Polymerization of Acrylic Acid Esters initiated by Tetrabutylammonium Alkyl- and Aryl-thiolates

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Tetrabutylammonium alkyl- and aryl-thiolates initiate the quantitative polymerization of acrylic acid esters at room temperature to form isotactic polymers having a narrow molecular weight distribution.

The polymerization of acrylic acid n-alkyl esters with formation of living polymers having narrow molecular weight distributions (*i.e.*, polydispersity values† of $D \leqslant 1.2$) has only recently been accomplished.[1] It involves group transfer polymerization[2] in which alkylthiosilanes are used as initiators and ZnI_2 as the catalyst.[1] In contrast to the low-yield classical anionic polymerization induced by such initiators as organolithium or sodium reagents at low temperatures,[3] this process is essentially quantitative at room temperature. Its success rests on repeated Michael additions of *O*-trimethylsilyl-ketene acetals, in which covalently bonded silyl groups migrate along

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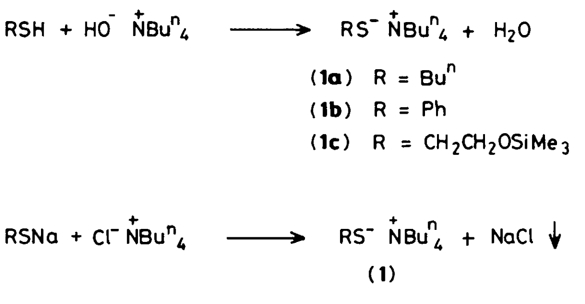
† The molecular weight distribution can be characterized by the polydispersity D; $D = M_w/M_n$ (ratio of the weight average molecular weight to the number average molecular weight). D-values of $\leqslant 1.2$ imply narrow molecular weight distributions.

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

Entry	Initiator	Solvent[b]	M_m (calc.) (kg/mol)	M_n (obs.) (kg/mol)	M_w (kg/mol)	D
1	**(1a)**	MeCN	1.37	1.28	1.47	1.15
2	**(1a)**	DMF	1.37	2.56	9.33	3.65
3	**(1a)**	$\mathrm{PhNO_2}$	1.37	1.46	1.66	1.14
4	**(1a)**	THF	1.37	1.69	4.15	2.45
5	**(1a)**	PhMe	1.37	1.75	4.82	2.75
6	**(1a)**	$\mathrm{PhNO_2}$–THF (1:1)	7.36	6.01	10.8	1.79
7	**(1a)**	THF	27.02	6.83	11.3	1.66
8	**(1b)**	THF	1.39	2.38	3.42	1.44
9	**(1b)**	DMSO	1.39	2.26	3.91	1.76
10	**(1b)**	MeCN	1.39	0.89	0.99	1.11
11	**(1c)**	$\mathrm{PhNO_2}$–THF (1:1)	2.00	1.26	1.44	1.14
12	**(1c)**	PhMe	1.07	1.03	1.32	1.28

[a] Consumption of monomer is quantitative in all cases. [b] DMF = dimethylformamide; THF = tetrahydrofuran; DMSO = dimethyl sulphoxide.



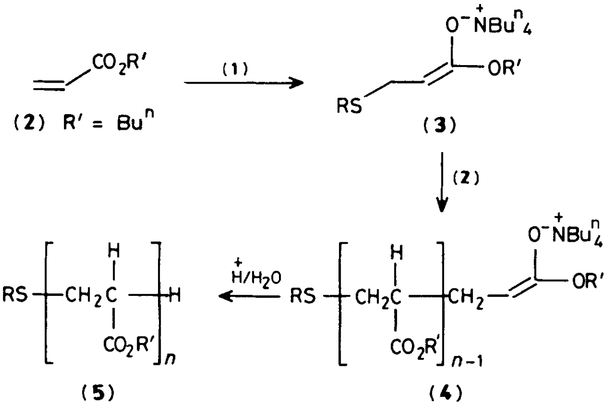
$$\mathrm{RSH} + \mathrm{HO^-}\overset{+}{\mathrm{N}}\mathrm{Bu^n_4} \longrightarrow \mathrm{RS^-}\overset{+}{\mathrm{N}}\mathrm{Bu^n_4} + \mathrm{H_2O}$$

(1a) R = $\mathrm{Bu^n}$
(1b) R = Ph
(1c) R = $\mathrm{CH_2CH_2OSiMe_3}$

$$\mathrm{RSNa} + \mathrm{Cl^-}\overset{+}{\mathrm{N}}\mathrm{Bu^n_4} \longrightarrow \mathrm{RS^-}\overset{+}{\mathrm{N}}\mathrm{Bu^n_4} + \mathrm{NaCl}\downarrow$$

(1)

Scheme 1



Scheme 2

the growing chain.[1,2] We now report a completely different method involving tetrabutylammonium alkyl- and aryl-thiolates $\mathrm{(RS)NBu^n_4}$ as initiators at room temperature in the absence of catalysts. The process is therefore a *metal-free anionic polymerization.*

The initiators (**1**) are readily accessible by treating a thiol with $\mathrm{(HO)NBu^n_4}$ in methanol, stripping off the solvent, and storing the residue *in vacuo* over $\mathrm{P_2O_5}$ (3 h; room temperature) to remove the water (Scheme 1). Alternatively, sodium thiolates (prepared from RSH and NaH) can be treated with $\mathrm{ClNBu^n_4}$, the equilibrium being completely on the desired side owing to the lattice energy of NaCl.[4] Freshly prepared ammonium alkylthiolates should be used in the polymerization as soon as possible, since decomposition *via* dealkylation to form thio-ethers occurs [$\mathrm{(PhS)NBu^n_4}$ is, however, stable for a long time].

Polymerization is accomplished by adding a defined amount of an acrylic acid ester to a defined amount of initiator‡ in the appropriate solvent at room temperature under nitrogen. It is spontaneous and exothermic, leading to quantitative consumption of monomer and formation of polyacrylates (following acidic work-up with dil. HCl) (Scheme 2). Typically, to a solution of the initiator (3 mmol) in the solvent (*ca.* 20 ml) is added dropwise butyl acrylate (30 mmol) within 15 min; the mixture is then stirred for an additional hour and then worked up.

Table 1 shows that the polymerization depends critically upon the solvent, the best choice often being acetonitrile, nitrobenzene, or a mixture of nitrobenzene and THF. In the case of the functionalized initiator (**1c**) prepared from the corresponding sodium thiolate and $\mathrm{ClNBu^n_4}$, the polymer has an hydroxy group on one end (following acidic work-up).

Several additional points deserve mention. Polymers having molecular weights of up to 1500 are characterized by excellent D-values ($\leqslant 1.20$) if the correct solvent is used. Moreover, the M_n (calc.) and M_n (obs.) values agree well in these cases. However, when aiming at higher molecular weights, the M_n (obs.) values are too low (entry 7). We attribute this to a side reaction involving thiolate elimination at one end of the polymer chain, a process that may well be induced by the basic nature of the growing chain end (ester enolate). The eliminated thiolate then starts a new chain. Indeed, the n.m.r. spectra of the higher molecular weight samples show the presence of olefinic protons (up to 20%). Thus, the present method is restricted to the synthesis of low-molecular weight polymers.

In the polymerization of n-butyl acrylate with $\mathrm{(Bu^nS)NBu^n_4}$ in MeCN (entry 1, Table 1), further acrylate was added two hours after completion of polymerization at room temperature. This led to a continuation of polymerization with quantitative formation of a polymer having a molecular weight

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‡ M_n (calc.) is determined by these two parameters.

distribution which is only slightly broadened ($D = 1.28$). However, since the M_n (obs.) value of 1.69 is small relative to the M_n (calc.) value (3.93), chain transfer processes must have occurred under these conditions (*e.g.*, thiolate elimination).

Finally, ^1H n.m.r. ([$^2H_8$]toluene) spectra of polymerized methyl acrylate show essentially only isotactic diads. This stands in contrast to the group-transfer polymerization of methyl acrylate using Bu^nSSiMe_3, which forms atactic polymers.[5] The polymerization of methyl acrylate induced by n-butyl-lithium and certain other organometallic reagents at low temperatures is known to lead to a primarily isotactic polymer, albeit in low yields.[6] This tacticity has been explained on the basis of a cyclic transition state of the Michael addition in which lithium is co-ordinated to two or more oxygen atoms.[6] We suggest that in the present metal-free case tight ion-pairs composed of enolates and ammonium ions are involved, and that strong electrostatic interactions result in a highly ordered transition state, thereby influencing polydispersity and tacticity. In the optimum cases studied, undesired back-biting and/or deprotonations appear to be slow. Nevertheless, the details of the mechanism remain to be elucidated. It is important to note that sodium and lithium n-butylthiolates in acetonitrile are inefficient initiators, leading to incomplete polymerization of n-butyl acrylate (<80% and 32% conversion, respectively) and broad molecular weight distributions ($D > 3$).

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