ADVANCED
MATERIALS

New Methods for the Anionic Polymerization of α-Activated Olefins

Group Transfer Polymerization
Metal-free Polymerization
Living Polymers

By Manfred T. Reetz*

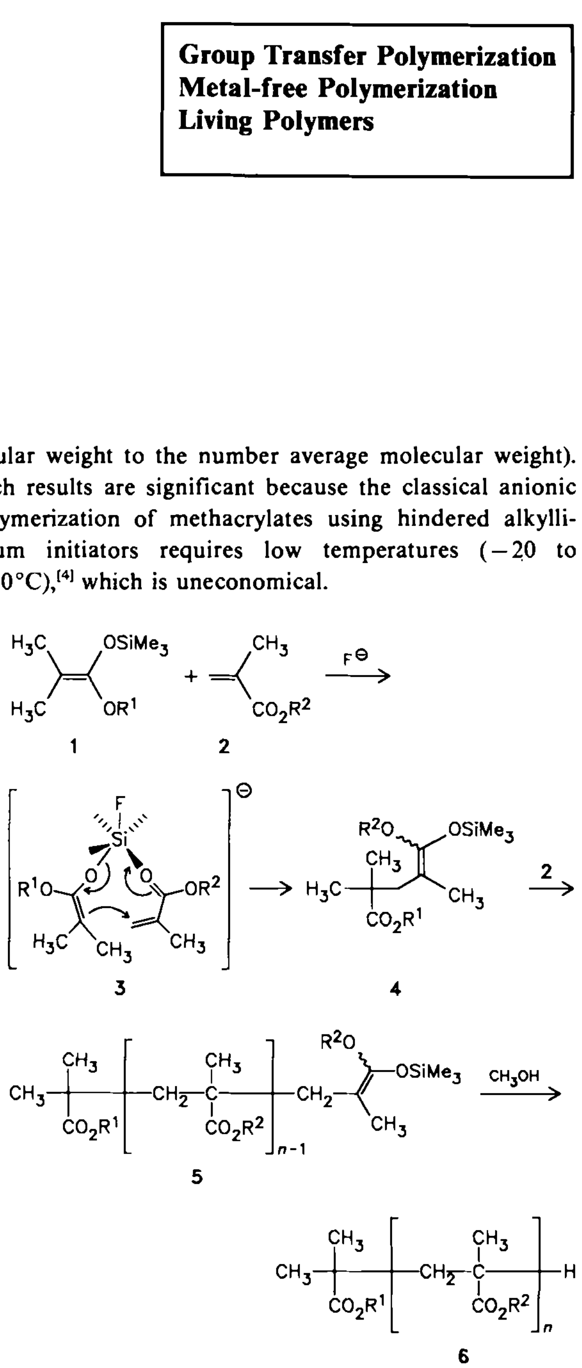
1. Introduction

One of the exciting developments in current polymer research concerns the controlled polymerization of monomers with formation of macromolecules having a defined molecular weight and a narrow molecular weight distribution. If a given process has the additional feature of yielding living polymers, such interesting reactions as functionalizations of the chain end and/or block and graft polymerizations are possible. The costs of these polymerizations may be higher than those of traditional processes lacking such characteristics. However, in certain applications this may be offset by the favorable properties of the polymers.

In recent years several different types of polymerizations have been developed with the aim of fulfilling some or all of the above mentioned requirements. These include cationic polymerizations of isobutylene and other electron rich olefins,[1] polymerization of cyclic olefins using olefin metathesis,[2] and anionic polymerizations of α-activated olefins such as acrylic and methacrylic acid esters.[3-12] This report deals with the latter area, with emphasis on the author's own research.

2. Group Transfer Polymerization

In 1983 *Webster* and co-workers at Du Pont startled the scientific community by introducing the so-called group transfer polymerization (GTP) of methacrylic acid esters **2** and other α-activated olefins.[3] Accordingly, the *O*-silyl ketene ketal **1** functions as the initiator in combination with a nucleophilic or electrophilic catalyst, e.g., fluorides or Lewis acids, respectively. It turned out that the former are better suited. Such fluorides as HF_2K, $FN\textit{n}Bu_4$ or $[Me_3SiF_2][S(NMe_2)_3]$ induce the quantitative polymerization of **2** at *room temperature* with formation of polymers having a narrow molecular weight distribution, i.e., D values of <1.3 ($D = M_w/M_n$; ratio of the weight average molecular weight to the number average molecular weight). Such results are significant because the classical anionic polymerization of methacrylates using hindered alkyllithium initiators requires low temperatures (-20 to -70 °C),[4] which is uneconomical.



$R^1 = CH_3$, *n*-alkyl, $CH_2CH_2OSiMe_3$
$R^2 = CH_3$, *n*-alkyl, allyl

The mechanism of GTP involves activation of the initiator by fluorides to form a pentavalent silicon species which then undergoes Michael addition to the monomer via the hexacoordinated intermediate **3**. Although the details of this step are still being studied,[5] it became clear that the silyl group migrates to the oxygen atom of the monomer, forming a new *O*-silyl ketene ketal **4** which in turn undergoes another Michael addition. Labeling experiments

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show that the silyl groups remain attached to the growing chain, i.e., they do not jump to other chains.[6]

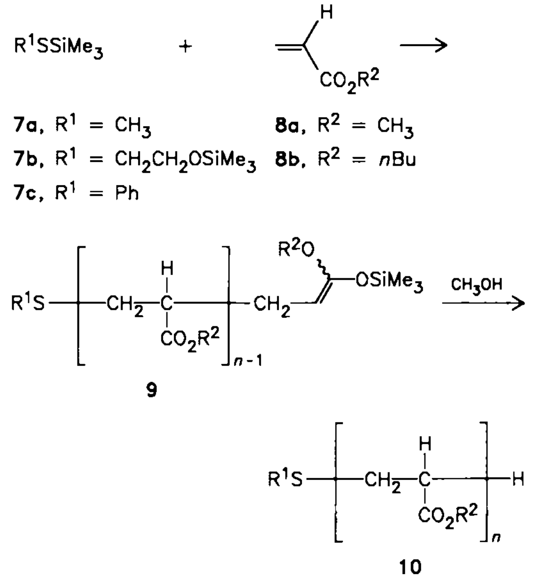
The molecular weight can be controlled by the amount of monomer added relative to the quantity of initiator used. Most of the reported molecular weights M_n lie between 1000 and 20000. There appear to be very few chain transfer or terminating events, which means that in a practical sense the polymers are living. Following the termination of a given polymerization, the same or a different methacrylic acid ester can be added, resulting in the continuation of polymerization.

Since the R^1 group in the initiator **1** can contain a protected functional group (e.g., $CH_2CH_2OSiMe_3$), one end of the polymer may bear a functional group (e.g., OH following hydrolytic deprotection) which can be used as an anchor point for the formation of graft polymers. Such functionalized polymers (chelic polymers) are useful for the production of dispersing agents and ABA block polymers.[7] Functionalization, coupling and dimerization at the chain end have also been reported.[3,7]

Since the details of the Dupont process have been delineated elsewhere,[7] no further information is given here, except to point out that *acrylic* acid esters were reported to cause problems.[7,8] Nucleophilic catalysts lead to broad molecular weight distributions. Lewis acid catalysts, especially ZnX_2, are better suited. They activate the monomer by coordinating at the carbonyl function. However, it was reported that the polymers are no longer living at room temperature, i.e., renewed addition of monomer following the termination of polymerization did *not* lead to a continuation of polymerization.[8]

It is generally accepted that the anionic polymerization of acrylates is more difficult than that of methacrylates.[4,7] Not only are the former monomers more reactive, but also the polymer chain contains C–H acidic positions which undergo undesirable deprotonations (metalations). In spite of this, we attempted the GTP of acrylic acid esters at room temperature using silylated thiols **7** as initiators. We were pleased to discover that ZnI_2 as catalyst (only 1% with respect to the *initiator*!) induces the quantitative polymerization of **8** in toluene with formation of *living* acrylates having excellent D-values (≈ 1.1).[9] Functionalized initiators (e.g. **7b**) behave similarly. This paves the way for preparing block, graft, chelic and telechelic polymers. In the polymerization of **8b** with **7b**/ZnI_2, further monomer was added at room temperature three hours after termination of polymerization; this led to a continuation of the polymerization with quantitative formation of a polymer having a molecular weight distribution which is only slightly broadened ($D = 1.25$). Following aqueous work-up, the isolated polymers are stable at higher temperatures, e.g., heating at 260°C for three hours causes no loss of sulfur.[10]

The success of group transfer polymerization rests upon the migration of covalently bonded O-silyl groups along the polymer chain under mild conditions,[3,9] in contrast to the highly polar lithium enolates in classical anionic polymerization. The reactivity is expected to increase in the following sequence: Si-enolates < Li-enolates < K-enolates < NR_4-enolates. At first glance the ionic end of the scale, i.e., a metal-free system with ammonium as the counterion, might be expected to lead to disastrous results at room temperature. Nevertheless, we decided to venture into this area.



7a, R^1 = CH$_3$ **8a**, R^2 = CH$_3$
7b, R^1 = CH$_2$CH$_2$OSiMe$_3$ **8b**, R^2 = nBu
7c, R^1 = Ph

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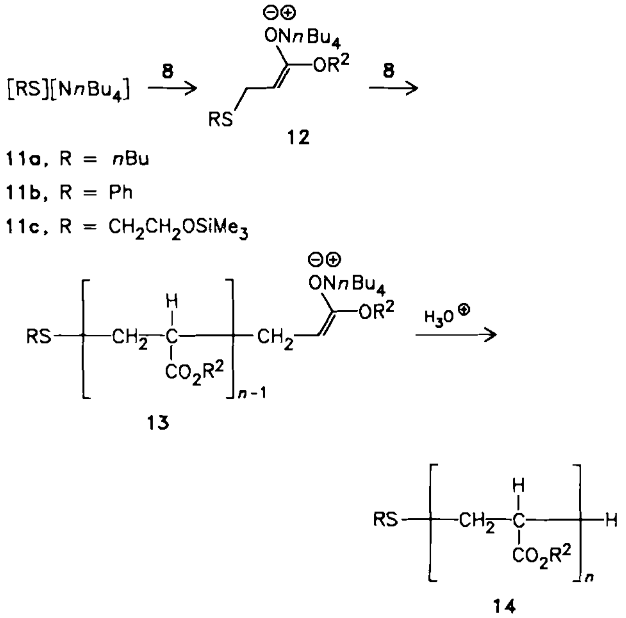
3. Metal-free Anionic Polymerization

We turned first to ammonium thiolates RSNnBu$_4$ as initiators for the anionic polymerization of acrylic acid esters.[11] They are accessible by deprotonation of the corresponding thiols by HONnBu$_4$ or by treating the sodium thiolates with ClNnBu$_4$.

Upon adding methyl or n-butyl acrylates to the initiators at *room temperature* in the absence of catalysts, essentially quantitative formation of polyacrylates was observed! Equally surprising is the discovery that under proper conditions the molecular weight distribution is very narrow.[11] The best results are obtained in acetonitrile, nitrobenzene or mixtures of nitrobenzene and THF, whereas dimethyl sulfoxide (DMSO) should be avoided. Typically, the initiator **11a** induces the polymerization of n-butyl acrylate at room temperature in acetonitrile, D being 1.15 ($M_n(\text{calc.}) = 1.37$; $M_n(\text{obs.}) = 1.28$; $M_w = 1.47$).

Mechanistically, the ammonium thiolates undergo rapid Michael additions to form an ammonium enolate **12** which in turn sets the stage for further Michael additions. In the case of the functionalized initiator **11c** the polymer has a hydroxy group on one end following acidic work-up, the D value being 1.14. In spite of the above positive aspects, the method has several limitations. The initiators are generally not stable for long periods of time due to decomposition via dealkylation of the ammonium ion. Moreover, when aiming at molecular weights of >2000, the M_n(obs.) values are much too low. This can be attributed to a side reaction involving thiolate elimination at one end of the polymer chain, a chain terminating process that is induced by the basic nature of the chain end.[11] The eliminated thiolate then starts a new chain. Since the D values are also poor in such cases, the process is limited to the synthesis of low molecular weight polymers. It is nevertheless important to note that sodium and lithium n-butylthiolates in acetonitrile are inefficient initiators, leading to incomplete polymerization and broad molecular weight distributions ($D>3$).[11]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11a, R = nBu
11b, R = Ph
11c, R = $CH_2CH_2OSiMe_3$

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In order to eliminate the above drawbacks, we explored the possibility of employing metal-free carbon nucleophiles as initiators.[12] In particular, C-H-acidic compounds were deprotonated with $HONnBu_4$ or their sodium salts treated with $ClNnBu_4$ to form the resonance-stabilized compounds **15**-**17**. They are stable at 0°C for months and can be handled at room temperature without any decomposition.

$[RC(CO_2R')_2][NnBu_4]$

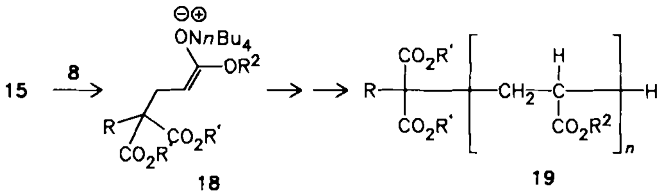
15a, $R = R' = C_2H_5$
15b, $R = C_2H_5$, $R' = CH_3$

$[CH_3C(CN)_2][NnBu_4]$
16

$[(CH_3)_2CNO_2][NnBu_4]$
17

Although a number of ammonium carbanions have been reported, they were generally not fully characterized.[13] In the present case the compounds were studied by NMR and IR spectroscopy.

Upon adding n-butyl acrylate to solutions of **15** at room temperature, a spontaneous exothermic reaction was observed with formation of polyacrylate (>95% conversion to **19** after aqueous workup). Thus, the doubly stabilized initiators **15** add in a Michael fashion to form less stabilized carbanions **18** which then continue chain growth until no more monomer is added. It is possible to add a different n-alkyl acrylate immediately following the consumption of monomer and to continue the polymerization with formation of a polymer having two well defined blocks.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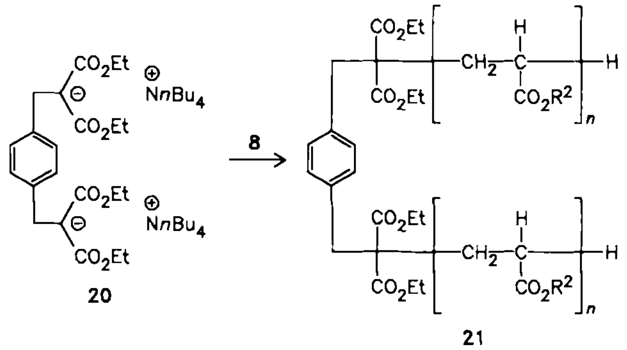
In contrast to the previous oligomerizations induced by thiolate anions, this new method allows the synthesis of polymers having molecular weights of >2000.[12] Moreover, the molecular weight distributions are surprisingly good (Table 1). For example, when aiming for a molecular weight of ca. 20000, M_n(calc.) and M_n(obs.) agree well, and the D value is 1.3 (entry 10 of Table 1). The other initiators also induce the polymerization of n-butyl acrylate, although the nitrostabilized initiator appears to be less efficient (entries 15 and 16 of Table 1).

Table 1. Polymerization of n-butyl acrylate **8b** at room temperature [a].

Entry	Initiator	Solvent	M_n(calc.) [kg mol^{-1}]	M_n(obs.) [kg mol^{-1}]	D
1	**15a**	THF	1.15	0.90	1.16
2	**15a**	THF	5.32	3.13	1.36
3	**15a**	THF	10.44	7.42	1.25
4	**15b**	THF	1.44	1.51	1.50
5	**15b**	Toluene	1.44	0.64	1.37
6	**15b**	THF	5.29	5.86	1.30
7	**15b**	Toluene	5.29	6.82	1.36
8	**15b**	Toluene	10.41	10.92	1.30
9	**15b**	THF	20.67	17.43	1.38
10	**15b**	Toluene	20.67	20.39	1.30
11	**16**	THF	1.36	0.61	1.14
12	**16**	Toluene	1.36	0.71	1.61
13	**16**	THF	5.21	2.59	1.43
14	**16**	Toluene	5.21	4.21	1.34
15	**17**	THF	1.37	0.85	2.71
16	**17**	Toluene	1.37	1.25	2.18

[a] During polymerization the temperature rises by 10-20°C.

In a similar manner, dianions such as **20** are effective initiators in the polymerization of n-butyl acrylate (e.g., M_n(calc.) = 1717; M_n(obs.) = 1624; $D = 1.1$).[12]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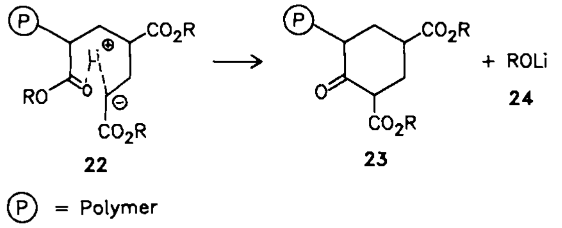
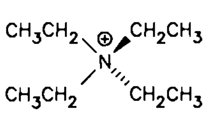
It is difficult at present to explain why the ammonium carbanions are such excellent initiators at room temperature. One of the major chain-terminating processes of the classical anionic polymerization of acrylates and methacrylates is the "back-biting" reaction.[4] This intramolecular Claisen condensation requires a metal ion such as Li$^{\oplus}$ or Na$^{\oplus}$ for the activation of the ester group and the ready expulsion of alkoxide ions (cf. 22 → 23 + 24). In the case of the present system, metal complexation is not possible. Even if the (reversible) addition step were to occur, it is likely that elimination of "naked" alkoxide is a kinetically and thermodynamically unfavorable process, certainly in comparison to chain propagation involving electrophilic monomers. Nevertheless, it remains to be tested how long the chain end survives following the complete consumption of monomer and prior to the addition of electrophiles (e.g., more monomer or H$_3$O$^{\oplus}$). It should be mentioned that the sodium salts of the above initiators are inefficient, leading to incomplete conversion and poor *D* values (> 3).[12]



22 **23**

Although detailed studies remain to be carried out, it is interesting to speculate about the mechanism. Strong electrostatic attractive forces between the anionic chain end and the ammonium counterions are likely to be involved.[11,12] Molecular orbital calculations on tetraalkylammonium ions show that the positive charge is *not* localized on the nitrogen atom as indicated by the traditional representation 25, but rather on the four α-carbon atoms, see 26.[10] This means that a tetraalkylammonium ion has a tetrahedral distribution of charge.



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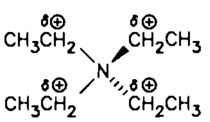

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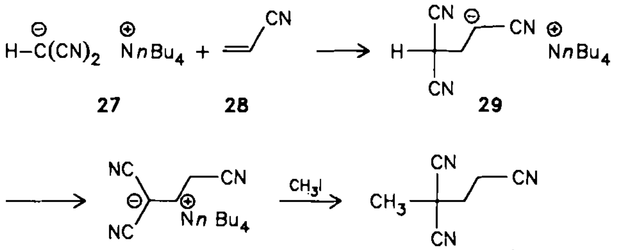
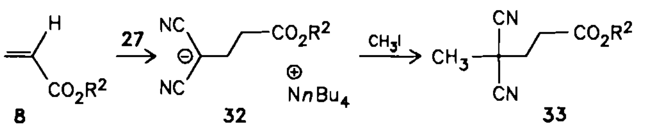
The monomer may well approach one corner of the tetrahedron; this process might be looked on as a kind of solvation. As the Michael addition then proceeds, the ester function turns into the new enolate chain end. Concomitantly, the previous enolate becomes an ester function along the chain, perhaps solvating intramolecularly until the next monomer approaches. In line with these speculations is the observation that bulky ammonium ions such as tetraoctylammonium are not well suited for metal-free polymerizations.[10] The reactions are often sluggish, leading to polymers with broad molecular weight distributions. The long groups pointing from the tetrahedral positions probably prevent a tight and ordered transition state.

Experiments directed toward the synthesis of ammonium malonates having protected functional groups are in progress.[10] A different strategy for the preparation of chelic polymers pertains to the reaction of the carbanion 27 bearing a hydrogen atom at the reactive center. We discovered that in 1 : 1 reactions with various Michael acceptors smooth exothermic additions occur. Following the complete consumption of the reaction components at room temperature, the crude product was quenched with methyl iodide. The products turned out to be 31 and 33, which means that proton transfer occurs (e.g. 29 → 30) prior to alkylation.[10] Thus, the initiator 30 can be prepared without undesired polymerization of the very reactive acrylonitrile! This chemistry also suggests that an easily hydrolyzable ester (e.g., 8, R^2 = *tert*-butyl) should react in the same manner, i.e., the *in situ* preparation of initiators of the type 32 (R^2 = *tert*-butyl) is probably an easy task. In experiments already performed, the nucleophilic *end* of the chain was *O*-silylated with Me$_3$SiCl.[10]



27 **28** **29** **30** **31** (90% isolated)



8 **32** **33**

(R^2 = *n*Bu; 71% isolated)

Finally, other α-activated olefins such as the extremely reactive acrylonitrile[10] as well as the less reactive methacrylates[12] can also be polymerized in a controlled manner. In the latter case the nitro-stabilized carbanion 17 is the best initiator, although an induction period of 30–60 s is generally observed.

4. Conclusions and Applications

Free radical initiation remains the method of choice for the production of high molecular weight homopolymeric acrylates and methacrylates. However, GTP with formation of living polymers results in a number of structural features generally not accessible by radical processes: narrow molecular weight distribution, controlled introduction of end groups, segmentation of chains in blocks, and accurate control of molecular weight in the range 1000 to

20000. GTP also produces polymers with linear backbones, in contrast to free radical polymerization in which branching may occur. One of the problems yet to be solved in GTP and metal-free polymerizations is the control of tacticity.[14]

As far as industrial applications are concerned, Dupont has invested great efforts towards developing such products as star polymers for use in toughening plastics and coatings, e.g., for the automobile industry. It remains to be seen whether the customer will pay a higher price for a more durable product. Other potential applications include thermoplastic elastomers, non-aqueous dispersions for the control of rheological properties,[7] and liquid crystalline polymers.[15] Chiral polymers made by GTP have also been reported.[16]

Although metal-free polymerization has only recently been developed, similar applications are in principle possible. The mechanism and theoretical basis also need to be explored. Finally, the question arises whether other types of anionic polymerizations (e.g., ring opening processes) can also be performed using metal-free initiators.

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[13] See e.g.: W. Schlenk, J. Holtz, *Chem. Ber. 49* (1916) 603; G. Wittig, M. Heintzeller, M. W. Wetterling, *Justus Liebigs Ann. Chem. 557* (1947) 201; E. B. Troughton, K. E. Molter, E. M. Arnett, *J. Am. Chem. Soc. 106* (1984) 6726.

[14] Poly(ethyl acrylate) of molecular weight 4000 (initiator: **15a**) is atactic, but solvent effects remain to be studied.[10] The thiolate induced polymerization of methyl acrylate (MW 1400) leads to an isotactic product as judged on the basis of ^{1}H-NMR studies.[11] GTP generally gives atactic polymers.

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Conference Report

Photovoltaic Solar Energy in Europe

More than 750 materials scientists, physicists, engineers, marketing specialists, and government officials from 45 countries met from 9-13 May 1988 at the "8th European Photovoltaic Solar Energy Conference and Exhibition" in Florence, the largest European Conference ever held on this topic. Photovoltaic (PV) energy has now reached maturity. Crystalline and polycrystalline silicon modules have proven to be the most reliable decentralized source of energy. Their still rather high cost limits their applications at present to the electrification of isolated sites, which are however abundant. Performance and reliability of stand-alone PV systems in the 10 W to 60 kW range have been evaluated during the past ten years by the US Army, several American and European agencies, and by Third World organizations.

Whereas the reliability of crystalline and polycrystalline silicon modules complies with military standards, many peripherical components such as inverters and battery regulators still have reliability problems. For most household applications, low voltage direct current is therefore preferable to 220 V alternating current, in spite of the high price and poor choice of dc household appliances. The storage of electrical energy has turned out to be a crucial problem for photovoltaics. According to *E. Voss* (Varta, Kelkheim), the lead-acid battery is at present the only viable system for power applications. Possible alternative storage systems for the future are Zn-Br and Cr-Fe batteries, whereas Ni-Cd batteries will not be cost-competitive.

Progress in photovoltaics is intimately linked with the development of new materials and processing technologies. Amorphous hydrogenated silicon, discovered as an electronic material by *Spear* and *Lecomber* (University of Dundee) in 1975, is today a $ 200 million per year business in non-PV applications, and has become one of the leading thin film solar cell materials.

Progress that has recently been made in the production of silicon cells is mainly due to the minimization of optical and recombination losses. Crystalline cells with recombination-free interfaces have been developed by *M. A. Green* in Kensington, Australia (passivated emitter and laser-