

## Group transfer polymerization of acrylonitrile in bulk at ambient temperature

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### Summary

Group transfer polymerization of acrylonitrile was conducted in bulk at room temperature with 1,1,3-trimethyl-5-methylen-2, 6-dioxa-1-silacyclohexen (TMDSCH) as the initiator and tetrabutylammonium bibenzoate (TBABB) as the catalyst. The experimental results showed that the new GTP initiator gave polyacrylonitrile in fairly good yields with well control of the molecular weight and polydispersity.

### Introduction

Since Group transfer polymerization (GTP) was first reported 20 years ago by Webster as a method for the synthesis of acrylic block copolymers [1-2], it has been extensively utilized for the preparation of various types of well-defined polymers, such as usual polymers, functional polymers and block copolymers with narrow molecular weight distribution [3-5]. GTP has turned out to be one of the most unique and useful polymerization technique in the research field of advanced polymerization chemistry, which commonly uses 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS) as initiator and a carboxylic acid salt as catalyst. Moreover, it has been applied to different kinds of monomers, including methyl methacrylate, glycidyl methacrylate, conjugated dienoates and acrylonitrile (AN) or methacrylonitrile [6-19]. However, GTP rate of AN is very high in the presence of initiator MTS, therefore, GTP of AN led to uncontrolled localized polymerization of the monomer before complete mixing could be achieved. Even if GTP of AN was carried out at low temperatures (-50 °C) with a batch polymerization, the molecular weight distribution is broad ( $M_w/M_n = 3.79$ ) because acrylonitrile is a very reactive monomer with propagation being much faster than initiation [6].

Recently, *bulk* GTP technique has been successfully applied by Patrickios [4] in the synthesis of linear homopolymers and randomly cross-linked homopolymer networks of 2-(dimethylamino)ethyl methacrylate of various molecular weights. The obvious advantages of bulk polymerization technique were that it may avoid causing uncontrolled localized polymerization of the monomer because addition of the

initiator to the monomer provides a better chance for complete mixing of the two before the polymerization starts. The development of new type of initiator may provide another solution to this problem because the structure of the initiator has a big effect on molecular weight control and polydispersity of polymer for GTP[6]. In this paper, we described our preliminary results of GTP of AN in bulk with the new initiator TMDSCH which has ring structure. In addition, this new initiator was also very efficient for GTP of AN in bulk.

## Experimental

### *Materials*

AN was purified by washing with 5% aqueous solution of NaOH and water, respectively, and distilled out at 78 °C after dried over anhydrous CaCl<sub>2</sub>, and calcium hydride. The GTP catalyst, tetrabutylammonium bibenzoate (TBABB) was synthesized according to the literature procedure [20]. The GTP initiator, TMDSCH was prepared by reaction of acetylacetone with dimethyldichlorosilane in the triethylamine as previously described [21]. All other reagents were used as received.

### *Instruments*

Gel permeation chromatography (GPC) measurements were carried out (PLgel 5 $\mu$ m MIXED-C, 300 $\times$ 7.5 mm columns, Polymer Laboratories, UK) with refractive index detector (polystyrene standards, DMF + 1 g/L<sup>-1</sup> LiBr as eluent, at 25 °C).

IR spectra were recorded on a Thermo Nicolet Avatar 370 spectrometer using KBr pellets. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AMX-400 spectrometer at room temperature in DMSO-d<sub>6</sub> with TMS as internal standard.

### *Polymerization*

All glassware must be dried completely. A typical polymerization procedure was detailed below: TBABB (95.2 mg, 0.2 mmol) and freshly distilled AN (5.0 mL, 76.0 mmol) were added into a Schleck tube which was sealed by a rubber septum and protected by N<sub>2</sub>, then TMDSCH (0.030 mL, 0.2 mmol) was added in one portion. The reaction was started immediately and caused an increase of temperature from 20 to 22 °C within 5 min. The polymerization mixture became extremely viscous as manifested by the decelerated motion of the stirring bar. After 3 h the reaction was terminated by adding 30 mL of DMF with 2 drops sulfuric acid, and the polymer was precipitated with aqueous methanol in a blender and dried to give 4.02 g (quantitative yield) of white powder.

## Results and Discussion

The main focus of this work is to develop the new effective GTP initiator for the controlled GTP of acrylonitrile in bulk at room temperature. To examine reactivity of initiator TMDSCH, we first used TMDSCH as initiator and TBABB as catalyst for the polymerization of AN in DMF, THF and DMSO, respectively. Contrary to our expectation, the polymerization reaction of AN was sluggish and after 15 h at 20 °C

gave PAN in 10-20% yields. But to our surprise the polydispersity of the polymers was 1.56. Comparison of our results (10-20% yields,  $M_w/M_n = 1.56$ ) with that of Sogah et al (91% yields,  $M_w/M_n = 3.79$ ) [6], we may speculated that TMDSCH was a less reactive initiator for classical GTP of AN than MTS, but could improve polydispersity of the polymers. Although the mechanism of the polymerization is very unclear, we think that the reactivity of the initiator and polydispersity of polymer observed are highly dependant upon the *ring* structure of the new initiator. The initiator possessing ring structure for GTP has not been reported so far.

Encouraged by dramatic improvement in the polydispersity, then we used TMDSCH as initiator and TBABB as catalyst for GTP of AN in bulk, e.g. in the absence of solvent. Gratifyingly, GTP of AN in bulk afforded an outstanding yield (92.2%) and a lower polydispersity (1.68) in the presence of TMDSCH (25.1 mmol/L) and TBABB (17.8 mmol/L).

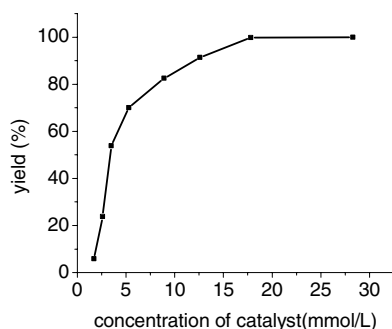
Finally, we investigated effect of the concentration of TMDSCH and TBABB on molar mass and polydispersity of the resultant polymers. The results are listed in Table 1. As can be seen from the table: 1) high yields of polymer (around 100 %) were achieved at room temperature (20 °C) under the conditions applied when the concentration of TBABB is higher than 17.8 mol/L; 2) the concentration of TMDSCH and that of TBABB do have a big influence on the yield, but a little influence on the polydispersity of the resultant polymers; 3) compared with classical GTP of AN, bulk GTP of AN provided lower polydispersity (1.51-1.85). These results showed that TMDSCH was a suitable initiator for synthesis of PAN by GTP in the bulk.

**Table 1.** Polymerization of AN with different catalyst and initiator system (monomer: 76mmol, Polymerization time 3 h at 20 °C)

Entry	[TMDSCH] (mmol/L)	[TBABB] (mmol/L)	Yield(%)	$M_n^a$ ( $10^{-4}$ )	$M_w/M_n$	Theor. $M_n$ ( $10^{-4}$ )
1	76.3	35.7	99.8	5.15	1.85	2.13
2	39.7	35.7	99.9	5.29	1.79	4.10
3	25.1	35.7	99.5	5.82	1.75	6.48
4	76.3	17.8	99.6	4.78	1.78	2.13
5	39.7	17.8	99.3	6.14	1.67	4.10
6	25.1	17.8	92.2	3.34	1.68	6.48
7	39.7	8.9	82.5	2.81	1.59	4.10
8	19.8	7.1	62.6	3.42	1.53	8.21
9	9.9	3.5	51.8	2.15	1.51	16.42

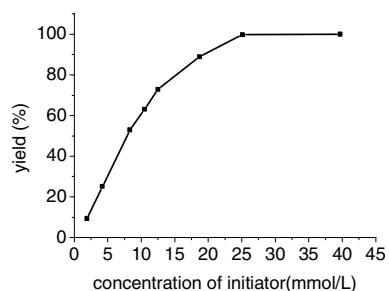
<sup>a</sup> values measured by GPC, calibrated with polystyrene standards

Figure 1 shows the influence of catalyst concentration on the yields of PAN. In the case of low concentration of TBABB, polymerization reactivity was not so high, and polymer yields was low. The polymer yields also increased with the increase in the amount of catalyst. The polymer yields reached a maximum value when concentration of catalyst was around 17.8 mmol/L.



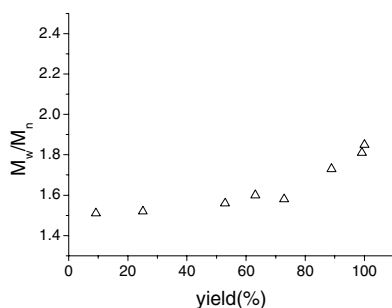
**Figure 1.** Dependence of the polymer yield on the concentration of catalyst (Polymerization conditions: 20 °C; 3 h; monomer: 76 mmol; [TMDSCH] = 39.7 mmol/L.)

Figure 2 indicates the effects of initiator concentration on the yield of PAN. The PAN yields increased with the increase in the concentration of initiator when the concentration of catalyst (35.7 mmol/L) is fixed. The polymer yield reached a maximum value when concentration of initiator was 25.1 mmol/L.



**Figure 2.** Dependence of the polymer yield on the concentration of initiator (Polymerization conditions: 20 °C; 3 h; monomer: 76 mmol; [TBABB] = 35.7 mmol/L.)

Figure 3 describes the molecular weight distributions of the polyacrylonitrile. In general, the polydispersity of the resultant polymers is from 1.5 to 1.85, which is much smaller than that of PAN from a conventional GTP (3.79) [6].



**Figure 3.** Dependence of polydispersity on the polymer yields (Polymerization conditions: 20 °C; 3 h; monomer: 76 mmol; [TBABB] = 35.7 mmol/L.)

## Conclusions

In summary, GTP of AN was successfully conducted in the bulk at room temperature with TMDSCH as the initiator and TBABB as the catalyst for the first time. The polydispersity of PAN is less than 1.9, which is much smaller than that of classical GTP. The experimental results show that the new initiator TMDSCH was a suitable initiator for synthesis of PAN by GTP in bulk. Therefore this method can expand GTP for preparing PAN more efficiently.

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