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Synthesis and characterization of graft copolymers of poly(vinyl chloride) with styrene and (meth)acrylates by atom transfer radical polymerization

*Hyun-jong Paik, Scott G. Gaynor, Krzysztof Matyjaszewski**

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, U.S.A.

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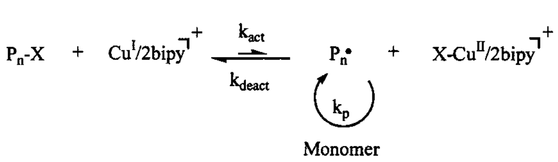
SUMMARY: Graft copolymers of poly(vinyl chloride) with styrene and (meth)acrylates were prepared by atom transfer radical polymerization. Poly(vinyl chloride) containing small amount of pendent chloroacetate units was used as a macroinitiator. The formation of the graft copolymer was confirmed with size exclusion chromatography (SEC), ^{1}H NMR and IR spectroscopy. The graft copolymers with increasing incorporation of butyl acrylate result in an increase of molecular weight. One glass transition temperature (T_g) was observed for all copolymers. T_g of the copolymer with butyl acrylate decreases with increasing content of butyl acrylate.

Introduction

Poly(vinyl chloride) (PVC) is a major commercial polymer[1]. Over 20 million metric tons of PVC a year is currently produced worldwide. PVC is light, flame-retardant, robust and durable; it has low permeability to gases and good weatherability and its physical and mechanical characteristics make it ideal for many different uses. PVC is well known for its compatibility with additives including plasticizers, heat stabilizers, lubricants, fillers, and other polymers which enable it to have a variety of mechanical properties. Chemical modification of PVC has also been of interest. One way to achieve this goal is by grafting from PVC[2]. Cationic[3], anionic[4] and radical[5] processes have been applied to prepare graft copolymers with PVC as a backbone.

The rapidly developing field of controlled radical polymerization provides another approach to prepare graft copolymers, especially with well-defined structures. In controlled radical polymerization, the concentration of growing radicals is suppressed to avoid termination[6]. This is made possible by using various means such as iniferters[7], 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO)[8,9], organometallic species[10], degenerative transfer[11] and atom transfer[12–16]. In particular, Roha et al. have reported the controlled free radical graft copolymerization of the PVC with xanthate and dithiocarbamate iniferter[17,18].

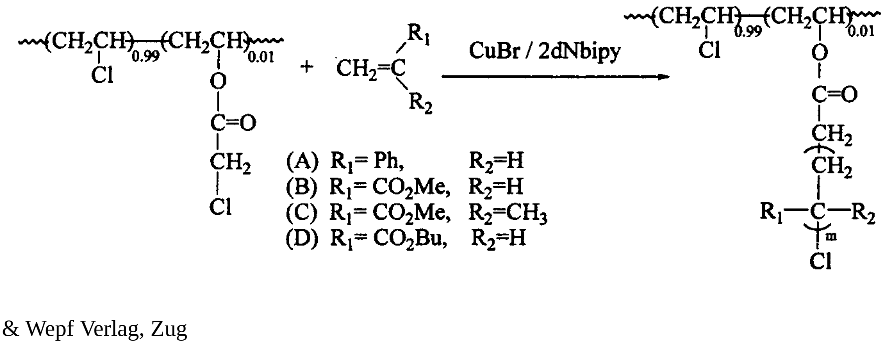
Scheme 1:



Atom transfer radical polymerization (ATRP) employs an equilibrium between dormant alkyl halides and active propagating radicals to maintain a low concentration of active species. The activated radical species can either propagate or be deactivated to reform the dormant species. This process is catalyzed by a transition metal compound such as cuprous halide complexed by 2,2′-bipyridine.

ATRP can be used to prepare well-defined polymers from many monomers, including substituted styrenes[13,19], (meth)acrylates[12,16,20,21], and acrylonitrile[22]. Atom transfer radical polymerization also has an advantage in utilizing a wide range of initiators. Alkyl halides with radical stabilizing substituents such as carbonyl, cyano, or aryl groups adjacent to the C-X, can be used as initiators. In

Scheme 2:



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addition to compounds containing activated carbon-halogen bonds, those compounds with weak halogen bonds, like RSO_2-X[15)] are good initiators. Any compounds, including macromolecular species, can potentially be used to initiate ATRP as long as they contain activated halogen atoms.

Here we present the preparation of grafted PVC with styrene and (meth)acrylates via ATRP using a macroinitiator: poly[(vinyl chloride)-*co*-(vinyl chloroacetate)] (PVC-1). The incorporated chloroacetate groups (1 mol-% compared to vinyl chloride) were utilized as initiators for ATRP (Scheme 2). The PVC backbone remained intact during ATRP because the secondary chlorine on the PVC backbone is too strongly bonded to initiate the polymerization by reaction with Cu(I) complex.

Experimental Part

Materials

All monomers were vacuum distilled over CaH_2 and stored under argon. 4,4′-Bis(5-nonyl)-2,2′-bipyridyl [dNbipy] was prepared by the procedure described in the previous article from this group[19)]. CuBr was purified according to literature procedure[23)]. Poly-[(vinyl chloride)-*co*-(vinyl chloroacetate)](PVC-1) was provided by Geon Company. The ^{1}H NMR study showed that 1 mol-% vinyl chloroacetate compared to vinyl chloride is incorporated in PVC-1.

Copolymerization procedure

The copolymerization was performed in a sealed tube or a Schlenk flask. Typical copolymerization was carried out as follows: To a glass tube, 0.0500 g (1.00×10^{-6} mol) PVC-1, 0.0100 g (6.97×10^{-5} mol) CuBr and 0.0570 g (1.39×10^{-4} mol) dNbipy were weighed under ambient atmosphere. 2.0 ml (1.74×10^{-2} mol) deaerated styrene were added using syringe under argon atmosphere. After three freeze-pump-thaw cycles, the glass tube was sealed under vacuum and the reaction mixture was heated at 110 °C for 12 h. The reaction mixture was dissolved in THF and then precipitated in methanol.

Polymerization of (meth)acrylates was carried out at 90 °C.

Characterization

Size exclusion chromatography (SEC) was performed using a Waters 712 WISP autosampler, 510 HPLC pump, 410 differential detector and following Waters SEC columns: guard, HR 0.5, HR 4E, HR 5E. All samples were run in tetrahydrofuran (THF) at 35 °C. Polystyrene standards were used for calibration. ^{1}H NMR spectra were recorded using Bruker AM 300. FT-IR was measured using ATI Mattson Infinite Series FT-IR Spectrometer. Differential scanning calorimetry (DSC) data were obtained using Rheometric Scientific DSC plus.

$\overline{M}_{n,total(NMR)}$ was estimated using formula:

$$\overline{M}_{n,total(NMR)} = \overline{M}_{n,(PVC\text{-}1)}\left(1 + x\frac{MW_{2nd\ monomer}}{MW_{vinyl\ chloride}}\right)$$

where x = molar ratio of 2nd monomer units to vinyl chloride units in copolymer, measured by ^{1}H NMR. The $\overline{M}_{n,(PVC\text{-}1)}$ value is based on the apparent MW of PVC-1 estimated by SEC using polystyrene standards.

Results and discussion

The graft polymerizations were performed with styrene (St), methyl acrylate (MA), methyl methacrylate (MMA) and butyl acrylate (BA) and films of these copolymers were prepared. These films were transparent, indicating that there was no macroscopic phase separation and no formation of large amounts of homopolymer. Size exclusion chromatography (SEC) showed that the molecular weight of the copolymer increased after the polymerization. The monomodal shape of the SEC trace of the obtained polymer suggests the formation of graft copolymer without homopolymerization (Fig. 1). The polydispersities of the resulting graft copolymers were relatively high owing to high polydispersities of the starting macroinitiator and due to the variable number of chloroacetate groups in one macroinitiator. The precise molecular weights of the copolymers could not be determined directly from the SEC data, owing to difference in hydrodynamic volumes between graft copolymers and linear polystyrene standards. This was confirmed by comparing the $\overline{M}_n$s of the polymers that were determined by SEC and ^{1}H NMR (Tab. 1).

The ^{1}H NMR spectrum indicates presence of both monomers in the final copolymers and allow for quantitative determination of the amount of incorporated second monomer (Fig. 2 and Tab. 1). In the NMR spectrum of the macroinitiator (Fig. 2(A)), the resonance at 4.1 ppm corresponds to CH_2Cl protons in the chloroacetate group. Consumption of these chlorine groups by initiation by ATRP was confirmed in the graft copolymers of styrene, MA and MMA (Fig. 2 (B), (C) and (D)). Clean disappearance of the signal corresponding to the α-protons from the chloroacetate group supports that it was consumed by initiation. The disappearance of this signal could not be confirmed for PVC-*g*-BA, because of overlap of the signal resulting from $-CO_2CH_2-$ in butyl acrylate (Fig. 2 (E)).

Incorporation of the second monomer in the product progressively increased with reaction time as shown in the ^{1}H NMR spectrum of PVC-*g*-PBA system in Fig. 3. An increase in molecular weight and amount of monomer incorporated in the grafts with time observed in SEC and ^{1}H NMR also supports the formation of graft copolymer (Tab. 2).

The formation of the graft copolymer was also supported by FT-IR analysis (Fig. 4). The spectra of the PVC macroinitiator showed the carbonyl stretch ($\nu = 1759$ cm^{-1}) in the chloroacetate groups (Fig. 4 (A)). After the copolymerization with butyl acrylate, a new carbonyl

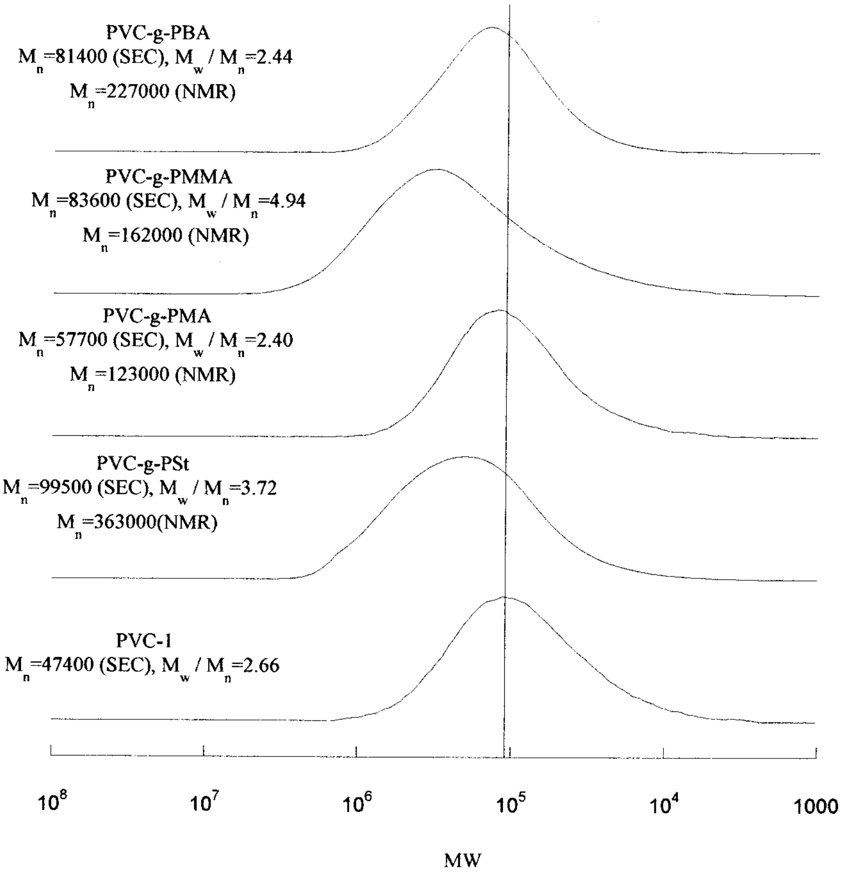

Fig. 1. SEC chromatograms of PVC-1 and graft copolymers

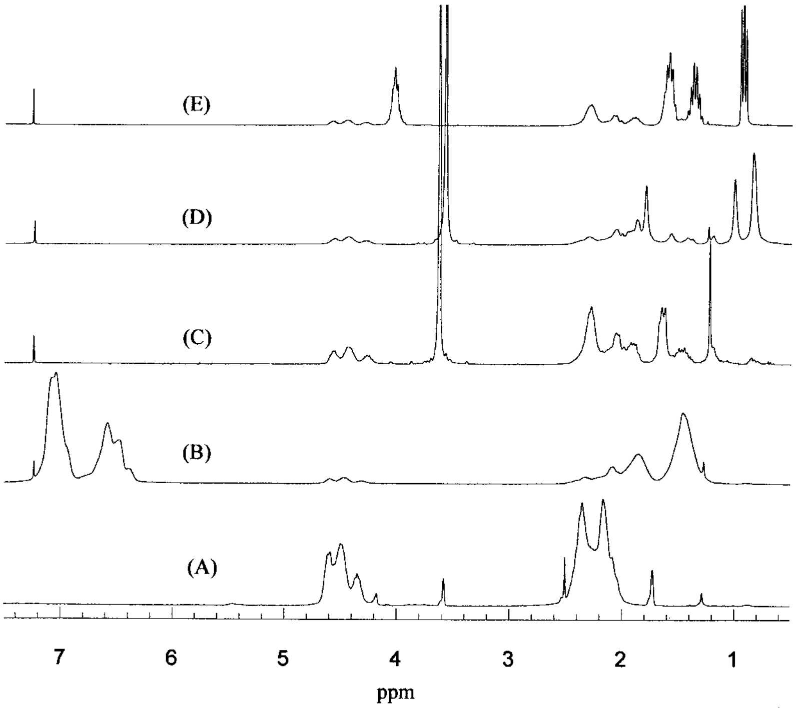

Fig. 2. ^{1}H NMR spectrum of (A) PVC-1, (B) PVC-*g*-PSt (80 mol-%), (C) PVC-*g*-PMA (50 mol-%), (D) PVC-*g*-PMMA (60 mol-%), (E) PVC-*g*-PBA (65 mol-%)

Tab. 1. Results of graft copolymerization of PVC with styrene (St), methyl acrylate (MA), methyl methacrylate (MMA) and butyl acrylate (BA)

2nd monomer	$\overline{M}_n$ (SEC)	$\overline{M}_n$ (NMR)	$\overline{M}_w/\overline{M}_n$ (SEC)	Content of 2nd monomer in mol-%	T_g/°C
–	47400	–	2.66	0	83
St	99500	363000	3.72	80	80
MA	57700	112700	2.40	50	21
MMA	83600	161500	4.94	60	111
BA	81400	227000	2.44	65	–19

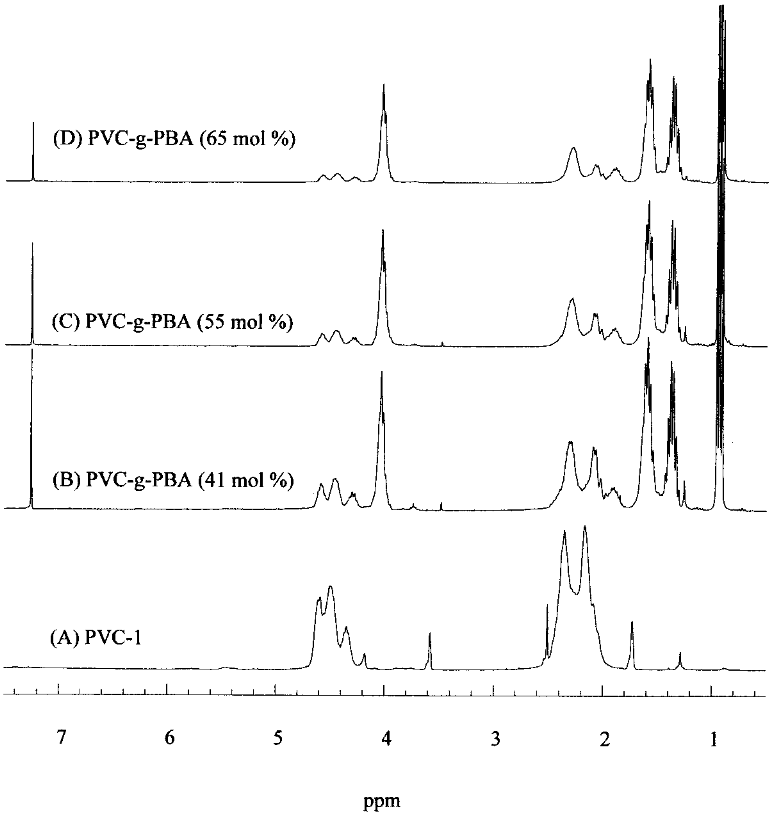

Fig. 3. ^{1}H NMR spectrum of PVC-1 and PVC-*g*-PBA

Tab. 2. Results of graft copolymerization of PVC with butyl acrylate (BA)[a)]

Time in h	$\overline{M}_n$ (SEC)	$\overline{M}_w/\overline{M}_n$ (SEC)	$\overline{M}_n$ (NMR)	Content of BA in mol-%	T_g/°C
0	47400	2.66	–	0	83
2.0	61500	2.28	114900	41	–4
4.3	79500	2.42	166100	55	–11
9.5	81400	2.44	227000	65	–19

[a)] [Butyl acrylate]$_0$ = 6.98 M, [CuBr]$_0$ = [dNbipy]$_0$/2 = 3.49 × 10^{-2} M, [PVC-1]$_0$ = 1.0 × 10^{-3} M, temp = 90 °C.

peak was observed at ν = 1730 cm^{-1} corresponding to the carbonyl stretching from butyl acrylate (Fig. 4 (B), (C)).

Thermal analysis (DSC) revealed only one T_g for all copolymers. The T_g of copolymers decreases with increasing content of butyl acrylate in the copolymer (Fig. 5). The results of PVC-*g*-PBA are summarized in Tab. 2.

In conclusion, the graft copolymers of poly(vinyl chloride) with styrene and (meth)acrylates were prepared by

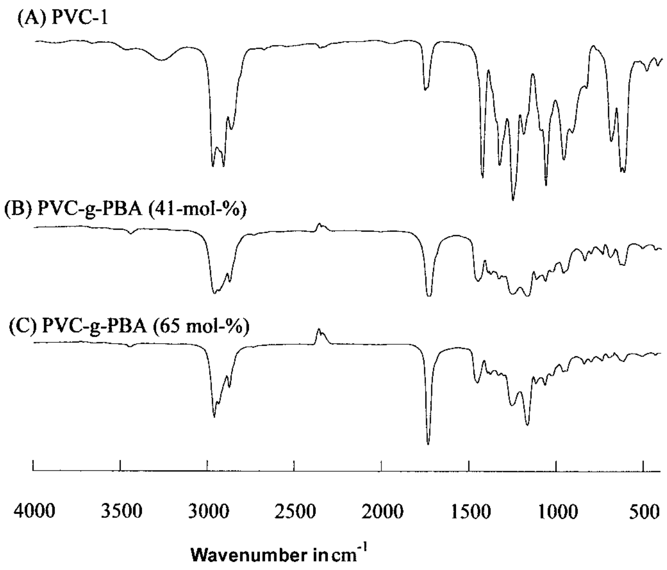

Fig. 4. FT-IR spectrum of PVC-1 and PVC-*g*-PBA

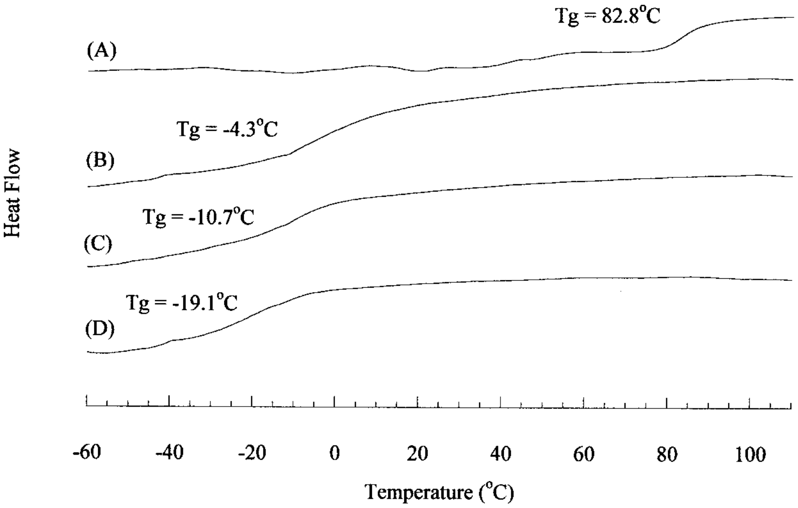

Fig. 5. DSC curves of (A) PVC-1, (B) PVC-*g*-PBA (41 mol-%), (C) PVC-*g*-PBA (55 mol-%), (D) PVC-*g*-PBA (65 mol-%)

atom transfer radical polymerization using poly(vinyl chloride) containing pendent chloroacetate units as a macroinitiator. The formation of the graft copolymer was supported by analysis of SEC, ^{1}H NMR and FT-IR. This new approach using as a macroinitiator, a copolymer with a small number of sites capable of initiating ATRP, can allow for the preparation of new materials.

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[1] P. V. Smallwood, “Vinyl Chloride Polymers, Polymerization”, in: *Encyclopedia of Polymer Science and Engineering*, vol 17, 2nd edition, H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges and J. I. Kroschwitz, Eds., Wiley, New York 1985, p. 295

[2] P. F. Rempp, P. J. Lutz, “Synthesis of Graft Copolymers”, in: *Comprehensive Polymer Science*, vol. 6, G. C. Eastmond, A. Ledwith, S. Russo and P. Sigwalt, Eds., Pergamon Press, Oxford 1989, p. 403

[3] J. P. Kennedy, *Appl. Polym. Symp.* **30**, 1 (1977)

[4] M. Kucera, Z. Salajka, K. Majerova, *Polymer* **26,** 1575 (1985)

[5] El-Sayed A. Hegazy, A. R. Evaid, S. A. El-Sharabasy, A. M. Mousa, A. Y. Hassan, *J. Appl. Polym. Sci.* **41**, 2941 (1990)

[6] D. Greszta, D. Mardare, K. Matyjaszewski, *Macromolecules* **27**, 638 (1994)

7) T. Otsu, M. Yoshida, *Makromol. Chem., Rapid Commun.* **3**, 127 (1982)

8) U.S. Pat. 4,581,429 (1986) D. H. Solomon, E. Rizzardo, P. Cacioli

9) M. K. Georges, R. P. N. Veregin, G. K. Kazmaier, G. K. Hamer, *Macromolecules* **26**, 2987 (1993)

10) B. B. Wayland, G. Poszmik, S. L. Mukerjee, M. Fryd, *J. Am. Chem. Soc.* **116**, 7943 (1994)

11) S. Gaynor, J. S. Wang, K. Matyjaszewski, *Macromolecules* **28**, 8051 (1995)

12) J.-S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.* **117**, 5614 (1995)

13) T. Patten, J. Xia, T. Abernathy, K. Matyjaszewski, *Science* **27**, 866 (1996)

14) M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules* **28**, 1721 (1995)

15) V. Percec, B. Barboiu, *Macromolecules* **28**, 7970 (1995)

16) C. Granel, P. Dubois, R. Jérôme, P. Teyssié, *Macromolecules* **29**, 8576 (1996)

17) M. Roha, H.-T. Wang, H. J. Harwood, A. Sebenik, *Macromol. Symp.* **91**, 81 (1995)

18) M. Huskic, M. Roha, H. J. Harwood, A. Sebenik, *Polym. Int.* **40**, 227 (1996)

19) K. Matyjaszewski, T. P. Patten, J. Xia, *J. Am. Chem. Soc.* **119**, 674 (1997)

20) H.-j. Paik, K. Matyjaszewski, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **37(2)**, 274 (1996)

21) T. Grimaud, K. Matyjaszewski, *Macromolecules* **30**, 2216 (1997)

22) K. Matyjaszewski, S. M. Jo, H.-j. Paik, S. G. Gaynor, *Macromolecules* **30**, 6398 (1997)

23) R. N. Keller, H. D. Wycoff, *Inorg. Synth.* **2**, 1 (1946)