

Group-transfer polymerization of benzyl methacrylate: A convenient method for synthesis of near-monodisperse poly(methacrylic acid)s

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Summary:

Group-transfer polymerization of benzyl methacrylate has been shown to proceed smoothly to give polymers of low ($\overline{M}_w / \overline{M}_n < 1.1$) polydispersity, with good control of molecular weight. Removal of the benzyl groups can be achieved easily *via* catalytic hydrogenation at room temperature and takes place without main chain scission. This is thus a very effective route for the synthesis of monodisperse poly(methacrylic acid)s.

Introduction

The production of polymers with narrow molecular weight distribution and controlled chain length is an important objective in polymer synthesis. It requires living reactions, with the initiation step sufficiently rapid, with respect to propagation, that all chain ends are formed together and have an equal chance of propagating.

As part of a programme of study of water-soluble homo- and block copolymers of narrow molecular weight distribution, we needed a controlled synthesis of poly(methacrylic acid). In principle, polymerization of such carboxylic acid monomers can be achieved by anionic or group-transfer methods but both require protection of the carboxylic acid function. Protective methods for protic monomers have been reviewed (1). For methacrylic acid they typically involve a suitable ester, with subsequent hydrolysis to liberate the free acid.

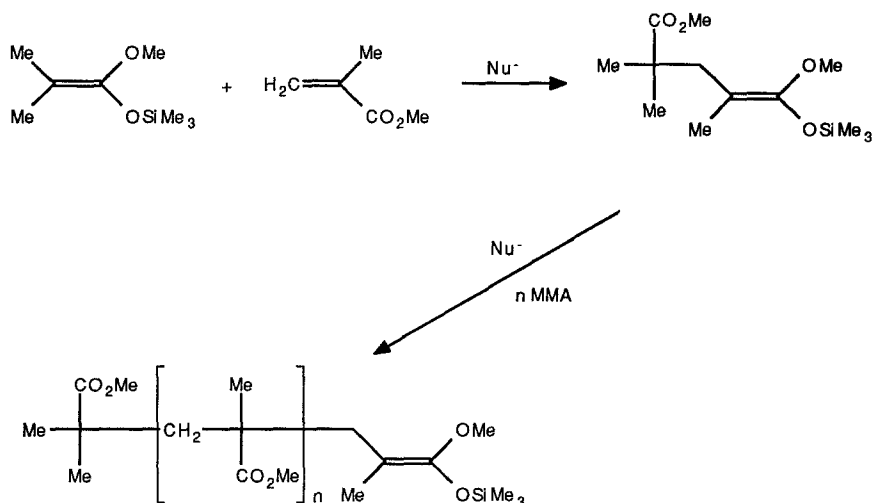
Polymerization of methacrylic esters by anionic initiation needs low temperatures to achieve living conditions (2), because the reactivity of the ester group towards nucleophilic attack allows termination reactions which compete with propagation. Teyssie et al. (3,4) have shown that this problem can be overcome to some extent by complexing the active centres with LiCl.

Group-transfer polymerization (GTP) is a newer approach which allows the synthesis of acrylic and methacrylic polymers in a living reaction at ambient temperature or above (5). It involves the sequential addition of monomer units to the silyl enolate of the terminal ester group (Scheme 1)

The "group-transfer" mechanism is not universally accepted in detail (6,7) and some authors consider that the polymerization is propagated by a small concentration of the free enolate anion.

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Scheme 1



GTP is typically initiated by a silyl ketyl acetal, the usual and simplest initiator being 1-methoxy-1-(trimethylsilyloxy)-2-methylpropene (MTS). It requires a catalyst, typically a nucleophile, and many anions have been reported as effective catalysts, typically fluoride and bifluoride.

Methyl methacrylate can be polymerized in both anionic and GTP conditions. However, hydrolysis of poly(methyl methacrylate) requires severe conditions (8,9) (potassium superoxide or sulfuric acid). In contrast, *p*-toluene sulfonic acid is sufficient to hydrolyse poly(*t*-butyl methacrylate) (10) but the polymer is not easily synthesised in a living reaction, particularly by GTP (11) and even this hydrolysis requires prolonged (7 hr) periods at elevated (80°C) temperatures. Trimethylsilyl methacrylate is polymerizable anionically at low temperatures and hydrolyses readily, but the monomer is difficult to handle and polymerization may be complicated by termination reactions, which depend on the counter-ion (12). GTP of this monomer is also difficult (13).

Another approach to protection of acid groups, which has been widely used in organic synthesis, is to use the benzyl ester, removing the benzyl group by hydrogenation (14). This is a very specific reaction, which can be performed at room temperature in the presence of a wide range of other functional groups. An attractive feature is that the catalyst, typically palladium on charcoal, is easily removed by filtration. The removal of benzyl groups from poly(benzyl methacrylate) by hydrogenation has been discussed by Caton et al. (15), who used polymers produced by free-radical initiation.

Very few reports of controlled polymerization of benzyl methacrylate (BzMA) have appeared. Yuki et al. (16) studied the stereochemistry of the polymer produced with *n*-butyl lithium, but gave no indication of molecular weight control. Cram and Sogah (17) obtained polymer with $\overline{M}_w / \overline{M}_n$ of 1.5 *via* anionic initiation to give low molecular weight polymer ($\overline{M}_n = 2100$).

BzMA is much cheaper than the *t*-butyl ester and is thus an attractive alternative for synthesis of poly(methacrylic acid) by routes requiring protected monomer. We have investigated polymerization of BzMA by GTP and the hydrogenation of the product.

Experimental

Materials.

Unless otherwise stated all reagents were purchased from Aldrich and purified by standard techniques. Benzyl methacrylate was supplied by TCI Chemicals. It was purified by passing through a column containing a mixture of neutral and basic alumina, followed by treatment with methyl-3-trimethylsiloxy-2-butenolate (Fluka) and tetrabutylammonium fluoride (TBAF) (Fluka) in acetonitrile (0.1 M solution), as described below.

Polymerization

Polymerizations were carried out in tetrahydrofuran, distilled immediately prior to use. All glassware was rigorously cleaned and dried in an oven at 130°C for at least 24 hours prior to use. It was assembled under a nitrogen purge and flamed out under vacuum. The reaction vessel was a round-bottom flask equipped with a magnetic stirrer, nitrogen purge and rubber septum for liquid transfer. All transfer was accomplished by double tipped needle techniques. Polymerizations were monitored by recording the reaction exotherm.

In a typical reaction, the vessel was charged with THF (50 ml), MTS (0.2 ml) and the catalyst, TBAF (1 mol% of the initiator). The solution was left to stir at room temperature for 15 min before the slow addition of BzMA (20 ml). A temperature rise of around 20°C was observed for all polymerizations, indicating rapid reaction. Polymerization was terminated, and the polymer recovered, by addition to an excess of methanol.

Hydrogenation

Hydrogenation of poly(BzMA) was performed in a mixture of ethyl acetate and methanol (10:1), in which the polymer remained soluble throughout the experiment. The polymer (2 g) was dissolved in 85 ml of solvent mixture and 0.5 g of 10% palladium/charcoal catalyst was added. The solution was stirred under an atmosphere of hydrogen at room temperature and the progress of the hydrogenation monitored either by measuring the gas absorption or by monitoring the formation of carboxylic acid groups by TLC, with bromophenol blue as the developing reagent. At the end of the reaction, the catalyst was filtered off and the polymer recovered by precipitation with an excess of diethyl ether.

Polymer Characterisation.

Molecular weights and molecular weight distributions were estimated by gel permeation chromatography in THF (flow rate 1 ml min⁻¹), using a Perkin-Elmer refractive-index detector and a Knauer ultra-violet detector. The Styragel column set was calibrated with polystyrene or poly(methyl methacrylate) standards.

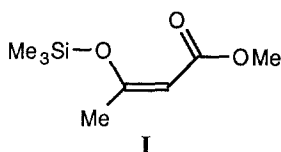
FTIR was performed on a Perkin Elmer Model 1720 spectrometer. ^1H nmr spectroscopy was carried out at 360 MHz, using a Bruker WM360 Fourier-Transform spectrometer.

Results and discussion

Monomer purification

Methacrylate ester monomers are usually produced by transesterification of methyl methacrylate with the corresponding alcohol and are often contaminated with traces of the alcohol, which is difficult to remove and interferes with polymerizations. Long et al. (18) reported that the alcohol impurity can be adequately removed from t-butyl methacrylate by reaction with aluminium alkyls. We did not find this method successful with BzMA. This monomer is very involatile (bp $230^\circ\text{C}/760$ mm) and, even under dynamic vacuum, it can be distilled only with heating. We found that this invariably resulted in polymerization if the monomer had been purified by this method.

Methyl 3-trimethylsiloxy-2-butenolate (MTB, **I**) readily silylates primary, secondary and tertiary alcohols under mild conditions. (19).



When 35 ml of BzMA was treated with 0.5 ml of **I** in the presence of TBAF (0.5 ml of 0.1 M solution) the monomer became orange, presumably due to formation of the anion of **I**. Monomer could be distilled from this mixture without polymerization and was readily polymerizable by GTP, as described below. Presumably the anion from **I** is too stable to initiate polymerization of BzMA.

Polymerization of BzMA

Polymerization of BzMA was performed in THF solution, with MTS as the initiator and TBAF as the catalyst. In all cases the reaction was smooth, typically giving an exotherm of around 20°C .

Table 1 shows the results of some typical polymerizations. In all cases the polydispersity was low and the control over molecular weight excellent. Results from duplicate polymerizations show good reproducibility. Because we do not have primary standards for GPC calibration, the molecular weights quoted are polystyrene equivalents; true molecular weights are discussed below.

Table 1
Results of typical GTP synthesis of poly(benzyl methacrylate)^a

10^3 [MTS]/mol l ⁻¹	\bar{M}_n (theory)	\bar{M}_n (expt)	\bar{M}_w (expt)	\bar{M}_w / \bar{M}_n
4.92	84000	72500	78500	1.08
9.84	42000	36800	39400	1.07
9.84	42000	34800	38400	1.10
19.68	21000	19000	20700	1.09
29.54	14000	12100	13000	1.08

a: [monomer] was 2.35 mol l⁻¹ in all cases. Molecular weights are polystyrene equivalents by GPC.

Hydrogenation of poly(benzyl methacrylate)

Hydrogenation of poly(BzMA) was performed using H₂ gas and a Pd/C catalyst at room temperature. The key to good conversion was found to be the use of a mixed (ethyl acetate/methanol 10:1) solvent which retains the polymer in solution throughout the reaction. In this solvent mixture the hydrogenation was typically complete in under 48 hours.

Hydrogenation was confirmed by ir spectroscopy. Before hydrogenation the polymer showed a sharp C=O stretching vibration at 1724 cm⁻¹. After hydrogenation this was replaced by a very broad band, centred at 1703 cm⁻¹ and identical to that from an authentic sample of poly(methacrylic acid).

Complete hydrogenation was confirmed by ¹H nmr. Figure 1 shows the spectra of the polymer before and after hydrogenation. The resonances from aromatic (7.3 ppm) and benzyl methylene (4.9 ppm) protons in the spectrum of the initial polymer are completely absent after hydrogenation. A broad resonance is observed at 12.3 ppm in the spectrum of the hydrogenated polymer, corresponding to the acid proton. The analytical results suggest that hydrogenation is at least 99% complete.

In order to assess whether there is any chain scission during hydrogenation, we submitted several samples of hydrogenated polymer for GPC analysis in DMF solution, *via* the SERC service at RAPRA. The results were disappointing. Although the unhydrogenated and hydrogenated copolymers were run sequentially, the GPC results indicated a substantial increase in molecular weight on hydrogenation and a broadening of the distribution. We concluded that comparison of the poly(BzMA) with the polyacid was invalid because of non-size exclusion effects.

To resolve this problem we methylated samples of the polyacid to convert them to poly(methyl methacrylate), which could be analysed by GPC in THF, and for which we had primary standards available. Methylation was performed by the method of Katchalski and Eisenberg (20), using diazomethane generated by the method of Lombardi (21). Table 2 shows a typical analysis.

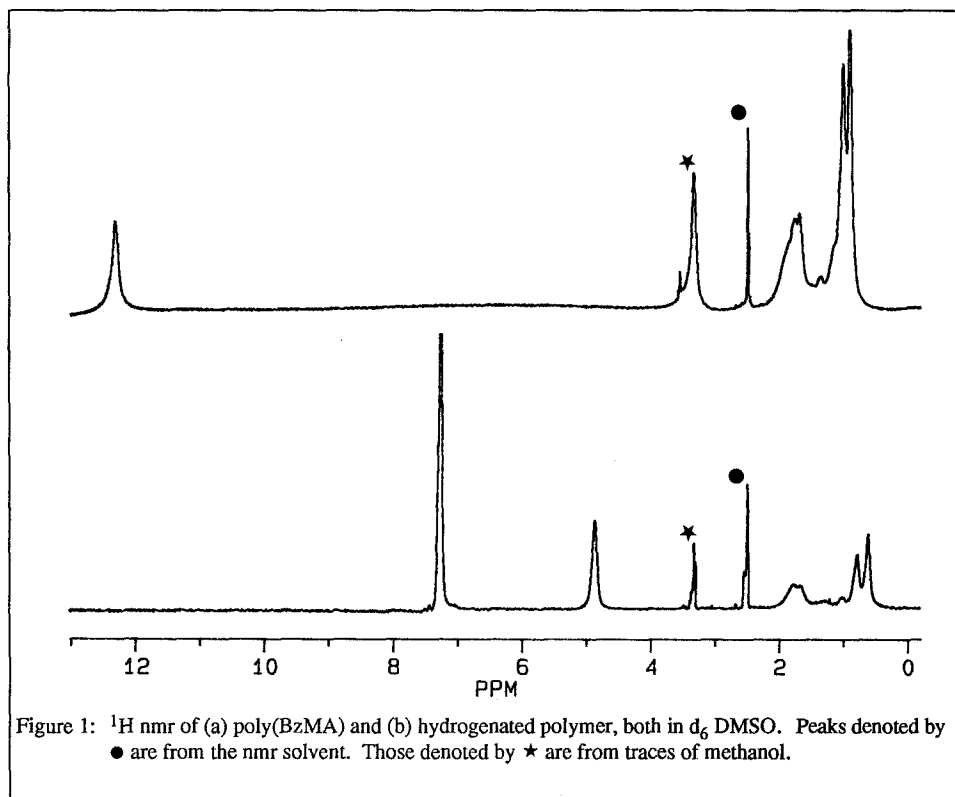


Table 2
GPC analysis of polymer before hydrogenation and after hydrogenation and methylation

Polymer	\bar{M}_n (theory)	\bar{M}_n (expt)	\bar{M}_w (expt)	\bar{M}_w / \bar{M}_n
Poly(BzMA)	14000	12100 ^a	13000 ^a	1.08
Poly(MMA)	8000	8300 ^b	8900 ^b	1.07

a) Polystyrene equivalent.

b) Calibrated with poly(MMA) standards

These data show that there is no chain scission on hydrogenation. They also allow us to obtain good molecular weight data, since narrow distribution poly(MMA) standards are available. The agreement between the theoretical and observed values of \bar{M}_n is excellent. Additionally, samples of poly(MMA) showed no response to the uv-detector of the GPC, where the poly(BzMA) gave a strong absorption. This is further evidence for the completeness of hydrogenation.

Conclusions

We have shown that GTP of benzyl methacrylate is a convenient and simple reaction, giving good molecular weight control and polymers of low polydispersity. Hydrogenation of these polymers is facile under mild conditions and the poly(methacrylic acid) is easily recovered after filtering off the hydrogenation catalyst. Methylation and GPC analysis shows that hydrogenation is quantitative and does not induce chain scission and that the poly(methacrylic acid)s have the desired molecular weight and low polydispersity. This is thus a very convenient route for preparation of monodisperse poly(methacrylic acid), with the potential for controlled structure block copolymers (13).

Acknowledgements

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