SYNTHETIC AND MECHANISTIC ASPECTS OF ANIONIC POLYMERIZATION OF (METH)ACRYLATES INITIATED BY METAL-FREE SALTS OF CH-ACIDIC COMPOUNDS

MANFRED T. REETZ,* STEPHAN HÜTTE AND RICHARD GODDARD

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim/Ruhr, Germany

The tetrabutylammonium salts of CH-acidic compounds (malonic acid diesters and diamides, nitropropane, phenylacetic and phenylpropionic acid esters and 9-ethylfluorene) serve as inexpensive initiators for the anionic polymerization of acrylates and methacrylates at room temperature. Molecular weights of 1500–25,000 can be reached, the molecular weight distributions being fairly narrow ($D = 1 \cdot 1$–$1 \cdot 4$ in optimized cases). Side-reactions as monitored by GC analyses include backbiting and Hofmann elimination, which means that the process is not a true living polymerization. The x-ray structural analyses of the tetrabutylammonium salts of phenylacetic and 2-phenylpropionic and 2-phenylbutyric acid esters show that anions and cations interact with one another via hydrogen bonding. Therefore, the initiators cannot be considered to be naked anions, a conclusion which very likely also applies to the growing polymer chain end during polymerization.

INTRODUCTION

(Meth)acrylic acid esters are an industrially important class of monomers because the corresponding polymers have a wide range of applications.[1] Traditionally, radical polymerizations have been used. However, control of molecular weight and molecular weight distribution is difficult, and there is no ready way to introduce specific end groups.[1] Conceptually, anionic polymerization is much better suited for solving such problems,[2] but here other difficulties arise. Side-reactions such as monomer termination, intermolecular polymer termination and intramolecular polymer termination (backbiting) occur during polymerization. For decades alkyllithium reagents in THF were used as initiators, reaction temperatures of −50 to −78 °C being necessary.[2] A breakthrough was achieved in 1983, when Webster and co-workers at Du Pont introduced the so-called group transfer polymerization (GTP).[3] Using O-silyl ketene ketals as initiators and anionic catalysts, they were able to polymerize methacrylic acid esters at room temperature, obtaining living polymers with controlled molecular weight (1500–30,000) and narrow molecular weight distributions ($D = 1 \cdot 1$–$1 \cdot 3$).[3]

More recently, several other initiating systems for the controlled polymerization of methacrylic esters have been reported. Most of them still require low temperatures

and/or expensive organometallic initiators. To this day, none of these processes have been adopted by industry. A promising method utilizes bulky alkyllithium reagents in the presence of excess LiX as initiators at 0 °C.[4] Other novel developments include initiator systems based on aluminium porphyrins[5] and organolanthanide complexes.[6]
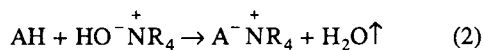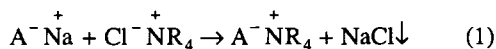
Our interest in group transfer polymerization[7] led us to a different approach, namely metal-free anionic polymerization.[8] Accordingly, tetraalkylammonium salts of CH-acidic organic compounds such as malonates or nitriles are used as anionic initiators in the absence of catalysts.[9] In typical experiments, acrylic acid esters are quantitatively polymerized at room temperature with the formation of polymers having fairly narrow molecular weight distributions ($D \approx 1 \cdot 3$), the typical molecular weight range being 1500–10,000, depending on the amount of initiator used. In spite of these useful features, it was observed that the calculated and experimental molecular weights are not always identical, which means that the process is not a true living polymerization.[10] Nevertheless, owing to the low cost of initiators and the ease of polymerization (room temperature), metal-free anionic initiators have attracted attention.[11–13]

In this paper, we describe new metal-free initiators derived from CH-acidic compounds with different reactivities in the polymerization of n-butyl acrylate (BA) and methyl methacrylate (MMA). Side reactions occurring during the polymerization process are

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* Author for correspondence.

examined, leading to the first mechanistic study of metal-free polymerization. Included is information about the structure of certain tetrabutylammonium ester enolates in the crystal and liquid state. These initiators can be regarded as models for the growing chain ends during the actual polymerization of (meth)acrylic acid esters.

We originally used two different methods for the synthesis of the anionic initiators $A^-N^+R_4$, namely salt exchange [equation (1)] and deprotonation [equation (2)].[9] Since the samples prepared by the former method often contain small amounts of the sodium salt, which may effect polymerization and influence reproducibility,[10] the second route is the method of choice. We have improved the original version by employing toluene to remove the water azeotropically at room temperature.[10,14] If higher temperatures are chosen, as described by a different group,[12] partial hydrolysis of ester moieties occurs, leading to oily impure initiators.[10]

$$A^-\overset{+}{Na} + Cl^-\overset{+}{NR_4} \rightarrow A^-\overset{+}{NR_4} + NaCl\downarrow \quad (1)$$

$$AH + HO^-\overset{+}{NR_4} \rightarrow A^-\overset{+}{NR_4} + H_2O\uparrow \quad (2)$$

EXPERIMENTAL

Materials. Dimethyl sulphoxide (DMSO), *n*-butyl acrylate (BA) and methyl methacrylate (MMA) were purified by distillation over calcium dihydride under high vacuum just before use. THF and toluene were refluxed over sodium tetraethylaluminium and DME and 1,4-dioxane over potassium benzophenone ketyl and distilled under inert gas conditions (argon).

Initiators. The general synthesis of metal-free initiators based on deprotonation of CH-acidic compounds by $HO^-N^+Bu_4$ has been already described.[14] All initiators, except when specifically noted, were prepared according to that procedure.

Tetrabutylammonium diethyl-2-ethylmalonate (1) and tetrabutylammonium diisopropyl-2-ethylmalonate (2) have been described and characterized previously.[14]

Tetrabutylammonium di-*tert*-butyl-2-ethylmalonate (3): colourless salt; crystallized from toluene; yield 68%. ^{1}H NMR (200 MHz; DMSO-d_6): δ (ppm) 0·80 (t; $^3J = 7·2$ Hz; 3 H; ^-C-CH$_2$-CH_3), 0·95 (t; $^3J = 7·0$ Hz; 12 H; CH$_3$-cation), 1·28–1·40 [m and s; 26 H; C(CH$_3$)$_3$ and N-CH$_2$-CH$_2$-CH_2], 1·59 (m; 8 H; N-CH$_2$-CH_2), 2·02 (q; $^3J = 7·1$ Hz; 4 H; O-CH$_2$), 3·19 (m; 8 H; N-CH$_2$). ^{13}C NMR (50 MHz; DMSO-d_6): δ (ppm) 13·3 (CH$_3$-cation), 16·5 (^-C-CH$_2$-CH$_2$), 19·0 (N-CH$_2$-CH$_2$-CH$_2$), 20·8 (^-C-CH$_2$), 22·9 (N-CH$_2$-CH$_2$), 29·2 [C(CH$_3$)$_3$], 57·3 (N-CH$_2$), 72·0 (O-C), 75·7 (O-C), 168·9 (C-carbonyl).

Tetrabutylammonium *N,N,N',N'*-tetraethylmalonic acid amide (4): colourless salt; yield 42%. IR (Nujol):

1600 cm^{-1}. ^{1}H NMR (200 MHz; DMSO-d_6): δ (ppm) 0·88–1·10 (m; 24 H; N-CH$_2$-CH_3; CH$_3$-cation), 1·30 (m; 8 H; N-CH$_2$-CH$_2$-CH_2), 1·56 (m; 8 H; N-CH$_2$-CH_2), 3·03–3·35 (m; 17 H; N-CH$_2$; $^-$CH; N-CH_2-CH$_3$). ^{13}C NMR (50 MHz; DMSO-d_6): δ (ppm) 13·4 (CH$_3$-cation), 14·4 (CH$_3$-anion), 19·1 (N-CH$_2$-CH$_2$-CH$_2$), 23·1 (N-CH$_2$-CH$_2$), 39·9 (N-CH$_2$-anion), 53·2 (C^-), 57·4 (N-CH$_2$-cation), 168·0 (C-carbonyl).

Tetrabutylammonium diethyl-2-*tert*-butylmalonate (5): colourless needles; crystallized from toluene; yield 20%. IR (Nujol): 1620 and 1548 cm^{-1}. ^{1}H NMR (200 MHz; DMSO-d_6): δ (ppm) 0·92 (t; $^3J = 7·4$ Hz; 12 H; CH$_3$-cation), 0·98, 1·11 and 1·15 [3 s; 9 H; C-(CH$_3$)$_3$], 1·03 and 1·04 (2 t; $^3J = 7·2$ Hz; 6 H; O-CH$_2$-CH_3), 1·30 (m; 8 H; N-CH$_2$-CH$_2$-CH_2), 1·56 (m; 8 H; N-CH$_2$-CH_2), 3·16 (m; 8 H; N-CH$_2$), 3·42, 3·68 (2 q; $^3J = 7·1$ Hz), 3·78–4·08 (m; 4 H; O-CH$_2$).

Tetraoctylammonium diethyl-2-ethylmalonate (6): tetraoctylammonium bromide was dissolved in ethanol and poured on to a strong alkaline ion exchanger. The resulting tetraoctylammonium hydroxide in ethanol was reacted with 2-ethylmalonic acid diethyl ester: pale yellow viscous oil; yield 74%. IR (Nujol): 1675 cm^{-1}. ^{1}H NMR (200 MHz; DMSO-d_6): δ (ppm) 0·78, 0·86 (2 t; 15 H; ^-C-CH$_2$-CH_3; CH$_3$-cation), 1·03 (t; $^3J = 7·1$ Hz; 6 H; O-CH$_2$-CH_3), 1·27 (m; 40 H; CH$_2$-alkyl chain: C$_3$–C$_7$), 1·56 (m; 8 H; N-CH$_2$-CH_2), 2·07 (q; $^3J = 7·1$ Hz; 2 H; ^-C-CH$_2$), 3·17 (m; 8 H; N-CH$_2$), 3·74 (q; $^3J = 7·1$ Hz; 4 H; O-CH$_2$). ^{13}C NMR (50 MHz; DMSO-d_6): δ (ppm) 13·8 (CH$_3$-cation), 15·4 (O-CH$_2$-CH$_3$), 16·4 (^-C-CH$_2$-CH$_3$), 20·8 (^-C-CH$_2$), 20·9, 25·6, 28·2, 31·0 (cation), 54·7 (O-CH$_2$), 57·5 (N-CH$_2$), 72·7 ($^-$C). The carbonyl signal could not be detected.

Tetrabutylammonium 2-nitropropanate (7): colourless prisms; crystallized from toluene; yield 57%. IR (Nujol): 1568 cm^{-1}. ^{1}H NMR (200 MHz; toluene-d_8): δ (ppm) 1·03 (t; $^3J = 6·7$ Hz; 12 H; CH$_3$), 1·45 (m; 8 H; N-CH$_2$-CH$_2$-CH_2), 1·63 (m; 8 H; N-CH$_2$-CH_2), 2·26 (s; 6 H; C-CH$_3$), 3·57 (m; 8 H; N-CH$_2$). ^{13}C NMR (50 MHz; toluene-d_8): δ (ppm) 14·2 (CH$_3$-cation), 20·1 (CH$_3$-anion), 20·4 (N-CH$_2$-CH$_2$-CH$_2$), 24·4 (N-CH$_2$-CH$_2$), 58·1 (N-CH$_2$), 103·6 ($^-$C).

Tetrabutylammonium 9-ethylfluorenyl (8): red needles; crystallized from DMF; yield 48%. ^{1}H NMR (200 MHz; DMSO-d_6): δ (ppm) 0·92 (t; $^3J = 7·0$ Hz; 12 H; CH$_3$-cation), 1·21 (t; $^3J = 7·4$ Hz; 3 H; CH$_3$-anion), 1·24 (sextet; $^3J = 7·0$ Hz; 8 H; N-CH$_2$-CH$_2$-CH_2), 1·49 (m; 8 H; N-CH$_2$-CH_2), 3·00 (q; $^3J = 7·4$ Hz; 2 H; ^-C-CH$_2$), 3·06 (m; 8 H; N-CH_2), 6·34 (3 t; $^3J = 7·1$ Hz; 2 H; C-H3; C-H8), 6·79 (3 t; $^3J = 7·3$ Hz; 2 H; C-H4; C-H7), 7·23 (3 d; $^3J = 7·9$ Hz; 2 H; C-H2; C-H9), 7·83 (3 d; $^3J = 7·8$ Hz; 2 H; C-H5; C-H6). ^{13}C NMR (50 MHz; DMSO-d_6): δ (ppm) 13·4 (CH$_3$), 16·5 (CH$_3$-anion), 18·9 (CH$_2$-anion), 19·2 (N-CH$_2$-CH$_2$-CH$_2$), 23·0 (N-CH$_2$-CH$_2$), 57·8 (N-CH$_2$), 95·7 (C^-), 106·7, 113·1, 118·3, 118·4, 120·5, 133·5 (aryl).

Potassium 9-ethylfluorenyl (9): 9-ethylfluorene was added dropwise to 1·1 equiv. of potassium hydride in THF. When hydrogen evolution ceased, the mixture was filtered and the solvent evaporated; yield 88% of a red salt. ^{1}H NMR (200 MHz; DMSO-d_6): δ (ppm) 1·30 (t; $^3J = 7·4$ Hz; 3 H; CH$_3$), 3·10 (q; $^3J = 7·4$ Hz; 2 H; CH$_2$), 6·44 (3 t; $^3J = 7·1$ Hz; 2 H; C-H3; C-H4), 6·89 (3 t; $^3J = 7·3$ Hz; 2 H; C-H4; C-H7), 7·33 (3 d; $^3J = 8·0$ Hz; 2 H; C-H2; C-H9), 7·93 (3 d; $^3J = 7·5$ Hz; 2 H; C-H5; C-H6). ^{13}C NMR (50 MHz; DMSO-d_6): δ (ppm) 16·5 (CH$_3$), 18·9 (CH$_2$), 95·5 (C$^-$), 106·8, 113·2, 118·3, 118·5, 120·5, 133·6 (aryl).

Lithium 9-ethylfluorenyl (10): n-Butyllithium (1·6 M in hexane) was added dropwise to 9-ethylfluorene in THF at −78 °C. The flask was allowed to warm to room temperature within 1 h and the solvent was evaporated; yield 41% of a red salt after crystallization from toluene. ^{1}H NMR (200 MHz; DMSO-d_6): δ (ppm) 1·21 (t; $^3J = 7·4$ Hz; 3 H; CH$_3$), 3·01 (q; $^3J = 7·4$ Hz; 2 H; CH$_2$), 6·35 (t; $^3J = 7·7$ Hz; 2 H; C-H3; C-H4), 6·80 (2 t; $^3J = 6·9$ Hz; 2 H; C-H4; C-H7), 7·24 (d; $^3J = 8·1$ Hz; 2 H; C-H2; C-H9), 7·85 (d; $^3J = 7·4$ Hz; 2 H; C-H5; C-H6). ^{13}C NMR (50 MHz; DMSO-d_6): δ (ppm) 16·7 (CH$_3$), 19·1 (CH$_2$), 95·4 (C$^-$), 106·7, 113·1, 118·2, 118·4, 120·4, 133·6 (aryl).

Tetrabutylammoniumphenylacetic acid ethyl ester enolate (11): yield 86% of pale-red prisms after crystallization from toluene. IR (Nujol): 1562, 1608 cm^{-1}. ^{1}H NMR (200 MHz; DMSO-d_6): δ (ppm) 0·92 (t; $^3J = 7·2$ Hz; 12 H; CH$_3$-cation), 1·01 (t; $^3J = 7·2$ Hz; 3 H; CH$_3$-anion), 1·30 (sextet; $^3J = 7·2$ Hz; 8 H; N-CH$_2$-CH$_2$-CH$_2$), 1·55 (m; 8 H; N-CH$_2$-CH$_2$), 3·14 (m; 8 H; N-CH$_2$), 3·70 (q; $^3J = 6·6$ Hz; 2 H; O-CH$_2$), 6·08 (t; $^3J = 6·6$ Hz; 1 H; CH-p), 6·68 (t; $^3J = 7·2$ Hz; 2 H; CH-m), 7·09 (m; 2 H; CH-o). ^{13}C NMR (50 MHz; DMSO-d_6): δ (ppm) 13·4 (CH$_3$-cation), 15·9 (CH$_3$-anion), 19·1 (N-CH$_2$-CH$_2$-CH$_2$), 23·0 (N-CH$_2$-CH$_2$), 54·2 (O-CH$_2$), 57·4 (N-CH$_2$), 112·1 (C-p), 119·4 (C-m), 126·9 (C-o), 147·5 (C-i), 164·8 (carbonyl). The ^{13}C NMR signal of the C-carbanion is broad and can be seen as a sharp signal in THF.

Crystal data for 11: C$_{26}$H$_{47}$NO$_2$, formula weight (FW) = 405·7, pale-red prisms, monoclinic, $P2_1/n$ (No. 14), $a = 10·767(2)$, $b = 17·291(3)$ and $c = 14·054(2)$ Å, $\beta = 101·95(1)°$, $V = 2559·8$ Å^3, $T = 100$ K, $Z = 4$, $d_{calcd} = 1·05$ g cm^{-3}, μ(MoKα) = 0·60 cm^{-1}, Enraf–Nonius CAD4 diffractometer, graphite monochromated MoKα radiation $\lambda = 0·71069$ Å, 6277 data collected ([sin Θ/λ]$_{max}$ 0·65 Å^{-1}, [±h, +k, +l]), 5836 independent ($R_{av} = 0·01$), 4340 observed [$I \geq 2\sigma(I)$], 450 parameters, final $R = 0·052$, $R_w = 0·058$ [$w = 1/\sigma^2(F_o)$], largest residual density = 0·36 e Å^{-3}. Atomic coordinates, bond lengths and angles and thermal parameters for 11, 12 and 13 have been deposited at the Cambridge Crystallographic Data Centre.

Tetrabutylammonium phenyl propionic acid ethylester-enolate (12): yield 37% of pale-yellow plates

after crystallization from toluene. IR (Nujol): 1548, 1497 cm^{-1}. ^{1}H NMR (200 MHz; DMSO-d_6): δ (ppm) 0·92 (t; $^3J = 7·1$ Hz; 12 H; CH$_3$-cation), 1·08 (t; $^3J = 7·0$ Hz; 3 H; CH$_2$-CH$_3$), 1·30 (sextet; $^3J = 7·3$ Hz; 8 H; N-CH$_2$-CH$_2$-CH$_2$), 1·53 (m; 8 H; N-CH$_2$-CH$_2$), 1·74 (s; C-CH$_3$), 3·13 (m; 8 H; N-CH$_2$), 3·79 (q; $^3J = 7·0$ Hz; 2 H; O-CH$_2$), 6·17 (t; $^3J = 7·0$ Hz; 1 H; CH-p), 6·80 (t; $^3J = 7·0$ Hz; 2 H; CH-m), 7·10–7·51 (m; 2 H; CH-o). ^{13}C NMR (50 MHz; DMSO-d_6): δ (ppm) 13·4 (CH$_3$-cation), 14·7 (CH$_2$-CH$_3$), 16·1 (C-CH$_3$), 19·1 (N-CH$_2$-CH$_2$-CH$_2$), 23·0 (N-CH$_2$-CH$_2$), 54·5 (O-CH$_2$), 57·5 (N-CH$_2$), 66·8 (C$^-$), 111·8 (C-p), 119·3 (C-m), 126·5 (C-o), 147·9 (C-i), 163·2 (carbonyl).

Crystal data for 12: C$_{27}$H$_{49}$NO$_2$, FW = 419·7, pale-yellow plates, monoclinic, $P2_1/c$ (No. 14), $a = 9·358(1)$, $b = 17·751(2)$ and $c = 15·878(1)$ Å, $\beta = 92·16(1)°$, $V = 2635·6$ Å^3, $T = 100$ K, $Z = 4$, $d_{calcd} = 1·06$ g cm^{-3}, μ(MoKα) = 0·60 cm^{-1}, Enraf–Nonius CAD4 diffractometer, graphite monochromated MoKα radiation $\lambda = 0·71069$ Å, 6433 data collected ([sin Θ/λ]$_{max}$ = 0·65 Å^{-1}, [±h, +k, +l]), 6010 independent ($R_{av} = 0·01$), 4316 observed [$I \geq 2\sigma(I)$], 467 parameters, final $R = 0·048$, $R_w = 0·048$ [$w = 1/\sigma^2(F_o)$], largest residual density = 0·23 e Å^{-3}.

Tetrabutylammoniumphenylbutanic acid ethyl ester enolate (13): yield 32% of pale-yellow plates after crystallization from toluene. IR (Nujol): 1549, 1600 cm^{-1}. ^{1}H NMR (200 MHz; DMSO-d_6): δ (ppm) 0·84 (t; $^3J = 7·1$ Hz; 3 H; C-CH$_2$-CH$_3$), 0·92 (t; $^3J = 7·0$ Hz; 12 H; CH$_3$-cation), 1·04 (t; $^3J = 7·0$ Hz; 3 H; O-CH$_2$-CH$_3$), 1·29 (sextet; $^3J = 7·2$ Hz; 8 H; N-CH$_2$-CH$_2$-CH$_2$), 1·55 (m; 8 H; N-CH$_2$-CH$_2$), 2·29 (q; $^3J = 7·1$ Hz; 2 H; C-CH$_2$), 3·14 (m; 8 H; N-CH$_2$), 3·77 (q; $^3J = 7·0$ Hz; 2 H; O-CH$_2$), 6·01 (t; $^3J = 7·4$ Hz; 1 H; CH-p), 6·75 (t; $^3J = 7·8$ Hz; 2 H; CH-m), 7·00–7·50 (m; 2 H; CH-o). ^{13}C NMR (50 MHz; DMSO-d_6): δ (ppm) 13·4 (CH$_3$-cation), 14·7 (O-CH$_2$-CH$_3$), 16·1 (C-CH$_2$-CH$_3$), 19·2 (N-CH$_2$-CH$_2$-CH$_2$), 20·7 (C-CH$_2$), 23·0 (N-CH$_2$-CH$_2$), 54·3 (O-CH$_2$), 57·4 (N-CH$_2$), 75·7 (C$^-$), 111·5 (C-p), 119·2 (C-m), 126·6 (C-o), 147·0 (C-i), 163·1 (carbonyl).

Crystal data for 13: C$_{28}$H$_{51}$NO$_2$, FW = 433·7, pale-yellow plates, monoclinic, $P2_1/c$ (No. 14), $a = 9·233(3)$, $b = 18·018(5)$ and $c = 16·278(3)$ Å, $\beta = 95·82(1)°$, $V = 2694·2$ Å^3, $T = 100$ K, $Z = 4$, $d_{calcd} = 1·07$ g cm^{-3}, μ(MoKα) = 0·61 cm^{-1}, Enraf–Nonius CAD4 diffractometer, graphite monochromated MoKα radiation $\lambda = 0·71069$ Å, 13,255 data collected ([sin Θ/λ]$_{max}$ 0·65 Å^{-1}, [±h, ±k, +l]), 6162 independent ($R_{av} = 0·06$), 4221 observed [$I \geq 2\sigma(I)$], 463 parameters, final $R = 0·059$, $R_w = 0·070$ [$w = 1/\sigma^2(F_o)$], 7, the alkyl group attached to O2 is disordered (50 : 50), largest residual density = 0·60 e Å^{-3}.

Tetrabutylammonium-4-vinyl(phenyl)acetic acid methyl ester enolate (15): yield 67% of light-yellow

crystals after crystallization from toluene. ^{1}H NMR (200 MHz; DMSO-d_6): δ (ppm) 0·92 (t; $^3J = 7·0$ Hz; 12 H; CH$_3$-cation), 1·29 (sextet; $^3J = 7·2$ Hz; 8 H; N-CH$_2$-CH$_2$-CH_2), 1·54 (m; 8 H; N-CH$_2$-CH_2), 2·30 (s; 1 H; $^-$CH), 3·13 (m; 8 H; N-CH$_2$), 3·24 (s; 3 H; O-CH$_2$), 4·62; 5·20; 6·34 (ABM system; $J_{AB} = 1·5$ Hz; $J_{AM} = 10·8$ Hz; $J_{MB} = 17·5$ Hz; 3 H; CH$_2$=CH), 6·74–7·29 (m; 4 H; C$_6$H$_4$). ^{13}C NMR (50 MHz; DMSO-d_6): δ (ppm) 13·4 (CH$_3$-cation), 19·1 (N-CH$_2$-CH$_2$-CH$_2$), 23·0 (N-CH$_2$-CH$_2$), 47·3 (O-CH$_3$), 57·5 (N-CH$_2$), 103·1 (CH$_2$=CH), 121·3, 125·5, 128·8, 137·9, 147·8, (C$_6$H$_4$; CH$_2$=CH), 165·5 (carbonyl), the carbanion C-atom is rather broad.

Polymerizations. The initiator was placed in a flame-dried flask under an argon atmosphere and dissolved in a carefully dried solvent at room temperature. Monomer was dissolved in the same weight of solvent by weight and added dropwise via a syringe pump (1 ml min^{-1}) into the stirred solution of initiator. The polymerization was quenched 1 h after the monomer addition by injection of 1 ml of 1 M HCl. Poly(n-butyl acrylates) were diluted with diethyl ether and washed with water in a separating funnel. The organic layers were dried over MgSO$_4$, filtered and the solvents were evaporated under vacuum. Poly(methyl methacrylates) were slowly poured into water–methanol (4:1). The immediately precipitated polymers were filtered and dried under vacuum in a drying oven at 45 °C.

Measurements. Gel permeation chromatographic (GPC) measurements were performed at 20 °C using THF as eluent with a flow rate of 1·0 ml min^{-1} with a differential refractor detector and a variable-wavelength UV detector. The molecular weight calibration curve was obtained by using standards of BA and MMA.

^{1}H and ^{13}C NMR measurements were performed in DMSO-d_6 using a Bruker AM-200 spectrometer, where the chemical shifts were determined with respect to the solvent as internal standard.

Cryoscopic measurements were performed by Dornis & Kolbe (Mülheim/Ruhr, Germany) in benzene using a Beckmann thermometer.

Quantitative GC measurements were done on quenched polymer solutions. Internal standards were pentane for methanol, butanol and MMA, heptane for 2-nitropropane and undecane for n-butanol, diethyl 2-ethylmalonate and tributylamine.

IR spectra were recorded on a Nicolet FT 7000 spectrophotometer.

RESULTS AND DISCUSSION

BA and MMA have been polymerized at room temperature with initiators **1–7**. All reactions turned out to be exothermic, the temperature rising by 5–10 °C. Table 1

Table 1. Polymerization of BA at room temperature in THF

Initiator	M_n(calcd)	M_n(obsd)	D	Yield (%)
1	2970	2670	1·17	96
1	4100	3140	1·29	83
1	6260	3910	1·48	97
1	12860	7800	1·48	87
1[a]	2820	2530	2·05	96
1[b]	3100	2080	1·19	95
1[c]	2740	1770	1·14	91
1[d]	3280	2440	1·50	94
1[e]	3300	1830	1·12	92
1[f]	3090	3200	2·04	98
3	2730	1560	1·15	94
5	3110	2250	1·17	94
5	6350	3370	1·21	66
6	2660	2230	1·17	98
6	12700	4780	1·73	80
7	4110	1360	1·13	63
7	5800	2030	1·25	66
7[f]	3180	2570	3·64	93

[a] The monomer solution is added at once.
[b] Polymerization in DME.
[c] 1,4-Dioxane.
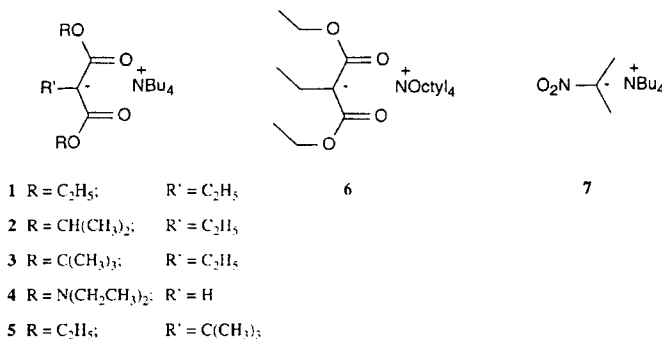[d] Toluene.
[e] DMSO.
[f] The polymerization temperature is 0 °C.

summarizes the results of the polymerization of BA with these metal-free initiators.

Polymerization of BA with initiator **1** always resulted in quantitative monomer conversion. The best results were obtained when poly(n-butyl acrylates) with M_n(calcd) of about 3000 were strived for. Here the molecular weight distribution D ranges between 1·14 and 1·30, and M_n(obsd) essentially corresponds to the theoretical value. It is important to add the monomer solution slowly since otherwise the polydispersity D rises, probably owing to the occurrence of more side reactions. The same behaviour was observed when the polymerization was performed at 0 °C. THF is the best solvent for this type of polymerization, followed by other polar solvents such as DME, 1,4-dioxane or DMSO, but in toluene the molecular weight distribution turns out to be rather broad.[10] When polymers of M_n larger than 5000 are desired, M_n(obsd) diverges from M_n(calcd), the former being smaller than the latter. No effect on this tendency was observed on changing the substituent on the carbon of the carbanion (Table 1). The same applies to changing the ammonium cation or using the nitro-stabilized carbanion **7**. Thus, initiators **5**, **6** and **7** are all similar in this respect. The factors responsible for side reactions are discussed below. Since initiator **3** polymerizes BA well and also contains two protected functional groups, a new tool for the synthesis of polymers with a defined difunctional end group is at hand: hydrolysis of the acid sensitive *tert*-butyl ester functions affords a

1 R = C$_2$H$_5$;   R' = C$_2$H$_5$

2 R = CH(CH$_3$)$_2$;   R' = C$_2$H$_5$

3 R = C(CH$_3$)$_3$;   R' = C$_2$H$_5$

4 R = N(CH$_2$CH$_3$)$_2$; R' = H

5 R = C$_2$H$_5$;   R' = C(CH$_3$)$_3$

macromonomer (dicarboxylic acid) which may be useful in further transformations.

Table 2 summarizes the results of the polymerization of the metal-free initiators with MMA at room temperature.

In contrast to the polymerization of BA, an induction period is generally observed. The increase in the reaction temperature starts suddenly and is about 10–15 °C. Initiators 1, 2, 5, 6 and 7 lead to polymers with M_n(obsd) much higher than M_n(calcd), even when the temperature of the polymerization rises to 50 °C, which in fact should increase the reactivity of the initiator. This observation lets us conclude that these initiators are not reactive or nucleophilic enough to start smooth polymerizations of MMA. Indeed, MMA is known to be much less reactive than BA in classical anionic polymerizations. The above behaviour has been observed in other polymerization systems previously and is known as 'slow initiation.'[15] Polydispersities as high as 1·50–2·88 are due to slow initiation, probably in

addition to side-reactions. Initiator 5 shows incomplete conversion. The reason for this may be the bulkiness of the α-substituent which hinders the 1,4-Michael addition. Nevertheless, we succeeded in the polymerization of MMA at room temperature with the bis-amide initiator 4, the most reactive in this series.[10] In this initiator the negative charge is not stabilized as well owing to the electron-donating amino groups in the amide function (higher pK_a value of the neutral precursor). Indeed, polymerizations with short induction periods led to poly(methyl methacrylates) with the desired M_n up to M_n(calcd) of 6000 with fairly narrow molecular weight distributions and complete conversion of monomer. Thus, the search for new and better metal-free initiators is a rewarding task.

The polymerization of (meth)acrylic acid esters at room temperature with metal-free initiators is accompanied by side and termination reactions.[10] In the classical anionic polymerization of (meth)acrylic acid esters they are known as monomer termination, intermolecular
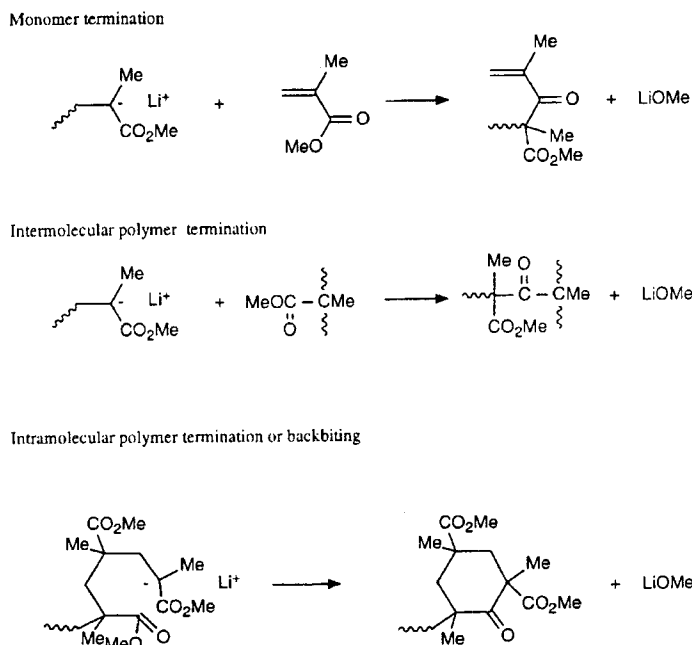
Table 2. Polymerization of MMA at room temperature in THF

Initiator	Induction period (s)	M_n(calcd)	M_n(obsd)	D	Yield (%)
1	150	3160	31750	2·50	92
1	210	11600	55200	1·80	85
2	210	2860	14500	2·88	86
2[a]	150	2880	7310	1·56	71
4	20	3360	3060	1·23	99
4	40	6930	5790	1·30	100
4	30	22140	14830	1·40	100
5[b]	–	3250	15930	1·56	23
5[b]	–	12050	16880	1·83	20
6	120	2960	25400	2·21	98
6[c]	15	3110	56310	1·50	100
6	270	9350	49050	1·55	78
7[c]	0	2870	15700	2·09	95
7	40	3000	11520	1·40	100
7	70	25000	27400	1·26	100

[a] The polymerization temperature is 50 °C.
[b] Very sluggish polymerization; induction period uncertain.
[c] The monomer solution is added at once.

Monomer termination

Intermolecular polymer termination

Intramolecular polymer termination or backbiting

Scheme 1. Possible side reactions during the polymerization of MMA initiated by organolithium reagents

polymer termination and intramolecular polymer termination (backbiting), as summarized in Scheme 1.[2]

The backbiting reaction, which is an intramolecular Claisen condensation, is believed to be dominant in classical anionic polymerization.[2] In all of these reactions alkoxide is released. Lithium, sodium and potassium alkoxides are not able to initiate further polymerization. In contrast, cesium methanolate formed during the polymerization of MMA is able to initiate a new chain growth with low initiation rate.[2] It is also important to point out that most Li enolates decompose at temperatures above −30 °C, forming ketenes and Li alkoxides.[16] This may also happen at the growing end of the polymer chain during polymerization.[10]

We examined our metal-free initiating system with respect to the occurrence of these side-reactions. Accordingly, quenched polymer solutions were analysed by qualitative and quantitative GC. Table 3 summarizes the results.

GC studies of the BA polymerization reaction mixtures show complete conversion of the initiator. In contrast, in the case of MMA polymerization a portion of the initiator is not consumed. Using initiator 1 this amount is rather low, but it must be emphasized that initiators containing ester groups are partially hydrolysed during quenching. Incomplete consumption of initiators indicates 'slow initiation.'

All polymer solutions show the presence of some n-butanol or methanol, originating from the ester moiety

of the monomer (BA or MMA, respectively). Bandermann has reached similar conclusions.[17] These observations clearly show the occurrence of side reactions of the type shown in Scheme 1. One expects more alcohol to be formed in the reaction of BA, since polymerization of this monomer is known to be more susceptible to 'backbiting' than that of MMA.[2] Indeed, this is observed in the present metal-free polymerizations. The formation of tributylamine is observed in all cases, an indication that Hofmann elimination occurs. In line with this is the observation that varying amounts of but-1-ene are detected in all cases. Owing to the volatility of this side-product, quantification was not attempted. It should be emphasized that there is some uncertainty in the interpretation of side-products detected by GC in that it is difficult to define the exact point at which these compounds are actually formed, i.e. during the actual process of polymerization or shortly thereafter and prior to quenching. It is also uncertain whether tetrabutylammonium butanolate or methanolate, which are formed in situ, initiate polymerization themselves. Such compounds cannot be isolated because they rapidly decompose via Hofmann elimination.[10] In spite of these difficulties in interpretation, backbiting and Hofmann eliminations clearly accompany metal-free anionic polymerization of acrylates and methacrylates.

In order to obtain some information about the rate of the initiation reaction in the polymerization of MMA

Table 3. GC measurements of crude solutions of poly(n-butyl acrylate) and poly(methyl methacrylate)

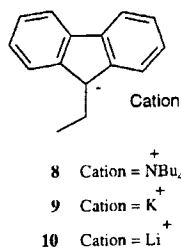| Monomer	Initiator	M_n(calcd)	Initiator recovered (%)[a]	Amount of alcohol (%)[a]	Amount of tributylamine (%)[a]
BA	1	4100	0	5·9	33·0
MMA	1	3160	3·6	25·2	21·0
BA	7	5800	0	36·6	4·3
MMA	7	2870	38·4	9·7	26·6

[a] With respect to the amount of initiator used in the polymerization.

induced by metal-free initiators, we examined the reaction by a 'titration method' using coloured initiators.[10] Since the tetrabutylammonium initiator 8 has a deep red colour which rapidly disappears on monomer addition, it is ideally suited for this purpose. The same applies to the red potassium and lithium analogues 9 and 10. For comparison these were also studied. The results of the polymerization of BA and MMA with 8, 9 and 10 are summarized in Table 4.

It is very surprising that initiation by the tetrabutylammonium salt 8 is *slower* than to those of the potassium and lithium salts 9 and 10, respectively. Traditionally it is believed that the reactivity of a


```
8   Cation = NBu₄⁺
9   Cation = K⁺
10  Cation = Li⁺
```

'carbanion' increases with increasing size of its cation.[2] In our series, we observe exactly the opposite and offer the following explanation. First, the Lewis acidity decreases with increasing size of the cation, resulting in less activation of the monomer. Second, it is known that tetrabutylammonium salts of enolates are not naked carbanions.[14] Rather, the tetrabutylammonium cations interact with carbanions such as malonates in solution via hydrogen bonding, leading to dimer formation.[14] Owing to the large size of the tetrabutylammonium cation, access to the carbanion is more difficult than one might expect on the basis of a truly naked carbanion. In the case of the fluorenyl initiator 8, stabilization between anion and cation via hydrogen bonding may also occur, resulting in steric shielding of the attacking nucleophilic species. Further, if the Michael addition actually occurs by way of electron transfer, the rate of such a process may well depend on the nature of the cation.

The preparative results obtained with initiator 8 are more or less comparable to those described for previous metal-free initiators,[9] although some differences become apparent. It is interesting to compare 8 with the Li⁺- and K⁺-containing initiators 9 and 10, which lead to incom-

Table 4. Polymerization of BA and MMA with the red-coloured initiators 8, 9 and 10 in THF at room temperature

Monomer	Initiator	Induction period (s)	Equiv. of monomer added until colour disappearance	M_n(calcd)	M_n(obsd)	D	Yield (%)
BA	8	0	5	3230	1500	1·24	100
BA	8	0	5	6020	2560	2·69	77
BA	9	0	3	3090	1260	1·14[b]	43
BA	9	0	3	5660	1290	1·14[b]	25
BA	10	0	1	3480	1140	1·06[b]	33
BA	10	0	1	5990	1180	1·05[b]	26
MMA	8	15	—[a]	4040	6720	1·37	100
MMA	8	15	—[a]	7530	11150	1·27	94
MMA	9	1	15	3020	790	3·44[c]	80
MMA	9	1	15	6530	2310	8·08[c]	95
MMA	10	1	3	8850	170	5·60[c]	18
MMA	10	1	3	17140	140	6·44[c]	9

[a] The colour did not disappear until all monomer had been added.
[b] Multimodal.
[c] Bimodal.

plete monomer conversion and bimodal (BA) polymers and to multimodal PMMA. Backbiting occurs to a greater extent in the metal-containing systems, probably because Claisen condensations are accelerated by electrophilic assistance of metal cations.[2] Steric shielding by the bulky ammonium ions may also play a role. This means that metal-free polymerization at room temperature is a much cleaner reaction relative to those containing Li^+ or K^+ ions. Although M_n(calcd) does not always correspond to M_n(obsd), experimental protocols can be given for obtaining a certain molecular weight.

For example, PMMA having a molecular weight of 11,150 and a narrow molecular weight distribution ($D = 1.27$) is readily synthesized simply by aiming for a molecular weight of 7530 (Table 4).

It may be that polymerization of (meth)acrylic acid esters induced by metal-free initiators is successful in optimized cases because of an equilibrium between an active growing chain end and a largely dormant aggregated species. In order to shed some light on this, we tried to synthesize metal-free initiators having an enolate structure related to that of the growing chain end. For this purpose the monoester enolates 11, 12 and 13 were prepared.

Relative to the large number of tetraalkylammonium enolates postulated as reactive intermediates in phase-transfer alkylations,[18] aldol additions and alkylations[19] and polymerizations,[9,11,12] only a few x-ray structures of such species have been described. It is important to emphasize once more than most Li enolates derived from most carboxylic acid esters are only stable below $-30\,°C$,[16] higher temperatures causing decomposition with formation of ketenes and Li alkoxides. We succeeded in the preparation of single crystals of 11, 12 and 13 at room temperature.[10] The results of the x-ray analyses are shown in Figures 1–3.

Enolates 11, 12 and 13 all have similar structures in the solid state. The phenyl group is always cis to the negatively charged enolate oxygen atom. The enolates are not true carbanions or naked anions, in contrast to previous statements concerning ammonium enolates.[18-20] Rather, anions and cations interact with one another by hydrogen bonding. In the case of 11 and 12, anions and cations alternate, two α-methylene units of each ammonium ion participating in C—H···O hydrogen
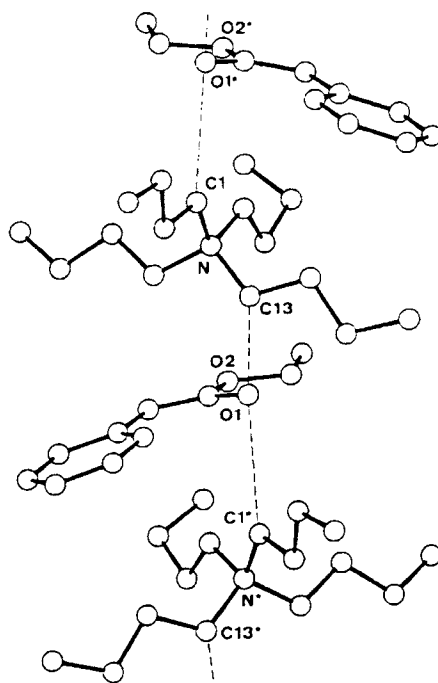

Figure 1. Structure of 11 in the crystal

bonding[21] with the enolate oxygen atoms. This means that each enolate oxygen atoms is stabilized from above and below, resulting in a one-dimensional 'polymer.' We have previously shown that ammonium enolates of malonates are also stabilized by such C—H···O hydrogen bonding,[21] in those cases as dimers (supramolecular ion pairs).[14] The C···O distances of the C—H···O units are about 3.2–3.4 Å (Table 5). In the case of 13, discrete ion pairs exist which loosely interact with one another, i.e. the C···O distances are short in the ion pair itself (typically 3.3 Å, indicative of relatively strong H-bonding) and long between two such pairs (3.64 Å, weak H-bonding, if any).

The n-butyl groups of the tetrabutylammonium ions in 12 and 13 take on the energetically preferred trans/trans
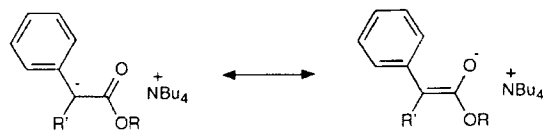
11   R = C$_2$H$_5$; R' = H

12   R = C$_2$H$_5$; R' = CH$_3$

13   R = C$_2$H$_5$, R' = C$_2$H$_5$

Table 5. Selected C—H···O hydrogen bonds in 11, 12 and 13

| Compound	Bond	C···O (Å)	H···O (Å)
11	C(13)—H(13B)···O(1)	3·246(2)	2·28(2)
	C(1)*—H(1B)*···O(1)	3·167(2)	2·50(2)
12	C(13)—H(13B)···O(1)	3·248(2)	2·31(2)
	C(1)*—H(1B)*···O(1)	3·394(2)	2·55(2)
13	C(13)—H(13B)···O(1)	3·265(3)	2·27(3)
	C(13)*—H(13B)*···O(1)*	3·640(3)	2·79(3)

* denotes symmetry related
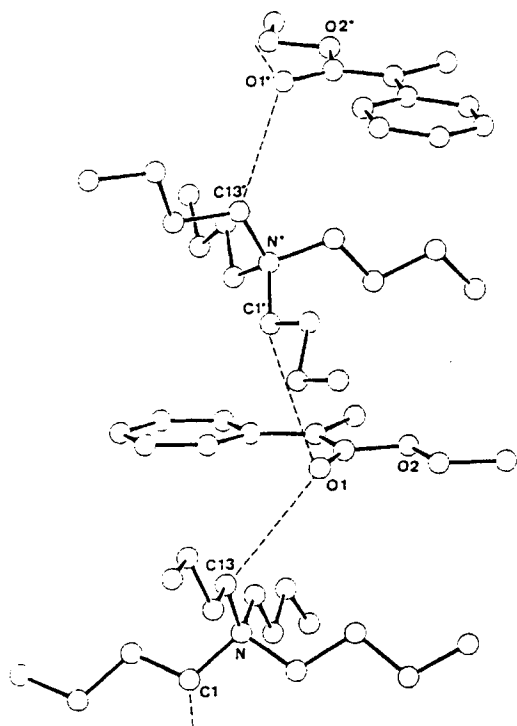
Figure 2. Structure of **12** in the crystal
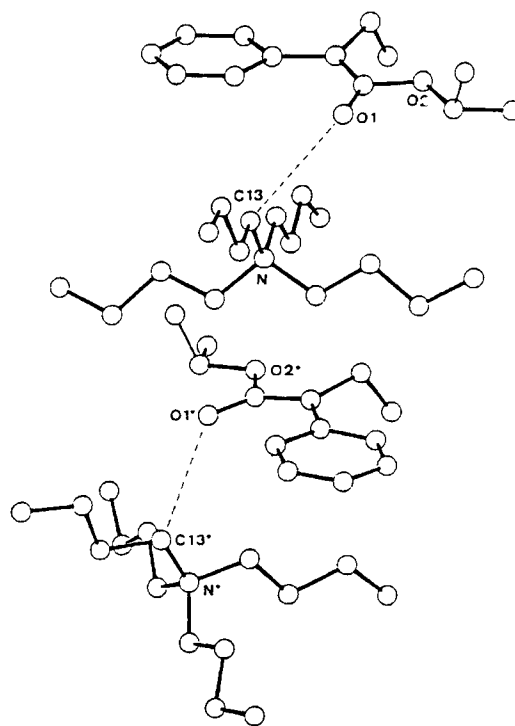
Figure 3. Structure of **13** in the crystal

conformation. In **11**, one alkyl group has rotated into the *trans/gauche* conformation, perhaps owing to packing effects. Analysis of the bond lengths and angles of the enolate portions of **11**, **12** and **13** reveals some expected but also unusual features (Table 6). All of the enolates are conjugated, almost planar systems. Of special interest is the fact that the ideal geometry around the sp^2-hybridized C-atoms in the 'olefinic' portion, namely 120°, is not observed. Rather, angle C(20)—C(19)—O(1) is wider and angle C(20)—C(19)—O(2) is smaller. At the same time, bond C(19)—O(1) shortens and bond C(19)—O(2) elongates. Such effects have been observed previously in the case of lithium enolates,[16] but the present distortions are much more pronounced. They can be interpreted by assuming that the enolates are 'on their way' to ketene and alkoxide ion. Thus, the x-ray structures can be viewed as a point along the reaction coordinate of enolate decomposition (Bürgi–Dunitz correlation principle).[22] Indeed, as stated previously, this may be one of the side-reactions at the growing end of the polymer.

In order to obtain information regarding possible aggregation in solution, freezing-point depression experiments were performed with **11**, **12** and **13** in benzene. Accordingly, **11** is a dimer ($MW_{calcd} = 406$; $MW_{obsd} = 822$) and **12** ($MW_{calcd} = 420$; $MW_{obsd} = 430$) and **13** ($MW_{calcd} = 434$; $MW_{obsd} = 445$) are monomers. Owing to

solubility problems at low temperatures, it was not possible to obtain data in THF. In view of these and the above x-ray data, it is reasonable to conclude that the growing end in the metal-free polymerization is not a naked anion. Rather, it is likely to be stabilized and partially shielded by undergoing H-bonding with the ammonium counter ion. This may occur in the form of monomeric ion pairs or dimers (supramolecular ion pairs).[14] It is tempting to postulate solvent-separated ion pairs as the active species which are robbed of the stabilizing H-bonding. However, evidence for such reactive species in equilibrium with the H-bonded ion pairs has not been obtained.

It needs to be emphasized that **11**, **12** and **13** are only *models* for the growing chain end in the polymerization of BA and MMA, particularly because they contain resonance-stabilizing phenyl groups. Nevertheless, these metal-free enolates are not as (resonance) stabilized as the anions of malonates. Indeed, compounds **11–13** and derivatives thereof are initiators for the polymerization of acrylates and methacrylates at room temperature. An example is the vinyl-substituted analogue **15** prepared from the ester **14**. It results in polymers having a styrene-type end group [equation (3)], i.e. the products are macromonomers for radical polymerizations leading to the formation of comb polymers. Typical results of metal-free polymerizations based on the initiator **15** are shown in Table 7.

Table 6. Important distances and angles in **11** (R = H), **12** [R = C(27)H₃] and **13** [R = C(27)H₂C(28)H₃]
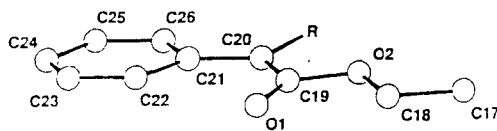
Compound	Distances (Å)		Angles (°)	
11	C(20)—C(19)	1·378(2)	C(19)—C(20)—C(21)	125·5(2)
	C(20)—C(21)	1·436(2)	O(1)—C(19)—O(2)	117·6(1)
	C(19)—O(1)	1·250(2)	O(1)—C(19)—C(20)	130·3(2)
	C(19)—O(2)	1·407(2)	O(2)—C(19)—C(20)	112·1(1)
			C(20)—C(21)—C(22)	124·1(2)
12	C(20)—C(19)	1·398(2)	C(19)—C(20)—C(21)	122·3(1)
	C(20)—C(21)	1·447(2)	C(19)—C(20)—C(27)	120·0(1)
	C(20)—C(27)	1·511(2)	C(21)—C(20)—C(27)	117·7(1)
	C(19)—O(1)	1·252(2)	O(1)—C(19)—O(2)	117·0(1)
	C(19)—O(2)	1·403(2)	O(1)—C(19)—C(20)	129·3(1)
			O(2)—C(19)—C(20)	113·7(1)
			C(20)—C(21)—C(22)	124·9(1)
13	C(20)—C(19)	1·396(3)	C(19)—C(20)—C(21)	121·3(2)
	C(20)—C(21)	1·455(3)	C(19)—C(20)—C(27)	119·5(2)
	C(20)—C(27)	1·515(3)	C(21)—C(20)—C(27)	119·2(2)
	C(19)—O(1)	1·249(3)	O(1)—C(19)—O(2)	117·4(2)
	C(19)—O(2)	1·407(3)	O(1)—C(19)—C(20)	130·1(2)
			O(2)—C(19)—C(20)	112·5(2)
			C(20)—C(21)—C(22)	124·2(2)

Table 7. Polymerization of BA and MMA by initiator **15** at room temperature in THF

Monomer	M_n(calcd)	M_n(obsd)	D	Yield (%)
BA	3110	2000	1·27	68
MMA	3300	4280	1·31	98
MMA	6130	6100	1·47	96
MMA	30100	11350	1·47	97

(3)
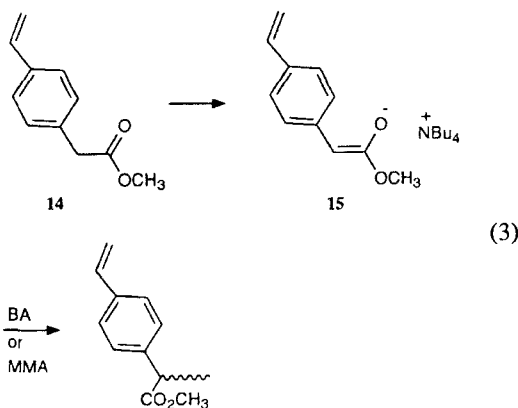
CONCLUSION

Metal-free anionic polymerization of acrylates and methacrylates using tetraalkylammonium salts of CH-acidic compounds at room temperature leads to polymers having narrow molecular weight distributions. The molecular weights range between 1500 and 25,000. The fact that M_n(calcd) and M_n(obsd) do not always correspond to one another is connected with side-reactions such as backbiting and Hofmann elimination, as evidenced by GC analyses of the crude polymerization products. Also, slow initiation occurs in the case of MMA. Hence the process is not a true living polymerization. Nevertheless, polymerizations in which the counter ion is Li⁺ or K⁺ are much less efficient at room temperature, low conversion and multimodal polymer products being the result. X-ray crystallographic studies of tetrabutylammonium ester enolates show that these initiators are not real carbanions (naked anions). Rather, anion and ammonium cation interact with one another by way of hydrogen bonding. It is therefore likely that the growing polymer chain end, which is also an ester enolate, interacts with the tetrabutylammonium cation in a similar manner.

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