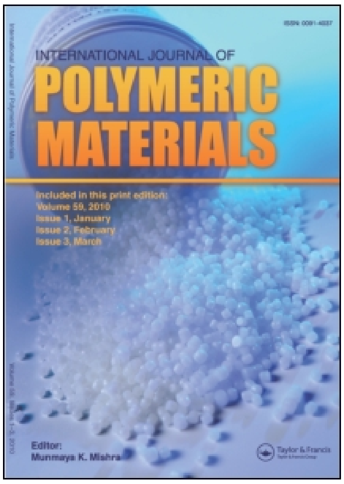


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Co-ordination Polymers of 1,6-bis(8-hydroxyquinolin-5-yl)-2,5-dioxa-3-methyl hexane

T. B. Shah[a]; H. S. Patel[a]; R. B. Dixit[a]
[a] Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India

To cite this Article Shah, T. B. , Patel, H. S. and Dixit, R. B.(2001) 'Co-ordination Polymers of 1,6-bis(8-hydroxyquinolin-5-yl)-2,5-dioxa-3-methyl hexane', International Journal of Polymeric Materials, 49: 3, 271 — 281
To link to this Article: DOI: 10.1080/00914030108039779
URL: http://dx.doi.org/10.1080/00914030108039779

Intern. J. Polymeric Mater., 2001, Vol. 49, pp. 271–281
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.

Co-ordination Polymers of 1,6-bis(8-hydroxyquinolin-5-yl)-2,5-dioxa-3-methyl hexane

T. B. SHAH*, H. S. PATEL and R. B. DIXIT

Department of Chemistry, Sardar Patel University,
Vallabh Vidyanagar-388120, Gujarat, India

(Received 28 July 1999)

Co-ordination polymers of novel bis oxine bidentate ligand namely 1,6-bis(8-hydroxyquinolin-5-yl)-2,5-dioxa-3-methyl hexane (BQDMH) have been prepared with different metal ion like Zn^{+2}, Cu^{+2}, Ni^{+2}, Co^{+2} and Mn^{+2}. The novel bis bidentate ligand (BQDMH) is synthesized by condensation of 5-chloromethyl-8-hydroxyquinoline hydrochloride with propylene glycol in presence of base catalyst. All these co-ordination polymers and parent ligand are characterized by elemental analysis, IR spectra and diffuse reflectance spectral studies for their structure determination. The thermal stability and number-average molecular weight ($\overline{M}_n$) of all these co-ordination polymers have estimated by thermogravimetric analysis and non-aqueous conductometric titration method respectively. Besides this all the co-ordination polymers have also characterized for their magnetic susceptibility and metal to ligand stoichiometry estimation.

Keywords: Bis bidentate ligand; Oxine and co-ordination polymer

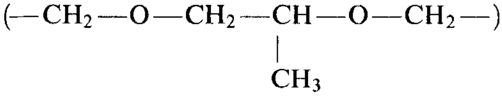
INTRODUCTION

Much research is being directed toward the preparation of polymeric chains, which are propagated, by the formation of metallic chelates. Some success has been achieved in formation of polychelates derived from polymeric ligand. An efficient method for synthesizing such type of polymers by introducing an inorganic component either chemically

---

*Corresponding author.

bonded or as a filler. The literature survey reveals that polymers bearing 8-hydroxyquinoline have potential application such as in waste water treatment for metal recovery, in protective coating and in biological activity [1–4]. Manolove *et al.* [5] have also reported that polymers bearing 8-quinolinol have additional potential applications for example, as water disinfectant, as antifouling paints, for antimicrobial surgical materials, as disinfectant in solutions, gels and ointments for medicinal uses [6–12]. Literature survey has revealed one of the promising methods to enhance the chelating ability of 8-quinolinol compounds is the formation of co-ordination polymers of a bidentate 8-quinolinol with different metal ions in which two 8-hydroxyquinolinyl end groups are joined by a linear aliphatic bridge usually at 5,5′-positions [13–15]. Recently we have also reported the synthesis and characterization of co-ordination polymers based on novel 8-hydroxyquinoline bis bidentate ligand containing an aliphatic bridge of dimethylene oxide ($-CH_2-O-CH_2$) [16]. This work has been further extended with a view to investigate the chelating ability of 8-quinolinol bidentate ligand with increasing the chain length of an aliphatic bridge between two 8-hydroxyquinoline moieties.

Accordingly, the present work deals with synthesis of bis oxine ligand namely 1,6-bis(8-hydroxyquinolin-5-yl)-2,5-dioxa-3-methyl hexane (BQDMH) and its co-ordination polymers with Zn^{+2}, Cu^{+2}, Ni^{+2}, CO^{+2} and Mn^{+2} metal ions. In this novel BQDMH ligand, the 5,5′-position of two oxine units are linked with each other through a linear aliphatic chain of 2,5-dioxa-3-methyl hexane  $(-CH_2-O-CH_2-\underset{\underset{CH_3}{|}}{CH}-O-CH_2-)$ at its 1 and 6 carbon atoms.

EXPERIMENTAL

Materials

All the chemicals were of AR grade.

Procedures

Synthesis of 1,6-bis(8-hydroxyquinolin-5-yl)-2,5-dioxa-3-methyl hexane (BQDMH)

The parent ligand (BQDMH) was prepared in two steps.

1. Preparation of 5-chloromethyl-8-hydroxyquinoline.

   5-Chloromethyl-8-hydroxyquinoline was prepared by reported method [17].
2. Synthesis of parent ligand (BQDMH).

   This was prepared by method reported for 5-alkoxy methylene-8-quinoline [17]. According to this method, the mixture of 5-chloromethyl-8-hydroxyquinoline hydrochloride (0.1 mole), propylene glycol (0.05 mole) in THF and sodium bicarbonate (0.1 mole) was refluxed for 2 hrs. with occasional shaking. The resulting solution was then made alkaline with dilute ammonia to precipitate out BQDMH ligand. It was then filtered off and dried. The yield of BQDMH was 65% and its melting point is 175°C.
3. Preparation of co-ordination polymers.

   All co-ordination polymers were synthesized by using metal acetates discussed in following.

   To a warm and clear solution of BQDMH (0.01 mole) in 20% aqueous formic acid was added a solution of metal acetate (0.01 mole) in 50% aqueous formic acid with constant stirring. After complete addition of the metal ion solution the pH of the reaction mixture was adjusted with dilute ammonia solution. The polymeric chelates separated out in the form of a suspension was digested on a water bath for one hour. Finally the solid polymers was collected by filtering, washing with hot water followed by acetone and DMF and was dried in air. The yield of all co-ordination polymers was almost quantitative.

Measurements

Elemental analysis for C, H and N analysis were carried out on Carlo Erba elemental analyzer (Italy). IR spectra of BQDMH and all the co-ordination polymers were scanned on a NICOLET-400 D FTIR

TABLE I Analytical data for the co-ordination polymer of BQDMH

BQDMH and its co-ordination polymers	*Elemental analysis*									
	C%		*H%*		*N%*		*M%*		μ_{eff}	
	Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*	*Calc.*	*Found*	*B.M*	$\overline{M}_n$
BQDMH	70.76	70.17	5.64	5.04	7.17	7.07				
BQDMH-Cu^{+2}	56.6	56.05	4.92	4.15	5.74	5.17	13.03	12.88	2.1	2206
BQDMH-Co^{+2}	57.15	56.93	4.96	4.55	5.79	5.37	12.20	11.33	4.5	2130
BQDMH-Ni^{+2}	57.17	56.90	4.97	4.67	5.80	5.66	12.16	10.56	3.5	2173
BQDMH-Mn^{+2}	57.62	57.13	5.01	4.87	5.84	5.17	11.47	10.13	5.5	2000
BQDMH-Zn^{+2}	56.39	56.19	4.90	4.19	5.71	5.21	13.35	13.07	D	2086

D = Dimagnetic.

spectrophotometer in KBr. The metal content analysis of co-ordination polymers were performed by decomposing a weighed amount of each co-ordination polymer followed by EDTA titration as reported in literature [18]. Although the number average molecular weight ($\overline{M}_n$) of polymer is considered as one of prerequisite property for its end use applications, no literature report hitherto has been made regarding estimation of $\overline{M}_n$ of co-ordination polymers. The reason may be due to either insolubility or unstability of co-ordination polymers in acid or base media. However, we have made an attempt for characterizing $\overline{M}_n$ of co-ordination polymers under controlled experimental conditions by using the method non-aqueous conductometric titration of end group analysis of phenolic —OH groups of polymer as reported in literature [19]. These data of $\overline{M}_n$ are reported in Table I.

Magnetic susceptibility measurements of all the co-ordination polymers were carried out at room temperature by the Gouy method. Mercury tetrathiocynato cobaltate(II) $Hg[Co(NCS)_4]$ was used as a calibrant. The diffuse reflectance spectra of all the solid co-ordination polymers were recorded on a Backman DK-2A spectrophotometer with a solid reflectance attachment. MgO was employed as the reference compound. Thermal stability of these co-ordination polymers was carried out by TGA on Du Pont 950 thermogravimetric analyzer.

RESULTS AND DISCUSSION

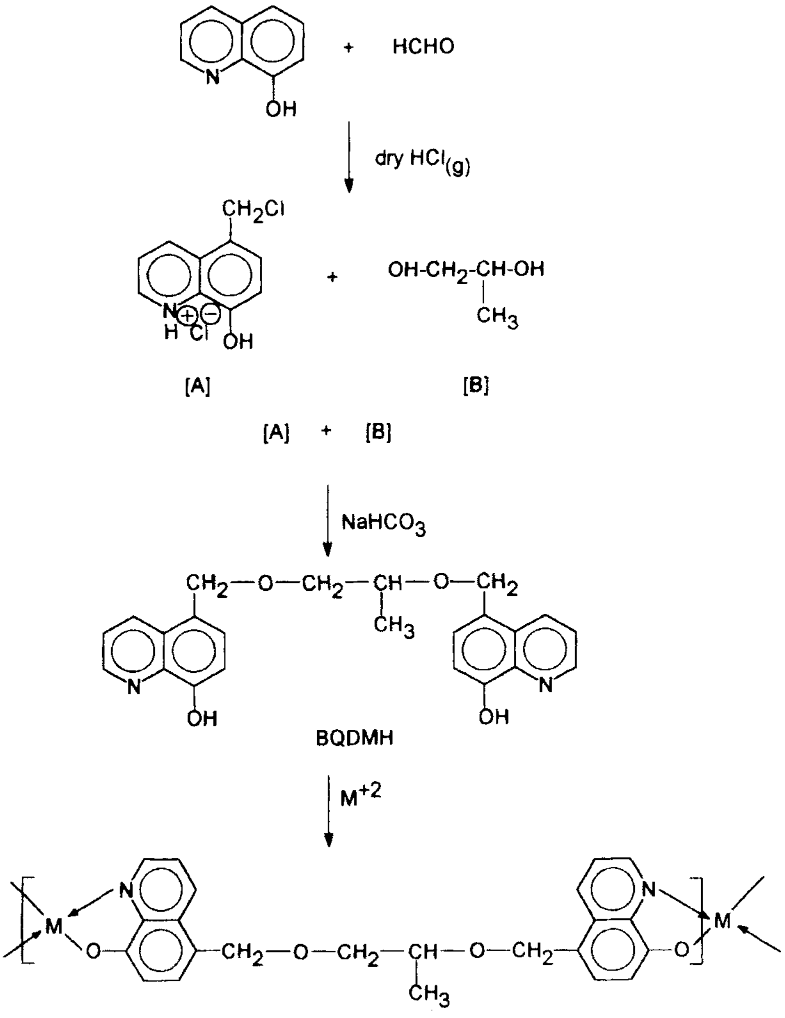
The synthesis of the bis(8-hydroxy-5-quinolyl)-2,5-dioxa-3-methyl hexane has not been reported previously. It was prepared by chloromethylation of oxine followed by the reaction of the product with propylene glycol. The ligand BQDMH was isolated in the form of light green powder. It is soluble in dioxane, DMF and DMSO. Results of elemental analysis of BQDMH for C, H and N are reported in Table I are found to be consistent with the predicted structure as shown in Scheme 1.

IR spectrum of BQDMH is shown in Figure 1. In the IR spectra of BQDMH a band of phenolic hydroxyl stretching is observed at 3342 cm^{-1} as well as the absorption bands at 1427, 1428, 1508 and 1589 cm^{-1} characteristics for 8-hydroxyquinoline moiety. The weak band at 2939 cm^{-1} attributes to aliphatic stretching vibration of methylene group (—CH_2—) and at 1118 cm^{-1} is due to C—O stretching of ether group of 2,5-dioxa hexane bridge. In addition to this evidences of structure of BQDMH has many characteristics absorption bands common to those occurred in 5,5′-methyline bis(8-hydroxyquinoline) further confirming the predicted structure as shown in Scheme 1.

The co-ordination polymers of BQDMH with different metal ions Zn^{+2}, Cu^{+2}, Ni^{+2}, Co^{+2} and Mn^{+2} are varying in color from light green to brown. IR spectra of all the co-ordination polymers of BQDMH are shown in Figure 1. They are resemble each other in general shape. But the comparison of the IR spectrum of the parent ligand BQDMH with its co-ordination polymers has revealed certain characteristics differences.

One of the significant difference to be expected between IR spectrum of parent ligand and its metal co-ordinated polymers is the presence of much broaden band in the region of 3300 - 3500 cm^{-1} due to O—H stretching vibration frequencies in IR spectrum of co-ordination polymer, as oxygen of this O—H of a parent ligand has formed co-ordination bond with metal ions.

This is explicable by the fact that water molecule might have strongly absorbed to the polymer sample during their formation. The another noticeable difference is that the band due to C═N stretching vibration of 8-hydroxyquinoline at 1589 cm^{-1} in IR spectrum of BQDMH is shifted to a lower frequency. The band at 1427 cm^{-1} in the IR spectra of BQDMH assigned to inplane —OH deformation [20] is shifted towards higher frequency in the spectra of the co-ordination polymers indicating due to the formation of metal—oxygen



Where: $M^{+2} = Cu^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2}, Zn^{+2}$

SCHEME 1

bond. This has been further confirmed by a weak band at 1118 cm^{-1} corresponding to C—O—M stretching frequency. Thus all these characteristics features of IR studies suggesting the structure of co-ordination polymer as shown in Scheme 1.

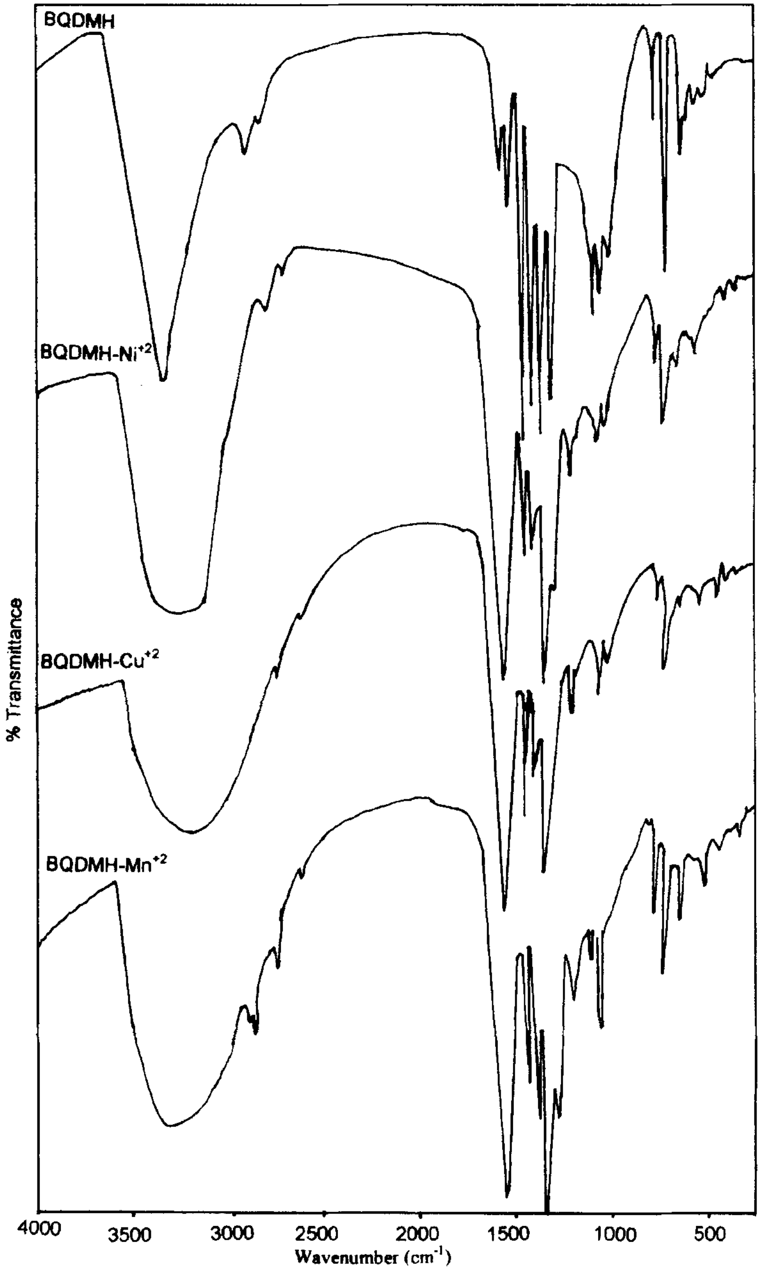


FIGURE 1 IR Spectra of BQDMH and its co-ordination polymer.

Examination of data about metal content in each polymer (Tab. I) revealed a 1 : 1 metal : ligand (M/L) stoichiometry in all the polymers.

The number-average molecular weight ($\overline{M}_n$) estimated by non-aqueous conductometric titration is reported in Table I. The discernible single break corresponding to free —OH group of end 8-hydroxyquinoline moiety was observed in titration curve. Result of non-aqueous conductometric titration reveals that there is not much variation in the number–average molecular weight of each co-ordination polymer as expected from their suggested scheme.

Magnetic moment (μ_{eff}) of all co-ordination polymers is given in Table II. Examination of these data reveals all co-ordination polymers other than that of Zn^{+2} are paramagnetic while that of Zn^{+2} is diamagnetic in nature.

The diffuse electronic spectrum of BQDMH-Cu^{+2} co-ordination polymer shows that two broad band at 15873 cm^{-1} and 23255 cm^{-1} due to $^2T_{2g} \rightarrow {}^2E_g$ transition and charge transfer spectra respectively suggesting a distorted octahedral structure for BQDMH-Cu^{+2} polymer which is further confirmed by higher value of μ_{eff} of BQDMH-Cu^{+2} polymer. The BQDMH-Ni^{+2} and BQDMH-Co^{+2} polymer give two absorption bands respectively at 15364 cm^{-1}, 19230 cm^{-1} and 15625 cm^{-1}, 22727 cm^{-1} corresponding to $^4T_{1g} \rightarrow {}^2T_{1g}$, $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition [15]. Thus absorption bands of diffuse reflactance spectra and the value of magnetic moment (μ_{eff}) have indicated an octahedral configuration for the BQDMH-Ni^{+2} and BQDMH-Co^{+2} polymers. The spectra of BQDMH-Mn^{+2} shows the weak bands at 15625 cm^{-1}, 11494 cm^{-1} assigned to the $^6A_{1g} \rightarrow 4T_{1g}(4G)$ and $^6A_{1g}(F) \rightarrow {}^4T_{1g}$ (4G) respectively and assigned an octahedral structure for BQDMH-Mn^{+2} polymer. As the spectrum

TABLE II Thermogravimetric analysis (TGA) of the co-ordination polymer of BQDMH

Co-ordination	*% Weight loss at different temperature (°C)*						
polymer	100	150	200	250	300	350	400
BQDMH-Cu^{+2}	12.5	13	13.5	29.5	84	84.5	
BQDMH-Co^{+2}	8.6	12.7	14.6	18.1	31.1	83.04	85.0
BQDMH-Ni^{+2}	9.55	11.12	13.75	20.07	57.93	82.65	83.18
BQDMH-Mn^{+2}	8.0	11.0	12.2	18.0	35.0	64.0	70.5
BQDMH-Zn^{+2}	7.9	10.5	12.0	17.8	32.0	61.0	65.5

of BQDMH-Zn^{+2} polymer is not well resolved it is not interpreted but its μ_{eff} value reveals it diamagnetic as expected.

The thermal behaviour of co-ordination polymers is investigated by performing thermogravimetric analysis (TGA). The TGA data of all the samples are presented in Table II and their thermogram are shown in Figure 2. Examination of percentage weight loss as a function of temperature reveals that all co-ordination polymers decomposed in a single step and almost have similar mode of decomposition indicating that decomposition reaction in co-ordination polymer are independent of nature of the metal ion present in co-ordination polymer. The rate of decomposition of all the co-ordination polymer is initially low upto 200°C temperature and gradually increases to

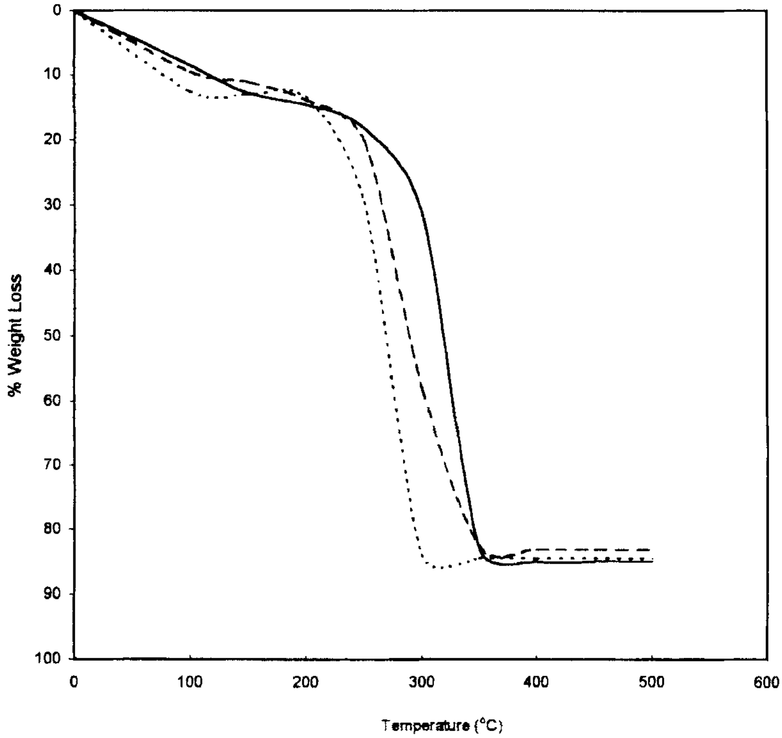
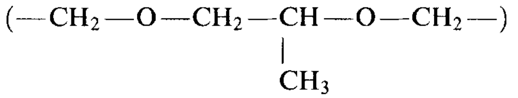
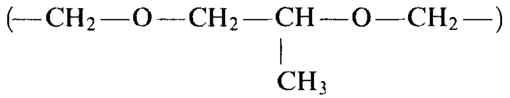


FIGURE 2 TG Thermogram of BQDMH-Cu^{+2} [------], BQDMH-Co^{+2} [————], BQDMH-Ni^{+2} [– – –].

maximum in the range 300°–350°C at which almost 85% loss in weight occurred.

Comparison of thermal stability of the present co-ordination polymers BQDMH with reported thermal stability of co-ordination polymers having bis(8-hydroxy-quinolinyl)methane (MBQ) reveals that the polymers containing  $(-CH_2-O-CH_2-\underset{CH_3}{\underset{|}{CH}}-O-CH_2-)$ bridge are thermally less stable than those containing methylene $(-CH_2-)$ and dimethylene oxide $(-CH_2-O-CH_2-)$ bridge. It may be because of higher aliphatic character of bridge  $(-CH_2-O-CH_2-\underset{CH_3}{\underset{|}{CH}}-O-CH_2-)$ containing two ether oxygen atom making it more labile to undergo decomposition.

On the basis of relative decomposition and the nature of thermogram of the co-ordination polymers order of thermal stability observed is as

$$Cu < Co < Ni < Mn.$$

Acknowledgement

The authors are thankful to Prof. H. C. Trivedi, Head, Department of Chemistry, Sardar Patel University for providing necessary research facilities.

References

[1] Geckeler, K. E. and Rongnong, Z. (1994). Ger-offen. DE 4227019 (Cl. C08F8/00), *Chem. Abstr.*, **121**, 10302r.
[2] Purohit, R. and Devi, S. (1991). *Analyst*, **116**, 825.
[3] Pittman, C. U., Ramachandran, K. S. Jr. and Lowyer, K. R. (1982). *J. Coat. Technol.*, **54**, 27.
[4] Albert, E. (1979). In: *Selective Toxicity*, Chapman and Hall, London.
[5] Manolova, N., Ignatova, M. and Rashkov, I. (1998). *Eur. Polym. J.*, **34**, 1133.
[6] Manolova, N., Rashkov, I., Panayotov, I. and Buchvarov, N. (1987). *Bulgarian Patent 43772*, Reg. No., 79270.
[7] Rashkov, I., Petrova, Ts., Manolova, N., Buchvarov, N. and Savov, E. (1990). *Commun Dept. Chem. Bulg. Acad. Sci.*, **23**, 465.

[8] Bankova, M., Manolova, N. and Rashkov, I. (1994). *Eur. Polym. J.*, **30**, 1179.
[9] Angelova, N., Manolova, N. and Rashkov, I. (1995). *Eur. Polym. J.*, **31**, 741.
[10] Bankova, M., Petrova, Ts., Manolova, N. and Rashkov, I. (1996). *Eur. Polym. J.*, **32**, 325.
[11] Bankova, M., Petrova, Ts., Manolova, N. and Rashkov, I. (1996). *Eur. Polym. J.*, **32**, 569.
[12] Bankova, M. N., Markova, N., Radoucheva, T., Dilova, K. and Rashkov, I. (1998). *Eur. Polym. J.*, **34**, 247.
[13] Horowitz, E. and Perros, T. P. (1964). *J. Inorg. Nucl. Chem.*, **26**, 139.
[14] Bailer, J. C. Jr., Judd, M. L. and McLean, M. J. (1969). *WADC, Technical Reports*, **58-61**, Part-II, p. 116.
[15] Patel, R. D., Patel, S. R. and Patel, H. S. (1987). *Eur. Polym. J.*, **23**, 229-232.
[16] Shah, T. B., Patel, H. S. and Dixit, R. B. (1999). *Oriental J. Chem.*, **15**(1), 107-112.
[17] Burkhalter, J. H. and Laib, R. I. (1961). *J. Org. Chem.*, **26**, 4078.
[18] Vogel, A. I. (1978). *Inorganic Quantitative Analysis*, 4th edn., ELBS London.
[19] Chatterjee, S. K. and Gupta, N. D. (1973). *J. Polym. Sci.*, Part A-1, **11**, 126.
[20] Charles, R. G., Freiser, H. F., Priedel, R., Hilliand, L. E. and Johnston, R. D. (1958). *Spectrochem. Acta*, **8**, 1.