

Group transfer polymerisation in hydrophobic ionic liquids†

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Received (in Cambridge, UK) 7th October 2004, Accepted 17th December 2004

First published as an Advance Article on the web 17th January 2005

DOI: 10.1039/b415548c

For the first time, group transfer polymerisation of methyl methacrylate (MMA) has been successfully carried out at ambient temperatures in an ionic liquid to produce living polymers of improved polydispersity.

Anionic polymerisation of methacrylates is widely accepted as being capable of producing living polymers with controlled molecular weights.¹ However, control of anionic polymerisation has been considered difficult in this case due to the presence of the ester group in the monomer; these tend to undergo side-reactions with the initiator, as well as with the propagating chain ends.^{2–4} Several methods of control of these processes have been proposed, including the addition of Lewis acids and inorganic salts.^{4–6} Organometallic initiators have been investigated, but these have been shown to bring about undesired side reactions involving the ester functionality and very low temperature conditions are needed to avoid these reactions.⁷

Group transfer polymerisation (GTP) is a relatively new method for polymerisation of acrylic and methacrylic monomers.^{8–10} The main advantage of GTP is that the reaction can be carried out at room temperature and above. Another advantage of GTP is better molecular weight control and narrower polydispersities. The initiation of MMA by the GTP initiator is described in Scheme 1. The GTP technique was discovered by Webster¹¹ and commercialised by DuPont. Traditionally it uses molecular solvents; in the present work we have investigated the use of ionic liquids as a means of providing a greener and improved method for this reaction.

Webster and co-workers¹² demonstrated the possibility of obtaining *living* GTP of methacrylic esters at room temperature by initiating with ketene silyl acetals in the presence of nucleophilic catalysts employing THF as solvent. Subsequently, other initiating systems have been proposed^{13–15} such as metal free cations,

ligand-modified classical cations, and aluminium co-ordinated initiating systems which are known to give controlled polymers of methacrylic esters at room temperature. GTP also proceeds in the presence of both Lewis acids and Lewis base catalysts such as fluorides.^{16,17} However, these fluoride catalysts produce high reaction rates and can become involved in side reactions. Hence catalysts which are less active than fluorides are of interest and there have been reports involving the use of weak bases such as tertabutylammonium cyanide.¹⁸ Lewis acids such as zinc halides and alkyl aluminium oxides work more effectively for acrylates than methacrylates in less basic solvents such as aromatic hydrocarbons.^{19,20} Success in controlling the living polymerisation appears to lie in the choice of the initiator, the catalyst, their concentrations, polarity of the solvent and an added salt which may stabilise the carbanion.^{20–23}

In recent years, room temperature ionic liquids (ILs) have been extensively investigated as replacement solvents for clean synthesis in a variety of chemical reactions.^{24–26} The major advantage in using these ionic liquids is their ability to dissolve a wide range of organic and ionic compounds to an appreciable extent. Their polarity, lack of volatility, and their high thermal stability are also important features. The use of ionic liquids as solvents in polymerisation reactions has recently been reported^{27–30} for free radical polymerisation, transition-metal mediated living free-radical polymerisation, cationic and charge transfer polymerisation. However, there are no reports of the application of ionic liquids as solvents for group transfer polymerisation.

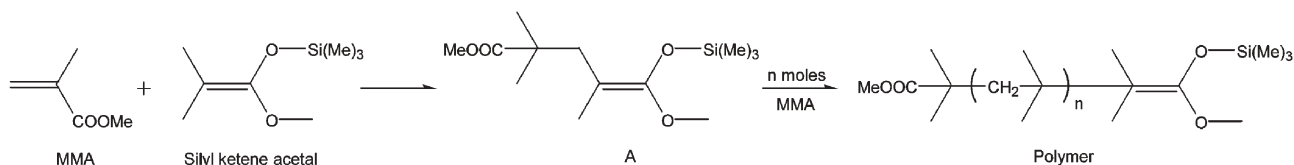
The main objective of the present study is to replace the traditional GTP solvents with an ionic liquid and also to investigate the potential for the special ionic solvent properties of the IL to enable the use of more mild catalysts, to obtain polymers with better polydispersities and at higher yields. These hypotheses are based on previous work in which we have found that the ionic liquid solvent provides an excellent medium for other polymerisation processes involving charged species.^{29,30} Yet another objective is to investigate the living nature of this polymerisation reaction in the IL, again on the basis of the special 'ionic' solvent properties of the IL.

In this communication, we report the group transfer polymerisation of MMA in an ionic liquid, with and without the addition of tetrabutylammonium bromide as catalyst. The results are

† Electronic supplementary information (ESI) available: graph of dependence of molecular weight produced (GPC) on the ratio of monomer to initiator and catalyst. See <http://www.rsc.org/suppdata/cc/b4/b415548c/>

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Scheme 1

compared with the polymers made by employing a conventional catalyst in a traditional solvent (THF). The ionic liquid chosen for this study was *N*-butyl, *N*-methyl pyrrolidinium bis-(trifluoromethanesulfonyl) amide, abbreviated as [p_{1,4}][tf₂N]. The tf₂N anion is chosen because of its weak basicity and its hydrophobicity.

Analytical grades of the monomer (MMA), tetrabutylammonium bromide (TBAB), the group transfer catalyst and 1-methoxy-1-(trimethylsiloxy)2-methyl-1-propene (the group transfer initiator), tetrahydrofuran (THF) and acetonitrile are used. The synthesis of [p_{1,4}][tf₂N] ionic liquid followed the procedures in the literature.³¹ Typically 0.0075 g (0.023 mmol) of tetrabutylammonium bromide is dissolved in 0.25 g of molecular solvent/ionic liquid solvent and 0.056 g (0.32 mmol) of group transfer initiator is added to 0.18 g (1.7 mmol) of MMA. The reaction mixture is stirred and thermostated. After the desired reaction time, the polymer is precipitated from methanol. Studies were also carried out to investigate molecular weights, using gel permeation chromatography (GPC).

Conventionally the group transfer polymerisation of methacrylates requires moderately anhydrous conditions. The present study involves relatively routine reaction conditions with no extra care to maintain anhydrous conditions. Initial trials used Lewis acid catalysts (HBOB = bis(oxalato)boric acid) in ionic liquid, but these were not successful. However, the yield of polymer is close to 100% in the case of experiments carried out using a Lewis base catalyst, TBAB, in IL (runs 4 and 6 of Table 1). The molecular weights produced in these cases were high and the polydispersities improved as compared with the traditional solvent based reactions. In the case of reactions carried out, under similar reaction conditions, with THF or with acetonitrile there is no polymer formation at all. A literature preparation (run 7) using a Lewis acid catalyst produced only 21% polymer yield and higher polydispersity.

Thus GTP proceeds smoothly to give high yields in ILs under circumstances where the reaction does not take place in traditional solvents. This may be due to the presence of relatively more water in the traditional solvents (the THF contained 0.1% water as determined by the Karl Fischer method) as compared to 0.03%

water in the ionic liquid. The molar concentration of water in the THF case is comparable to the amount of catalyst present.

To substantiate that MMA undergoes *group transfer* polymerisation, as opposed to free radical or ionic polymerisation, experiments were carried out at 60 °C in IL with the nucleophilic catalyst, but without the addition of initiator. The polymerisation did not occur (run 2). Another set of experiments was carried out without the addition of solvent, to assess the role of solvent. The polymerisation did not occur (run 3). The experiments were also carried out without the addition of catalyst and, in accord with expectation, polymerisation did occur, but only to the extent of 40% (run 1). This is presumably due to the lack of activation of the initiator by the catalytic nucleophile (in this case the bromide ion). It also indicates that the tf₂N anion is perhaps mildly active as a nucleophile to provide this function. Thus all of these experiments demonstrate that the initiator and ionic liquid solvent are necessary for the group transfer polymerisation to occur under these conditions. However, catalyst is not absolutely necessary, unlike the conventional group transfer polymerisation in which a nucleophilic catalyst is required.

To examine the living nature of this polymerisation in IL, a second aliquot of MMA (0.9 mmol) was added to the reaction mixture (run 1a of Table 2) just before the initial charge of the monomer had been completely polymerised. The reaction continued to complete polymerisation of the second aliquot (Table 2). It was found that there was an increase in the number average molecular weight (run 1a GPC results), as required if a living polymerisation is occurring. However the number average molecular weight obtained is less than the predicted M_n . This difference could be due to the observed gelling of the polymer in the IL which limits the increase in molecular weights. The living nature is further demonstrated by the plot of the ratio of monomer to catalyst and initiator concentrations against number average molecular weight. A linear region of the plot indicates the living nature of the process.³² This is in accordance with the observation that the living nature of GTP depends on the nature and concentration of catalyst.³³ The catalyst present in the system, while increasing the rate of the polymerisation, also appears to stabilise the living species.

Table 1 Molecular weights and % conversion of polymethylmethacrylate prepared in IL

Run	Catalyst/Polym <i>T</i>	Solvent used	Initiator (yes/no)	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	PDI	Yield (%)
1	—, 60 °C	IL	yes	49	25	1.9	40
2	TBAB, 60 °C	IL	no	—	—	—	—
3	TBAB, 60 °C	—	yes	—	—	—	—
4	TBAB, 60 °C	IL	yes	65	36	1.8	90
5*	TBAB, 20 °C	IL	yes	60	34	1.8	25
6**	TBAB, 60 °C	IL	yes	76	45	1.7	99
7 ^a	iBu ₂ AlCl 30 °C	MC	yes	0.8	0.3	2.4	21

^a Reaction time = 240 min; 5* reaction after 93 hours; 6** reaction after 20 hours; 7^a = literature;²⁰ MC = methylene chloride.

Table 2 Living polymerisation in an ionic liquid at 60 °C

Run	Cat/mmol	MMA/mmol	Yield (%)	Solvent	$M_w \times 10^{-4}$	Predicted $M_n \times 10^{-4}$	$M_n \times 10^{-4}$ (GPC)	PDI
1	0.07	1.7	99	IL	55	28.8	28	1.9
1 ^a	—	0.9	90	IL	65	49.2	32	1.9

^a Second stage addition of monomer; catalyst = TBAB; GTP initiator = 0.32 mmol.

Thus, these studies on the group transfer polymerisation of MMA in [p_{1,4}][tf₂N] IL show that the reaction can give high yields under relatively mild conditions in the IL with or without the addition of a nucleophilic catalyst. The addition of a nucleophilic catalyst such as TBAB provides higher rates of polymerisation and at a particular concentration of catalyst the polymerisation was observed to be living. The addition of catalyst also provides better molecular weight control. The growing propagating species may be stabilised by the ionic liquid, in particular against side reactions.

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