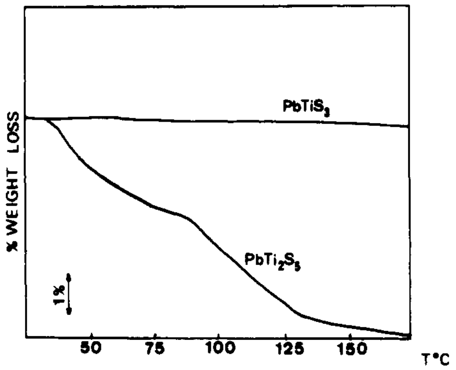

Figure 3. TG traces of $Li_{0.2}PbTiS_3$ and $Li_{2.0}(H_2O)_{1.5}PBTi_2S_5$. These samples were prepared from lithiated samples after being exposed to water vapor.

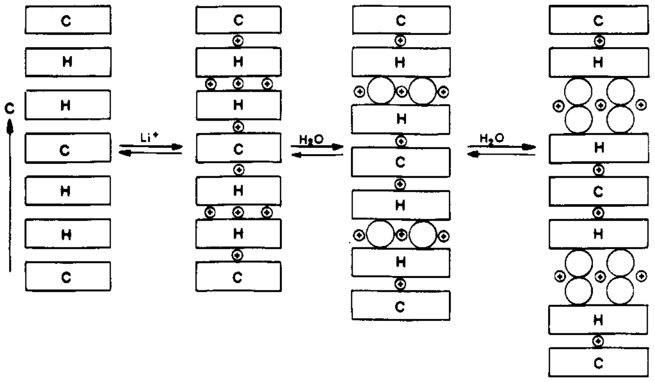

Figure 4. Scheme of lithiation/hydration reactions of $PbTi_2S_5$. C and H denote PbS (NaCl related) and TiS_2 (CdI_2 related) negatively charged layers.

that the pattern followed is that shown in Figure 4, which is similar to that described by Lerf and Schöllhorn.[4] This behavior was checked by halting the recording of the TG curve at the end of the first step and immediately recording the XRD pattern. The basal spacing of the low-temperature intercalation product was expanded by ca. 3 Å/HHC unit. The product obtained after the second step of the TG curve showed a similar basal spacing than the non-hydrated lithiated samples. Thus, the hydration seems to be a reversible process. Heating the samples above 175 °C led to a partial decomposition of the misfit structure, finally leading to an amorphous state. From the quantitative evaluation fo the TG data for the 1:2:5 phase, compositions of the hydrated phases close to $Li_2(H_2O)_{0,6}PbTi_2S_5$ and $Li_2(H_2O)_{1.5}PbTi_2S_5$ can be obtained. These values are similar to those found for $A_x(H_2O)_yMS_2$ (A: Na, K; M: Ti, Nb, Ta).[4] A final point of interest is the fact that no staging was observed in the hydrated phases. Staging has been found in amonium intercalates of TiS_2 and NbS_2.[11] Only stage I was detected in the hydrated samples, were the interlayer HH space of all HHC units contained 1 or 2 water molecules.

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Registry No. Pb, 7439-92-1; Ti, 7440-32-6; S, 7704-34-9; $PbTiS_3$, 12066-65-8; H_2O, 7732-18-5.

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Synthesis and Properties of Polyoxometalates Based Inorganic–Organic Polymers

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The synthesis of mixed organic–inorganic materials is a growing field of research.[1] The challenge for these new materials is to optimize both the inorganic and the organic components on a molecular scale. Such advanced materials must exhibit specific properties (electronic, optic, catalytic, ...) and easily be shaped as coatings or monoliths. Polyoxometalates (POM's) have been widely studied as small compact oxide clusters.[2] Their redox properties and high electronic density are ideal for their use as catalysts, stains for electron microscopy, cross-linking reagents, and photochromic or electrochromic materials.[3] Many studies are dealing with their stabilization by entrapment in polymeric networks.[4]

This communication presents for the first time, to the best of our knowledge, the synthesis and characterization of negatively charged macromolecules based on organically functionalized POM's anchored to an organic polymeric backbone. Organically modified POM's are anchored together through chemical bonds in order to obtain macromolecules. This study concerns the chemistry of a new class of organic–inorganic polymers. They could be promising materials for photo- or electrochromics.

The synthesis of mixed organic–inorganic polymers has been performed as follows: The organically modified POM precursors have been synthesized by reacting trichloro(or trialkoxy)silane with lacunar $K_4SiW_{11}O_{39}$ following a procedure previously described.[5–7] The organic functionalization is obtained via trichlorosilanes $RSiCl_3$ (R = vinyl ($CH{=}CH_2$), allyl ($CH_2CH{=}CH_2$), 3-(methacryloxy)propyl [methacryl] ($(CH_2)_3OC(O)C(CH_3){=}CH_2$)) purchased from Dynamit Nobel Company or triethoxystyrilsilane ($(OEt)_3Si(C_6H_4CH{=}CH_2)$) [styryl] synthesized by reaction of Grignard derivative with $Si(OEt)_4$ in THF.[8,9]

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(7) Triethoxystyrylsilane was added to a K_4SiW_{11} aqueous solution, under vigorous stirring, and the pH was adjusted to pH 1 by addition of HCl. After 20 h of stirring, NBu_4Br was added, and the precipitate was washed with water and *i*-PrOH, leading to styryl-derivitized heteropolytungstate (yield = 60%).

(8) $MgBrC_6H_4CH{=}CH_2$ was prepared by slow addition of 5.5 g (0.03 mol) of 4-bromostyrene to 0.73 g (0.03 mol) of magnesium turnings in THF, under argon atmosphere. The solution was kept boiling for 20 h. To this solution was added dropwise 5 g (0.024 mol) of tetraethoxysilane in THF. The solution was refluxed for 15 h. The resulting gum has been purified by vacuum distillation and 3 g (0.011 mol) of triethoxystyrylsilane ($(OEt)_3SiC_6H_4CH{=}CH_2$) was obtained (T_b = 120 °C/0.1 mmHg, yield = 50%, purity checked by NMR and mass spectrometry).

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Table I. Most Significant Properties of Polymers Obtained from $SiW_{11}SiR$:Catalyst:Solvent Systems

nature of the monomer $SiW_{11}SiR$	polymerization conditions: solvent, catalyst (ratio), temperature	hydrodynamic radius,[a] Å	polymerization yield,[b] %
$SiW_{11}SiR$	none	10[c]	
$SiW_{11}Si$(vinyl)	DMF, POB (2%), 70 °C	50	5
$SiW_{11}Si$(allyl)	DMF, *t*-BuPOB (2%), 110 °C	1200	20
$SiW_{11}Si$(methacryl)	DMF, POB (0.5%), 95°C	150	65
	DMF, POB (5%), 95 °C	800	70
$SiW_{11}Si$(styryl)	PC, POB (2%), 80 °C	100	100
	DMSO, AIBN (8%), 60 °C	80	100

[a] Hydrodynamic radius is obtained from QELS measurements (Brookhaven Instrument BI2030 Digital Correlator), for polymer solutions in DMF ($c = 0.3$–0.02 M, filtration 0.2 μm, $T = 20$ °C, quadratic fit). [b] Polymerization yields are obtained from NMR spectra (relative areas determination). NMR spectrometers: ^1H, Bruker AM 250; ^{29}Si CP-MAS, Bruker MSL 400. [c] This value, measured by QELS ($C = 0.5$ M) corresponds to hydrodynamic radius of Keggin oxopolymetalates.[2]

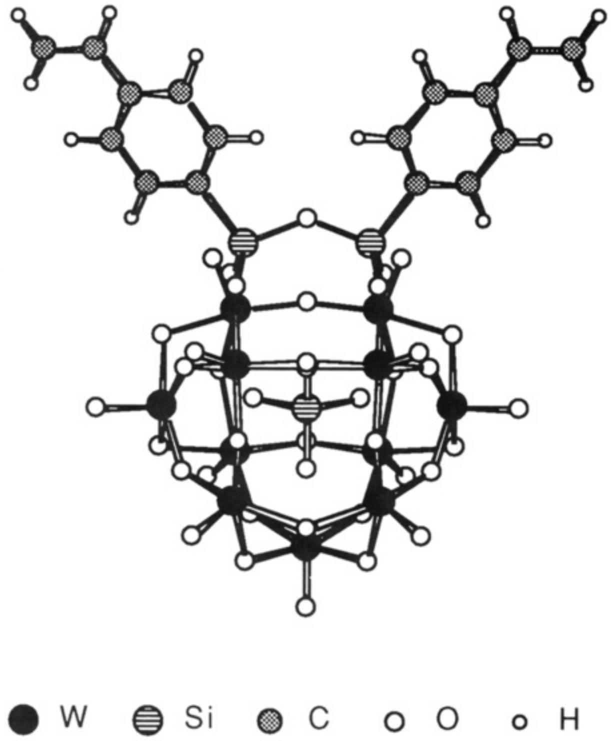

Figure 1. Structure of the $[SiW_{11}Sistyryl]^{4-}$ monomer.

Tetrabutylammonium salts $(SiW_{11}O_{40}(SiR)_2)^{4-}\cdot 4TBA^+$ [$SiW_{11}SiR$] have been obtained with high purity[10] and are readily soluble in aprotic polar solvents. A recent spectroscopic study[6] is in agreement with the structural model (Figure 1) proposed by Knoth.[5] Each POM carries two bifunctional groups (vinyl, allyl, methacryl, styryl) for further organic polymerization reactions.

The influence of the solvent (DMF, DMSO, acetonitrile [ACN], and propylene carbonate [PC]) and the radical initiator (benzoyl peroxide (POB), AIBN, and *tert*-butyl peroxide (*t*-BuPO)) on polymerization have been tested for each monomer unit. A typical synthesis was carried out as follows:

$SiW_{11}Si$(methacryl) (0.5 g) was dissolved in the minimum volume of solvent (DMF, ACN, PC). The solutions were filtered on a 0.2-μm Millipore filter, poured in a closed vessel, heated, and degassed under argon. Then, the radical initiator was added with different ratios ($R = 0.5\%$ to 8%, R is the weight ratio between initiator and organic function). Then, the hermetically closed tube was kept in a thermostated oven for 72 h (60 °C for AIBN, 90 °C for POB, 120 °C for *t*-BuPO).

The mean hydrodynamic radius of polymers in solution (DMF) has been determined by using quasi elastic light scattering measurements (QELS). The polymerization yield has been determined by using ^1H quantitative NMR measurements of polymeric solution in DMSO-d_6 (99.9%). Areas of the ^1H resonances corresponding to the remaining ethylenic protons have been compared with those of the TBA cations ($SiW_{11}(CH_2)_3OC(O)C(CH_3){=}CH_2$) $\delta[^1H] = 5.62, 6.05$ ppm; $N(CH^{(1)}{}_2CH^{(2)}{}_2CH^{(3)}{}_2CH^{(4)}{}_3)$, $\delta[^1H] = {}^{(4)}0.95, {}^{(3)}1.40, {}^{(2)}1.55, {}^{(1)}3.10$ ppm).

The nature of the solvent influences greatly the polymerization yield Y, e.g. Y is around 10% maximum for $SiW_{11}Si$(styryl) in DMF and 100% in PC or ACN. Table I summarizes the best results obtained for each monomer with an optimized solvent–initiator system. $SiW_{11}Si$(vinyl) is quite unreactive toward radical polymerization[11] and polymerization of $SiW_{11}Si$(styryl) is extensive. The reactivity of the different organically modified POM follows the order $SiW_{11}Si$(vinyl) ≪ $SiW_{11}Si$(allyl) < $SiW_{11}Si$(methacryl) < $SiW_{11}Si$(styryl). These results are quite comparable with those obtained with $(OX)_3SiR$ and X_3SiR monomers (X being the polymerizable radical).[12] Note that best polymerization yields do not always correspond to polymers with highest hydrodynamic radius.

For solid-state characteristic purposes, the mixed organic inorganic compounds were precipitated with water, washed, and dried. The infrared spectrum of the $SiW_{11}Si$(methacrylate) polymer below 1100 cm^{-1} exhibits the set vibrations characteristic of the oxometalate network (ν_{SiO}, 1050 cm^{-1}; ν_{SiO}, 1020 cm^{-1}; $\nu_{W=O}$, 900 cm^{-1}; ν_{WOW}, 860, 760, 710 cm^{-1}; ν_{SiC}, 615 cm^{-1}), indicating that the POM backbone remains unchanged after the polymerization reaction (no degradation of the polyanion occurs in the reaction bath). A decrease of the intensity of the $\nu_{C=C}$ vibration (1590 cm^{-1}) is observed in agreement with the occurrence of the polymerization reaction.

High-resolution ^{29}Si NMR spectra have been recorded in both the liquid and solid state (cross-polarization magic angle spinning (CP-MAS)). The ^{29}Si NMR resonance corresponding to the modified silica clusters $RSiO_n$ ($\delta = -65/-70$ ppm)) was not observed. Such experiments confirm that polymerization of both compounds occurs without degradation of the polyanionic structure. The decoupled $\{^1H\}$–^{29}Si spectra (liquid), recorded with a sequence $[\pi/2\text{–acquisition–delay}]_n$ (acquisition + delay =

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[10] The structure of this compound $[SiW_{11}O_{40}(SiC_8H_7)_2)^{4-}\cdot 4(C_4H_9)_4N^+]$ was established by time of flight spectrometry (M_w: found, 3920; calcd, 3922) and a multispectroscopic study (^{29}Si and ^{183}W NMR).[6] The purity (>98%) was checked by mass elemental analysis (Found: C, 24.6; H, 4.0; N, 1.7; O, 16.7; Si, 2.0; W, 51.0. Calcd for $C_{80}H_{158}N_4O_{40}Si_3W_{11}$: C, 24.47; H, 4.06; N, 1.43; O, 16.31; Si, 2.14; W, 51.59.) and NMR and IR spectroscopy.

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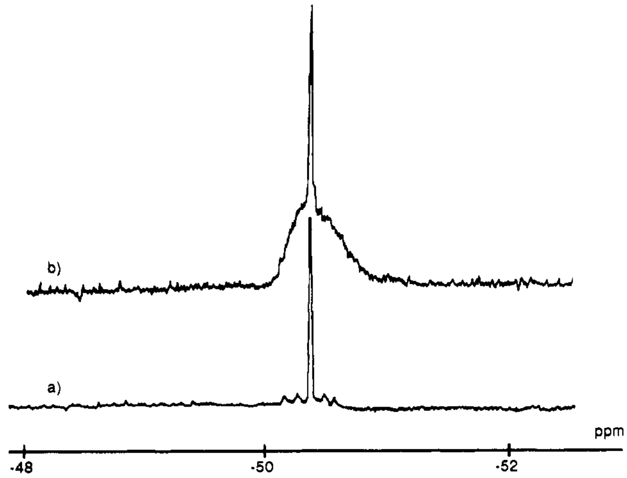


Figure 2. {^{1}H}–^{29}Si decoupled NMR liquid spectrum of SiW$_{11}$Si(methacryl) polymer (polymerization conditions, POB (2% ratio), DMF, 90 °C; polymer yield, 70%): solvent, DMSO-d_6; sequence, [π/2–acquisiton–delay]$_n$, (acquisition + delay = 0.2 s (a) and 10 s (b)).

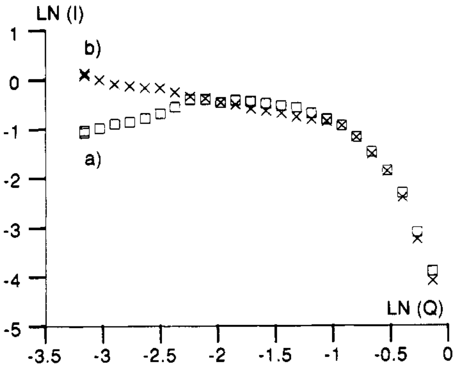
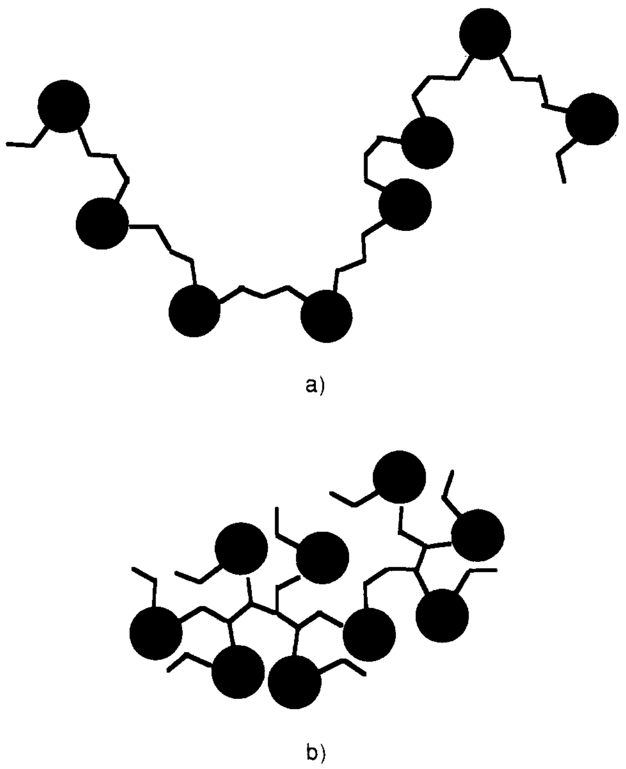


Figure 3. Small-angle X-ray scattering experiments: (a) SiW$_{11}$Si(methacryl) in DMF; (b) polymerized SiW$_{11}$Si(methacryl) in DMF (polymerization conditions, POB (2% ratio), DMF, 90 °C; polym. yield, 70%).

0.2, 0.5, 1, 10 s) exhibit two ^{29}Si resonances located at the same chemical shift (−52.9 ppm) but with different relaxation times (Figure 2). Such a ^{29}Si NMR chemical shift corresponds to the organically modified silicon atom. The narrow signal (0.5 Hz), with a long relaxation time, corresponds to species with a quite fast molecular motion. It remains from non polymerized POM precursors. The broad signal (30 Hz), with a longer relaxation time, should correspond to low mobility species.[13] Such a signal could be assigned to POM polymeric species. Furthermore, CP-MAS experiments performed on SiW$_{11}$Si(allyl) system presents two ^{29}Si resonances with different chemical shifts: −57 and −52.9 ppm signals corresponding respectively to the initial molecules (POMSiCH$_2$CH=CH$_2$), and to polymer species (POMSiCH$_2$CH$_2$CH$_2$CH$_2$).

Figure 3 presents the small angle X-ray scattering curves (ln $I = f(\ln Q)$ plot) of both solution of monomeric species and polymerized SiW$_{11}$Si(methacrylate) colloids in DMF at the same concentration. They present a quite different shape. Monomeric particles are represented by a scattering profile which presents a maximum. At large scattering angle (Guinier zone), the curve is a line with a slope of −4. It is representative of the compact structure of polyanionic units. It ended at Q values which correspond to the size of the POM (typically 10–15 Å). The maximum located at Q = 0.15 Å^{-1} corresponds to the calculated average distance between polyanion (d = 62 Å for C = 10^{-2} M). The depression of the scattered intensity observed at small Q values corresponds to repulsion interactions between polyoxometalates.


a)

b)

Figure 4. Proposed strutures for SiW$_{11}$SiR polymers (each POM is represented by one black disk): (a) linear structure; (b) branched, compact structure.

Polymers obtained from SiW$_{11}$Si(methacryl) are represented by a two-zone curve. At large scattering vector, we observe a −4 slope corresponding to the compact Keggin structure. At small scattering vector, a linear regime with a slope of −0.5 is observed up to Q = 3.2 Å^{-1} (d = 150 Å). Such a slope could be assigned to scattering by polymers with an unusually low density.[14] Thus it could be explained both by the finite size of the polymers or by the structure of the particles, the flexibility of the long organic chains (more than 15 chemical bonds), allowing a random distribution of distances between compact and strongly scattering POM centers.

These results show that inorganic–organic polymers based on POM units can be synthesized via radical polymerization. However, inorganic–organic polymers with different spacial repetitions and structures (linear or branched and compact) are probably obtained depending on polymerization conditions (Figure 4). Such conformational differences are evidenced by ^{1}H NMR on SiW$_{11}$Si(styryl) systems. Figure 5 presents the pattern of the phenyl signal for two polymers. No signals were observed for the vinyl functions indicating complete polymerization. Broad and complex signal are representative of the polymerized systems. However, their shape, totally different, could correspond to a different macromolecular network.[13]

The cyclic voltamogram of SiW$_{11}$Si(methacrylate) polymers in DMF/Bu$_4$NBF$_4$ electrolyte is shown in Figure

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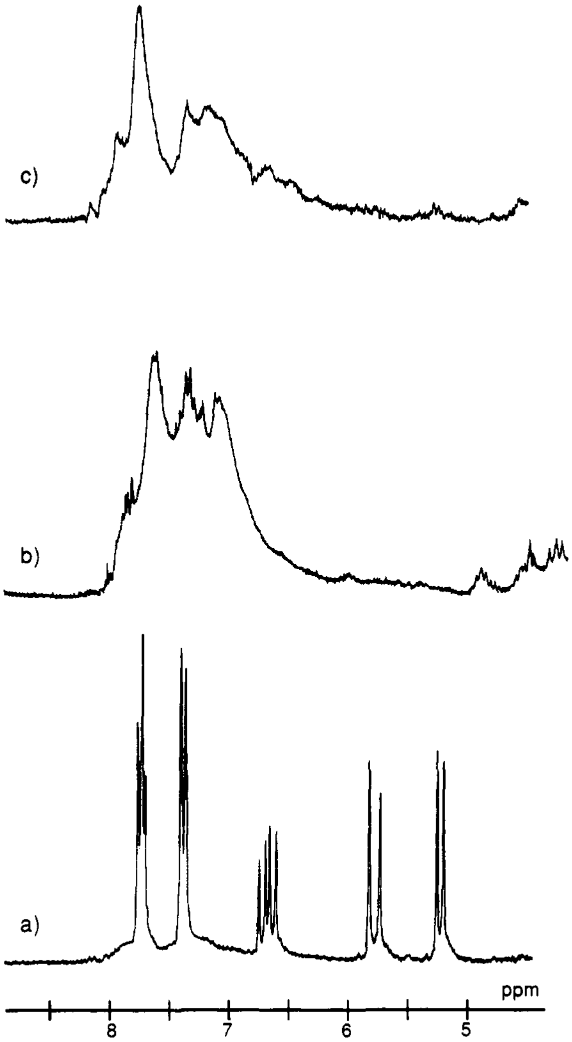

Figure 5. ^{1}H NMR spectrum of SiW11Si(styryl) based polymers: (a) $SiW_{11}Si$(styryl) monomer; (b) polymer, AIBN (8% ratio), DMSO, 60 °C; polymer yield 100%; (c) polymer, POB (6% ratio), PC, 80 °C; polymer yield 100%.

6. It is characteristic of a reversible reduction of the polymetalate structure, with two successive one-electron processes.[15] Upon UV irradiation, these solutions turn blue. Their visible spectrum is characterized by a wide absorption band in the visible–near-IR range centered upon 1000 nm. Such behavior is characteristic of a intervalence transition W^{5+}–W^{6+} in mixed valence polymetalates.[16] Therefore, the electrochemical or photochemical behavior of the POM active molecules do not depend on their spatial proximity inside these mixed organic inorganic polymers.

Transparent thin films can be deposited from these POM–polymeric solutions, on different kinds of substrates (glass, plastics, metals). They turn reversibly to blue upon UV irradiation or electrochemical reduction.

These mixed organic–inorganic structures present interesting materials for electrode modification in heterogeneous catalysis, electrocatalysis, and photochromic and electrochromic devices. In order to increase the polymerization yield, the structure, and the mechanical properties of the material, copolymerization of the modified oxopolymetalate and organic monomer, such as methyl methacrylate or styrene, was investigated.

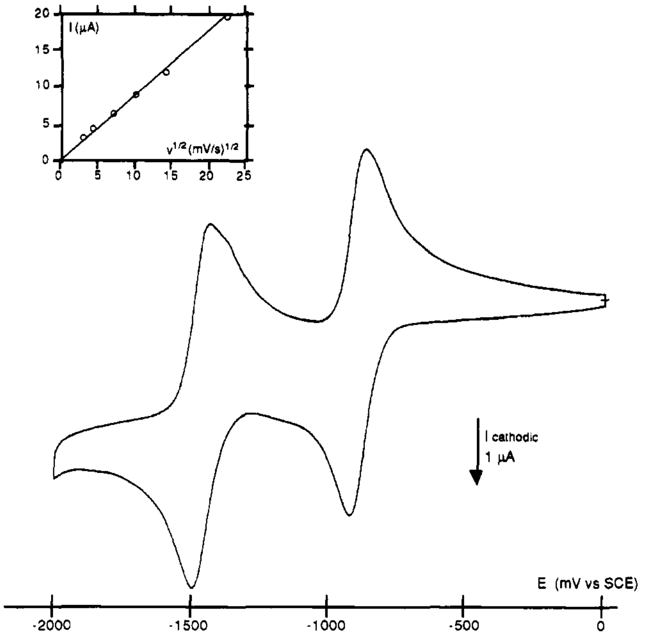

Figure 6. Cyclic voltamogram of $SiW_{11}Si$(methacryl) polymer (10^{-3} M) in DMF/Bu_4NBF_4 (10^{-1} M), scanning rate 100 mV/s. (polymerization conditions, POB (2% ratio), DMF, 90 °C; polymer yield, 70%). The inset shows the dependence of the cathodic peak current upon (scan rate)$^{1/2}$ [diffusion process].

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Growth of Epitaxial (100) GaAs Films Using the Single-Source Precursor $[Me_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$

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Considerable attention has been directed recently at finding alternatives to the traditional sources used to produce III–V compound semiconductor films, trimethyl and triethyl group 13 molecules, and group 15 hydrides.[1] This has been motivated by the toxic nature of the hydrides and the pyrophoric nature of the group 13 sources. In addition, the thermal stability of the hydrides imposes the need for a high growth temperature (ca. 650–700 °C) during chemical vapor deposition (CVD). As a consequence of the high growth temperature, an excess of the hydride must used to maintain a sufficient overpressure since this prevents the group 15 component from prefer-

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