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End-capping of living poly(2-methyl-2-oxazoline) with maleic acid

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Abstract

A series of functionalized poly(2-oxazoline)s were synthesized by quenching poly(2-methyl-2-oxazoline) living chains (mono- or bifunctional) with maleic acid as nucleophilic agent. By varying the functionality of the initiating system and the ratio of the nucleophile to oxazolinium ends, three different compounds – two macromers and/or an unsaturated polyester – were obtained. The use of a macromolecular proton scavenger was found to be an easy, efficient alternative to the laborious approach performed with triethylamine. The coupling products were copolymerized with styrene by solution or dispersion polymerization. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Macromer; Poly(2-methyl-2-oxazoline); Functional polymers

1. Introduction

Five-membered cyclic imino ethers, especially 2-substituted-2-oxazolines, are important monomers for the obtention of polyethylenimine derivatives. The continuous growing interest in their study is related to both their chemistry and their areas of application [1–4].

A rich polymer chemistry is associated to these monomers. They can undergo facile ring-opening cationic polymerization of a living nature in appropriate reaction conditions or can participate in addition reactions with many electrophiles (zwitterionic copolymerization, coupling reactions of bis-oxazoline monomers).

The versatility of the 2-substituted-2-oxazolines allows the synthesis of a large range of macromolecular compounds: homopolymers, copolymers and functionalized polymers. Last years, the quenching of the living oxazolinium species with various nucleophiles was extensively used as a facile and convenient approach for the obtention of polymeric materials with a controlled architecture [1–6]. Macromers with acryloyl [7], vinylester [8], styryl [9], butadiene [10] polymerizable end groups have already been reported. However, by our knowledge, there are only few investigations on the chemistry of the coupling reactions involving bifunctional living chains [2,11].

This article presents the use of the direct termination of the growing living oxazolinium macrocations in the synthesis of functional poly(*N*-acyliminoethylene)s with unsaturated end groups or with polymerizable groups inserted into the main chain. Some preliminary experiments on their application in the obtention of amphiphilic gels and graft copolymers or for the preparation of monodisperse polymer particles are reported.

2. Experimental part

2.1. Materials

2-Methyl-2-oxazoline (MOZO, Aldrich) was purified by distillation just before use. Chloroform was dried by

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refluxing on phosphorus pentoxide and distillation. Ethyl ether, previously dried over natrium wire, was used after distillation. *N*,*N*-dimethylformamide (DMF, Fluka) was stored on molecular sieves. Maleic acid (MA, Aldrich), 1,4-dibromo-2-butene (DBB, Aldrich), benzyl bromide (BB, Aldrich), benzoyl peroxide (BP, Aldrich), triethylamine (TEA, Merck), aluminium oxide (Fluka) were used as received, without further purification. 2,2-Azobisisobutyronitrile (AIBN, Aldrich) was recrystallized from methanol. Styrene (St), methyl methacrylate (MMA) and butyl acrylate (BA) were distilled under vacuum prior to use.

The copolymers of vinylpyridine with divinylbenzene (SVPy) with a content of 7.7% N, used as macromolecular proton scavengers, were obtained by suspension copolymerization with BP as initiator [12].

2.2. *Coupling reaction of living poly(2-methyl-2-oxazoline) with maleic acid*

The coupling reactions were performed in a glass ampoule of a peculiar shape, dotted with a stopcock equipped gas inlet and a lateral arm having a viscometric function, consisting of a reservoir and a capillary tube.

A typical run for the preparation of poly(2-methyl-2-oxazoline) (PMOZO) unsaturated polyester **(3)** was as follows (sample 5, Table 1). A mixture of MOZO (2.01 g, 23.6 mmol) and DBB (0.5 g, 2.36 mmol) in carefully dried chloroform (3.0 ml) was heated under argon atmosphere at 54°C for 24 h. After cooling, adequate amounts of proton scavenger – TEA (0.66 ml, 2.36 mmol, entry 5, Table 1) or SVPy (0.14 g, entry 6, Table 1) – and MA (0.27 g, 2.36 mmol) were added. The ampoule was then kept at the adopted reaction temperature (54°C) for 4 h. The reaction product was separated by filtration (the macromolecular catalyst) or by passing on alumina chromatographic columns (TEA) followed by precipitation in anhydrous ethyl ether. The white precipitate was filtered and dried in vacuo.

A similar procedure was used for the preparation of mono- or bifunctional macromers **(1)** and **(2)** (see Scheme 1), considering the required amounts of MA and proton scavenger, respectively.

2.3. *Copolymerization*

The copolymerization of the unsaturated polyester **(3)** and macromers **(1)** and **(2)** with vinyl monomers was realized in solution or dispersion. In the first case, the reaction was performed in sealed glass ampoules, in DMF, under argon atmosphere, at 80°C for 22 h, using AIBN as initiator. A total comonomer concentration of 4.3 mol l^{-1} was used.

Table 1
Macromers synthesis by end-capping method

No.	Sample code	Initiating system	Scavenger type	Product type	$\frac{[\mathrm{MOZO}]_0}{[\mathrm{I}]_0}$	DP$_{\mathrm{PMOZO}}$[a]	$\frac{[\mathrm{MA}]_0}{[\mathrm{I}]_0}$	[MA]/[I] in product	Coupling efficiency[b]	Product composition (%)	Yield (%)	M_n	M_w/M_n[c]
1	P_1	BB	TEA	**(1)**	10	10.2	1.1	0.95	0.95	95 **(1)**	75	1074[d]	
2	P_2	BB	SVPy	**(2)**	10	10.5	0.5	0.59	0.90	80 **(2)**	91	1700[d]	
3	P_3	BB	TEA	**(2)**	10	10.7	0.5	0.54	0.95	90 **(2)**	70	1800[d]	
4	P_4	DBB	–	**(3)**	10	10.3	1	1.50	0.67	–	50	1190	6.0
5	P_5	DBB	TEA	**(3)**	10	10.2	1	1.10	0.90	–	75	4720	2.4
6	P_6	DBB	SVPy	**(3)**	10	10.2	1	1.05	0.95	–	92	6110	2.0
7	P_7	DBB	TEA	**(3)**	15	14.0	1	0.90	1.00	–	77	9800	2.8
8	P_8	DBB	SVPy	**(3)**	25	23.0	1	1.05	0.95	–	90	17 200	3.0

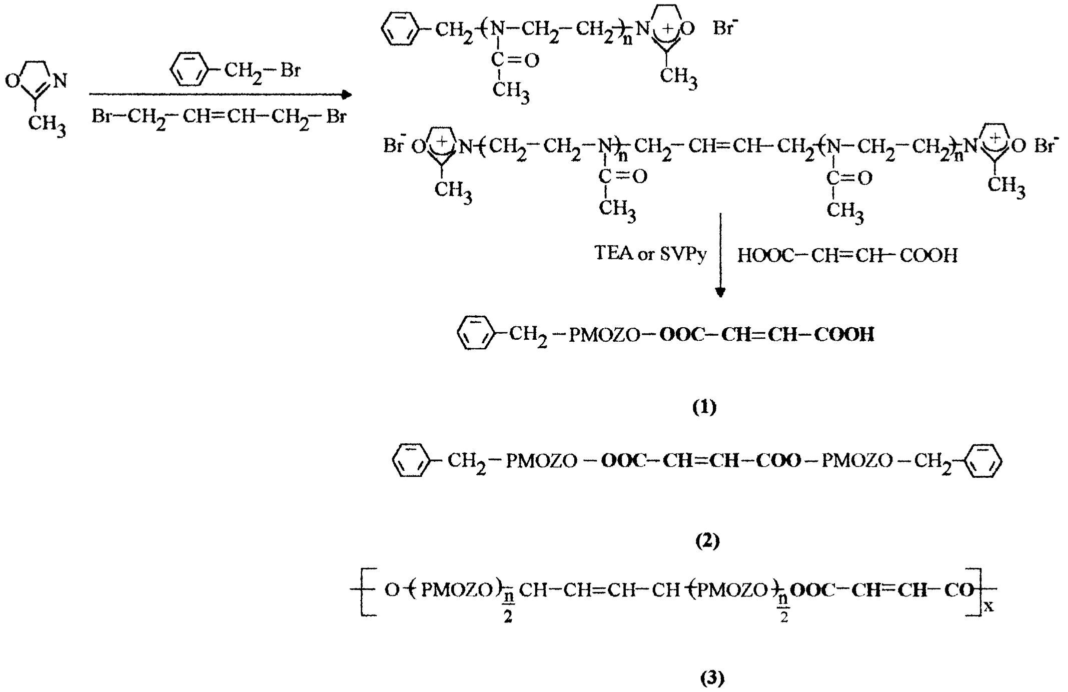
Reaction conditions: $[\mathrm{MOZO}]_0 = 3.5$ mol l^{-1}, $T = 54$°C, $CHCl_3$.

[a] From ^{1}H-NMR spectra.

[b] Calculated from ^{1}H-NMR spectra.

[c] Calculated from GPC data.

[d] Calculated from ^{1}H-NMR spectra.



Scheme 1. Macromonomers synthesis.

For dispersion copolymerization, a typical example is as follows. The required amounts from a solution of BP in St (4.5 ml, 41 mmol St containing 0.3 g, 1.2 mmol BP) were added to a mixture of mono- (0.16 g P_1, 0.15 mmol) or a bifunctional macromer (0.25 g P_2, 0.15 mmol) in 90/10 v/v% absolute ethanol/water (45 ml). The solution was purged 10 min with argon and then kept for 6 h at 30°C in a thermostated quartz sealed ampoule equipped with magnetic stirrer, placed at 16 cm distance from a high pressure mercury lamp of 500 W. The resulted polymer particles were separated by centrifugation of the dispersion, purified by washing with methanol, dried in vacuo and analyzed.

2.4. Measurements

^{1}H- and ^{13}C-NMR spectra were recorded on a 250 Bruker AC spectrometer, using $CDCl_3$ or DMSO-d_6 as solvents.

The IR spectra were recorded on a Specord M-80 infrared spectrometer. Gel permeation chromatography (GPC) analysis was performed by using a PL-EMD 950 chromatograph with evaporative mass detector with $CHCl_3$ as eluent. The composition of the polymers was determined by elemental analysis (N%).

Electron microscopy studies were performed on a TESLA BS 513A apparatus. The samples were prepared by spraying the diluted solutions of the reaction mixture (1% in a 90/10 v/v ethanol/water mixture) on copper grids covered with carbon.

3. Results and discussion

Synthetic approaches based on the living nature of cationic ring-opening polymerization of 2-oxazolines [1–3] were preferentially used to prepare a large variety of poly(*N*-acetyliminoethylene) macromonomers or functional polymers. Kobayashi and coworkers reported the use of the end-capping with nucleophilic quenching compounds having carboxylic groups (meth/acryloyl [7] or fatty acids [13]) in the synthesis of functional polymers acting as macromers or nonionic emulsifiers. A similar approach was considered to obtain bifunctional macromers [11]. However, to our knowledge, no data were reported on the us e of dicarboxylic acids as nucleophilic terminators. Depending on the chemical nature of the initiating system and on the ratio of the bifunctional nucleophilic agent to oxazolinium species, such a compound offers the possibility to yield different products, i.e. two macromers and an unsaturated polyester. MA was chosen as a quenching compound with the aim to obtain polymerizable functional poly(*N*-acetyliminoethylene). The possible alternatives are given in Scheme 6. To investigate the influence of the functionality of the growing living chains on reaction development, two different compounds were used for the initiation of the cationic polymerization of MOZO (i.e. BB and DBB, known to give rise to a fast initiation) [14]. In accordance with literature data, the chain length was controlled by the initial monomer to initiator ratio (see Table 1).

Two different proton acceptors were used in this reaction: a low molecular one, TEA or a macromolecular one, poly(4-vinylpyridine-co-divinylbenzene) (SVPy). Vinylpyridine containing polymers are frequently employed as catalyst resins or supports in the immobilization of catalysts [15]. Generally, the vinylpyridine based catalyst was evidenced to be superior to other resins containing strong acid cation exchange groups as it did not cause side reactions when placed in contact with substrate functionalities. The following of the coupling process gave no indication sustaining the occurrence of secondary reactions such as the formation of macromolecular betaine products [16]. ^{1}H-NMR spectra confirmed this observation.

As compared to poly(*N*-acetyliminoethylene), the ^{1}H-NMR spectra of the products present new peaks at $\delta = 6.1$–6.25 ppm (the signal d in Fig. 1) and $\delta = 9$ ppm, attributed to the protons of the unsaturated and carboxylic groups from the MA moieties, respectively.

The ^{13}C-NMR spectrum also confirms the performing of the coupling reaction (Fig. 2). These data are completed by the IR spectra, which revealed the presence of a new absorption band at 1750 cm^{-1}, characteristic to the ester carbonyl stretching vibration.

The degree of functionalization, expressed as the number of the coupled carboxylic groups per theoretical

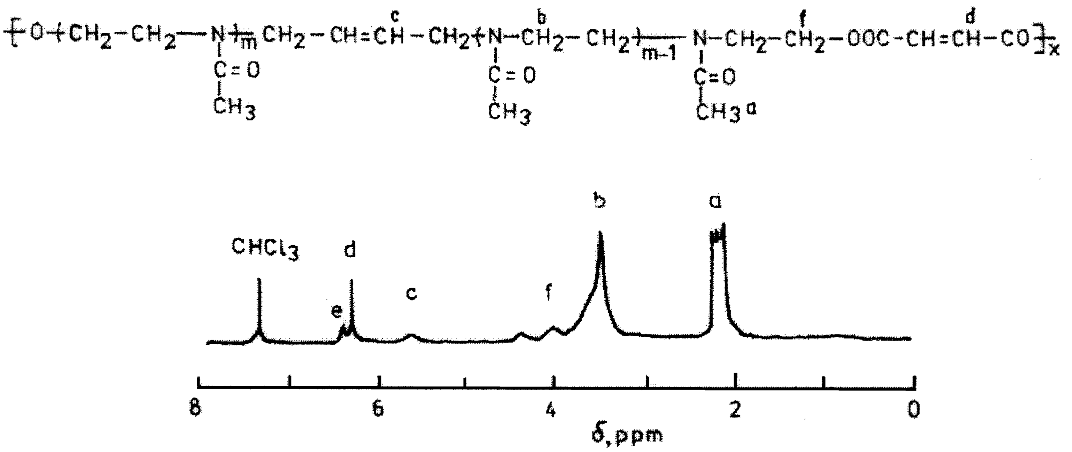


Fig. 1. ^{1}H-NMR spectrum of the unsaturated PMOZO polyester in CDCl$_3$ (sample P$_5$, Table 1).

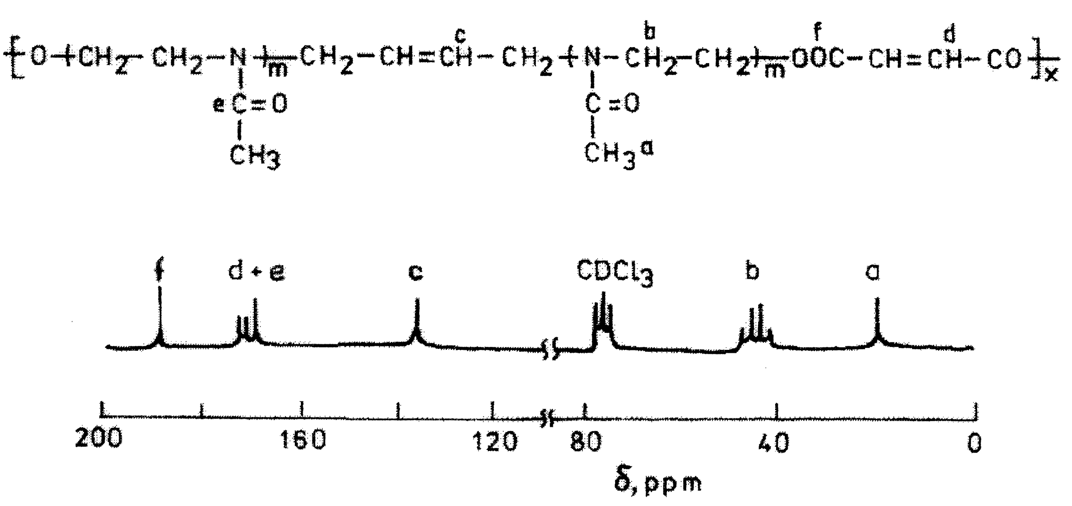


Fig. 2. ^{13}C-NMR spectrum of the unsaturated PMOZO polyester in CDCl$_3$ (sample P$_5$, Table 1).

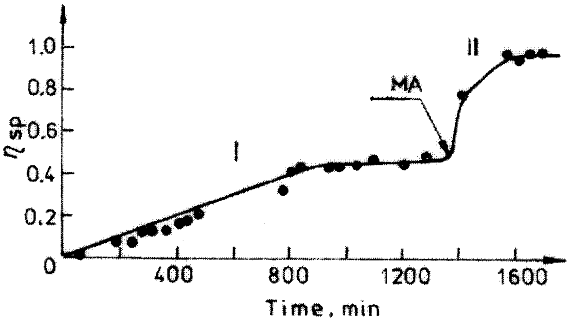


Fig. 3. η_{sp} vs time plot for the reaction mixture during polymerization (I) and coupling (II) steps. Reaction conditions: $[MOZO]_0 = 1$ mol l^{-1}, $[BB]_0 = 0.1$ mol l^{-1}, $[MA]_0 = 0.1$ mol l^{-1}, $T = 54$°C, $CHCl_3$, TEA.

Table 2
Copolymerization data

Sample code	M_1[a]	M_2	F[b]	f[c]	Yield (%)
C_1	P_2	St	0.03	0.01	56
C_2	P_2	BA	0.03	0.005	53
C_3	P_2	MMA	0.03	0.006	52
C_4	P_5	St	0.10[d]	0.33	73

[a] According to Table 1; reaction conditions: $[M_1] = 0.13$ mol l^{-1}, $[M_2] = 4.2$ mol l^{-1}, AIBN 3 wt.% relative to total monomer, 80°C, Ar, 22 h (M_1 = macromer, M_2 = vinyl comonomer).

[b] $F = [M_1]/([M_1] + [M_2])$ in feed.

[c] $f = [M_1]/([M_1] + [M_2])$ in copolymer.

[d] $[P_5]$ was calculated relative to the PMOZO sequences inserted in the main chain of the unsaturated polyester.

number of the coupling ones, was determined from the integral ratio of the peaks ascertained to the protons of the inserted polymerizable groups and those ascertained to initiator moieties (situated at 5.4 ppm for DBB and 7.0–7.5 for BB). The data evidenced that the coupling reaction was quite efficient in all studied cases (Table 1). It can be observed that a higher efficiency was reached in the presence of SVPy beads as compared to TEA (Table 1, samples 2 and 6).

The development of the reaction carried out with bifunctional living chains and stoichiometric amounts of MA was followed by a viscometric technique. As can be seen in Fig. 3, after a first stage, corresponding to the living cationic polymerization, a jump in the viscosity of the reaction system is registered at the addition of MA, an evident proof of the coupling. The reaction is rapid enough, i.e., in about 30 min the plot reaches a constant value. The comparison of the graphs obtained in different reaction conditions – without proton scavenger, in the presence of TEA or of the macromolecular SVPy – evidenced that a higher coupling efficiency was realized in the last case (Fig. 4, Table 1, samples 4–6). Higher dimensions were obtained for the final unsaturated polyester in the presence of the macromolecular catalyst. Moreover, the alternative using TEA is more laborious and lower total yields are obtained (Table 1, samples 1,3,5,7). The hydrolysis of the acetyl groups was avoided by the adoption of an accurate procedure with respect to the addition order of the components of the reaction system, the required time for the SVPy beads swelling being carefully assured. The rate of coupling is lower as compared to the procedure using TEA, probably due to the diffusion-controlled character of the process. An excess of proton scavenger was used.

The possibility to obtain two different macromers depending on the amount of the added dicarboxylic acid suggests that the coupling reaction is of a "two-step

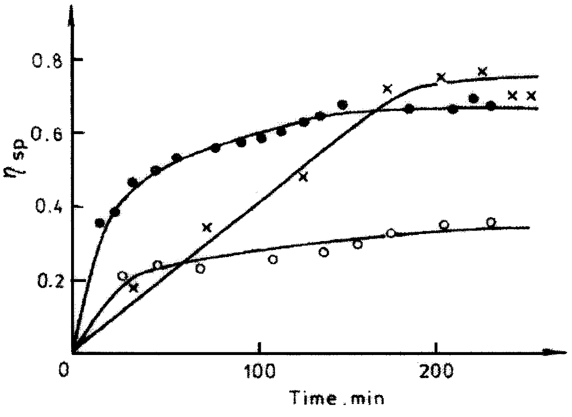


Fig. 4. Influence of the nature of the proton scavenger on reaction development: (○) without catalyst, (●) with TEA (0.24 mol), (×) with macromolecular catalyst (0.02 g SVPy mmol^{-1} DBB, $\varphi = 0.8$ mm).

Fig. 5. Transmission electron micrograph of the microparticles obtained by dispersion copolymerization of PMOZO macromer **(1)** with styrene in ethanol/water mixture. Reaction conditions: 10 vol% monomers, 3 wt.% macromer relative to total monomer, 3 wt.% PB relative to monomers, 30°C, 6 h UV irradiation.

reaction" type. This can be explained by both the steric hindrances and the modification of electron density in the second carboxylic group after the coupling of the first one with the PMOZO living macrocation.

The resulted products can be used in the preparation of new functional macromolecular compounds (i.e. by hydrosilation), amphiphilic gels, graft copolymers with well-defined structure, and micronsize monodisperse polymeric particles. In the last case, they act both as comonomers and steric stabilizers.

Some preliminary experiments were carried out to investigate the behavior of the prepared compounds in homo-/copolymerization, especially for the macromers. As expected, macromer **(2)** did not homopolymerize, most probably due to the important steric effects. It hardly gave copolymers with comonomers such as St, MMA and BA (Table 2). Due to the low reactivity, the final products retained only about 30% from the feeded PMOZO macromers. As compared to this macromer (0.5×10^{-3} polymerizable groups/g – Table 2, C_1), the copolymerization of the unsaturated polyester (1.2×10^{-3} polymerizable groups/g) gave copolymers in a high yield and with a relatively high content in PMOZO units (Table 2, C_4).

The dispersion polymerization experiments of the macromers **(1)** and **(2)** with St in 90/10 v/v 1% ethanol/water polar mixture, in the presence of BP as initiator, demonstrated that the synthesized macromers are able to act as stabilizers in dispersion polymerization (Fig. 5). The calculated values of the particle size distribution, for similar polymerization conditions, were of 1.16 and 1.20 for the experiments performed with **(1)** and **(2)**, respectively. Considering the biocompatibility of PMOZO, such materials might be of interest for biomedical applications. Further studies are necessary to determine the optimum required reaction conditions.

References

[1] Kobayashi S. Prog Polym Sci 1990;15:751.
[2] Aoi K, Okada M. Prog Polym Sci 1996;21:151.
[3] Kobayashi S, Uyama H. Trends Macromol Res 1994;1:121.
[4] Simionescu CI, David G. In: Salamone JC, editor. The polymeric materials encyclopedia, vol. 7. Boca Raton: CRC Press; 1996. p. 5334.
[5] Kobayashi S, Uyama H, Higuchi N. Macromolecules 1990;23:54.
[6] Shimano Y, Sato K, Kobayashi S. J Polym Sci Part A: Polym Chem 1995;33:2715.
[7] Kobayashi S, Masuda E, Shoda S, Shimano Y. Macromolecules 1989;22:2878.
[8] Uyama H, Kobayashi S. Macromolecules 1991;24:614.
[9] Miyamoto M, Hayashizaki K, Tokumizu M, Saegusa T. Macromolecules 1990;23:4718.
[10] Kobayashi S, Uyama H, Narita Y, Ishiyama J. Macromolecules 1992;25:3232.
[11] Christova D, Velichova R, Goethals EJ. Macromol Rapid Commun 1997;18:1067.
[12] Vlad CD, Neagu V, Stoleriu A. Polym-Plast Technol Engng 1999;38(2):275.
[13] Kobayashi S, Uyama H. Macromolecules 1991;24: 5473.
[14] Kobayashi S, Uyama H, Narita Y. Macromolecules 1990;23:353.
[15] Frechet JMJ, Meftahi MV. Brit Polym J 1984;16:193.
[16] Barboiu V, Streba E, Luca C, Simionescu CI. J Polym Sci Part A: Polym Chem 1995;33:389.