu(II) complex were studied at various H₂O₂ concentrations (Table 5) and

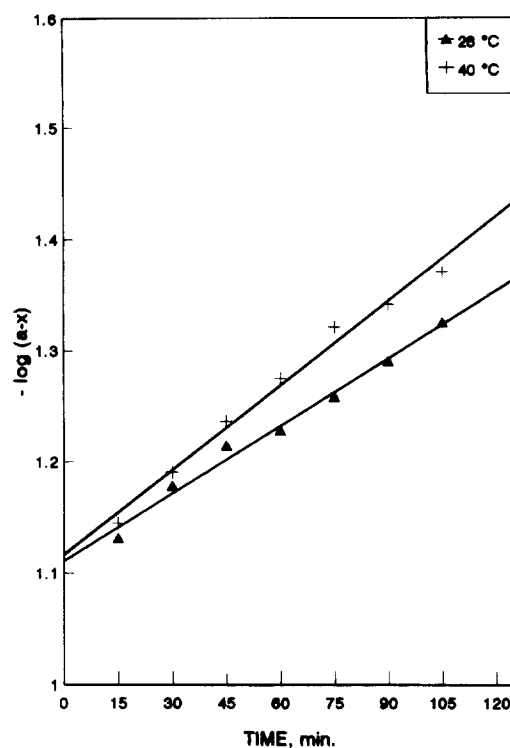


Figure 4 Kinetics of catalytic decomposition of H₂O₂ by 8 mol% TEGDMA-crosslinked polyacrylamide amine-Cu(II) complex

complex concentrations (Table 6). The increase in H₂O₂ concentration and in complex concentration increases the extent of H₂O₂ decomposition.

The dependence of catalytic activity of the 8 mol% crosslinked polymer Cu(II) complex on pH was studied using two buffers; borax (pH 9.2) and ammonium sulfate (pH 5.5). The H₂O₂ decomposition was higher at the pH of borax buffer; 92% conversion was observed at pH 9.2 and 75% conversion at pH 5.5 over a comparable time duration of 2 h. The catalytic efficiency was found to be enhanced by raising the temperature. The decomposition of H₂O₂ was followed at 301 and 313 K using the 8 mol% TEGDMA-crosslinked polymeric copper complex. The decomposition was 78% at 301 K and 90% at 313 K.

The reuse of the 8 mol% TEGDMA-crosslinked polyacrylamide amine-Cu(II) complex was investigated for four cycles. The supported catalyst was found to retain its activity for repeated use.

Time course of catalytic decomposition of H₂O₂

The time course of the catalysis by TEGDMA-crosslinked polyacrylamide amine-Cu(II) complexes was followed (Figure 3). The kinetics of H₂O₂ was followed at two different temperatures: 301 and 313 K. The linear plot of -log(a - x) versus time (Figure 4) indicates that the reaction follows a first order kinetics with respect to H₂O₂²¹. Rate constants *k*₁ and *k*₂ were obtained from the slope of the curve. Activation energy *E* was calculated using the equation:

$$\ln \frac{k_2}{k_1} = \frac{E}{8.314} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

The activation energy value of the TEGDMA-crosslinked polyacrylamide amine-Cu(II) complex is found to be 10.26 kJ mol⁻¹.

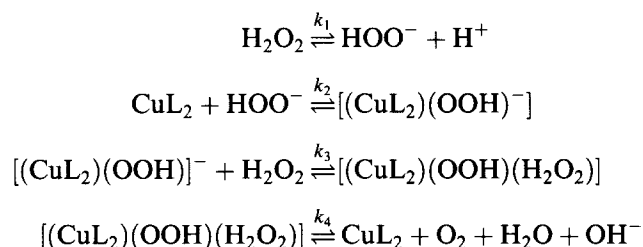
The kinetics and mechanism of catalytic decomposition of H_2O_2 in homogeneous systems have been widely investigated²¹⁻³⁰. The catalytic activity of inorganic oxide supported metal ions and chelated metal complexes are also reported²¹. The catalytic decomposition of H_2O_2 , using DVB-crosslinked polystyrene supported ethylenediamine and glycine cobalt complexes, follows a first order kinetics with respect to $[\text{H}_2\text{O}_2]$ ²².

From literature data for catalase induced reactions the activation energy is only 8.4 kJ mol^{-1} ²³ and the thermal decomposition of H_2O_2 requires 201 kJ mol^{-1} ²⁴. When using a copper complex of a copolymer of 2-methyl-5-vinyl-pyridine and acrylic acid this value is 73.5 kJ mol^{-1} ²⁵. The activation energy of a Cu complex of polymethacrylate aspartic acid is reported to be 33.6 kJ mol^{-1} and of glutamic acid 23.1 kJ mol^{-1} ²⁶.

The decomposition of H_2O_2 in the presence of Cu complexes of polyelectrolytes is reported to be proportional to $[\text{H}^+]$, $[\text{H}_2\text{O}_2]$ and $[\text{CuL}_2]$ ²⁶, i.e.

$$[\text{H}_2\text{O}_2] \text{ decomposed} = \frac{-d[\text{H}_2\text{O}_2]}{dt} \\ = k[\text{CuL}_2][\text{H}_2\text{O}_2][\text{H}^+]$$

This relationship is explained by the following reaction steps²⁷⁻³⁰.



The mechanism involves reduction of the Cu(II) complex to Cu(I) and reoxidation of Cu(I) to Cu(II) during step 4²³.

CONCLUSION

Metal complexes of TEGDMA-crosslinked polyacrylamide amine act as catalysts in the decomposition of H_2O_2 . The trend in catalytic efficiency is in the order $\text{Mn(II)} > \text{Cu(II)} > \text{Fe(III)} > \text{Cr(III)} > \text{Pb(II)}$ complexes. The extent of decomposition decreases as the crosslink density increases. The catalytic decomposition depends upon on the concentration of H_2O_2 , amount of the catalyst, temperature and pH. The rate of the reaction is

first order. The activation energy of the 8% TEGDMA-crosslinked polyacrylamide amine-Cu(II) complex is found to be $10.26 \text{ kJ mol}^{-1}$.

REFERENCES

- Lieto, J., Milstein, D., Albright, R. L., Minkewicz, J. V. and Gates, B. C., *Chem. Tech.*, 1983, **46**.
- Copper, C. A., McCullough, R. L., Gates, B. C. and Seferis, J. C., *J. Catal.*, 1980, **63**, 378.
- Copper, C. A., McCullough, R. L., Gates, B. C. and Seferis, J. C., *J. Polym. Sci., Polym. Phys.*, 1982, **20**, 173.
- Kaneko, M. and Tsuchida, E., *Macromol. Rev.*, 1981, **16**, 397.
- Pittman, C. U., in *Polymer-Supported Reactions in Organic Synthesis*, ed. P. Hodge and D. C. Sherrington. Wiley, Chichester, UK, 1980, p. 249.
- Murrell, L. L., in *Advanced Materials in Catalysis*, ed. J. L. Burton and R. L. Garten. Academic Press, New York, 1976, p. 166.
- Grubbs, R. H., *Chem. Tech.*, 1977, **7**, 512.
- Hartley, F. R., Muray, S. G. and Nicholson, P. N., *J. Mol. Catal.*, 1982, **16**, 363.
- Trost, B. M. and Keinan, E., *J. Am. Chem. Soc.*, 1978, **100**, 7779.
- Grubbs, R. H. and Kroll, L. C., *J. Am. Chem. Soc.*, 1971, **93**, 3062.
- Grubbs, R. H., Kroll, L. C. and Sweet, E. M., *Am. Chem. Soc., Polym. Prepr.*, 1972, **13**, 828.
- Grubbs, R. H., Kroll, L. C. and Sweet, E. M., *J. Macromol. Sci. Chem.*, 1973, **7**, 1047.
- Pracejus, H. and Bursian, M., East German Patent No. 92031, 1972; *Chem. Abs.*, 1973, **78**, 72591.
- Jurewicz, A. T., Rollmann, L. D. and Whitehurst, D. D., *Adv. Chem. Ser.*, 1974, **132**, 240.
- Jose, L., Mathew, B. and Pillai, V. N. R., *Polymer*, 1993, **34**, 3963.
- Vogel, A. I., *A Text Book of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis*. Longman, New York, 1978.
- Nicolaus, V. and Wohrle, D., *Angew. Chem.*, 1992, **198**, 179.
- Sarin, V. K., Kent, S. B. H., Tam, J. P. and Merrifield, R. B., *Anal. Biol. Chem.*, 1981, **117**, 147.
- Mathew, B. and Pillai, V. N. R., *Polym. Bull.*, 1991, **26**, 603.
- Egawa, H., Nonaka, T. and Nakayama, M., *J. Makromol. Sci. Chem.*, 1988, **25**, 1407.
- Ram, R. N., *Ind. J. Tech.*, 1985, **23**, 237.
- Gokak, D. T., Kamath, B. V. and Ram, R. N., *J. Appl. Polym. Sci.*, 1988, **35**, 1523.
- Weil, J. H., *Biochimie Generale*. Masson, France, 1987.
- Sigel, H., *Angew. Chem.*, 1969, **81**, 161.
- Bekturov, E. A., Kudaibergenov, S. E. and Segitov, V. B., *Polymer*, 1986, **27**, 1269.
- Lekhiri, A., Castellano, A., Morcellet, J. and Morcellet, M., *Eur. Polym. J.*, 1991, **27**, 1271.
- Sigel, H. and Muller, U., *Helv. Chem. Acta*, 1966, **49**, 671.
- Sigel, H., Flierl, H. and Griesser, R., *J. Am. Chem. Soc.*, 1969, **91**, 1061.
- Erdey, L. and Inczedy, I., *Acta Chim. Hung.*, 1955, **7**, 93.
- Erlenmeyer, H., Flierl, C. and Sigel, H., *Chimica*, 1969, **22**, 433.