Group Transfer Polymerization

Synthesis and Group Transfer Polymerization and Copolymerization of p-Vinylbenzyl Methacrylate

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SUMMARY

p-Vinylbenzyl methacrylate was synthesized by the phase transfer catalyzed esterification of potassium methacrylate with p-chloro-methylstyrene. p-Vinylbenzyl methacrylate was homopolymerized and copolymerized with methyl methacrylate by group transfer polymerization through the methacryloyl group, resulting in reactive polymethacrylates containing pendant styrene groups.

INTRODUCTION

Recently, a new addition polymerization technique known as group transfer polymerization (GTP) was developed (1-7). It uses silyl ketene acetals and other organosilicon compounds as initiators, and either nucleophilic (eg. HF_2^-, CN^-, F^-, N_3^-) (1,2) or electrophilic (Lewis acids) (3) catalysts to polymerize polar monomers such as methacrylates, acrylates, acrylamides, etc. through a living mechanism. Therefore, it has the important advantages associated with living polymers, including the capability to give polymers with narrow molecular weight distribution, the ability to control the molecular weight by the ratio of monomer to initiator, and the ability to synthesize telechelics (4,5) and block copolymers (7). Also, it proceeds rapidly at room temperature and it can be used to polymerize acrylates through a living mechanism, both in contrast to anionic polymerization which can only be used to polymerize methacrylates at low temperature by a living mechanism (8,9). Despite the unique chemistry and advantages of GTP, little has been done to exploit its potential of polymerizing unusual monomers (2,7,10). One of the most important potential applications of GTP would be the polymerization of polar double bonds to the exclusion of nonpolar double bonds. Of particular interest is the electrophilic catalyzed GTP of 2-methacryloyloxyethyl acrylate, which gives a polymer containing pendant methacryloyl groups (7). We are interested in functional polymers containing pendant or terminal styrene groups, since they represent a novel class of thermally reactive oligomers (11-14). The goal of this paper is to present the synthesis and group transfer polymerization and copolymerization of the bifunctional monomer p-vinylbenzyl methacrylate. This is the first example of a monomer polymerized selectively at a polar

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vinyl group in the presence of a styrenic substituent, resulting in a reactive polymethacrylate containing pendant styrene groups. This novel class of reactive polymethacrylates is very useful for the synthesis of novel polymer networks and interpenetrating polymer networks.

EXPERIMENTAL

A. Materials and Methods

Methacrylic acid (Aldrich) and dimethylketene methyl trimethylsilyl acetal (Polysciences, Inc.) were used as received. p-Chloromethylstyrene was synthesized according to a literature procedure (15). Methyl methacrylate (MMA) (Aldrich) was dried and purified by passage through a column of sodium sulfate sandwiched between basic activated alumina just prior to each polymerization. Tris(dimethylamino)sulfonium bifluoride used as catalyst was generously donated by Dr. Hertler of E. I. du Pont de Nemours and Company. Tetrahydrofuran (THF) used as polymerization solvent was refluxed over lithium aluminum hydride and distilled under argon just prior to each polymerization. All other reagents were used as received. Polymerizations were carried out under argon in polymerization vials equipped with septums. All glassware and syringes were dried at 120°C at least 12 hrs. before use. Polymerizations were performed by a batch process in which catalyst was added to a solution of monomer, initiator, and solvent. Average molecular weights and polydispersities ($\overline{M}w/\overline{M}n$) were determined by gel permeation chromatography (GPC) with a Perkin-Elmer series 10LC equipped with LC-100 column oven, LC-100 autosampler and Sigma 15 data station. The measurements were made using an UV detector, THF as solvent (1 ml/min, 40°C), a set of PL-gel columns (10^2, 5×10^2, 10^3, 10^4, and 10^5 Å), and a calibration plot constructed with polystyrene standards. Glass transition temperatures (Tg) were determined with a Perkin-Elmer differential scanning calorimeter (model DSC-4) at a heating rate of 20°C/min. Indium was used as the calibration standard. All glass transition temperatures reported were read during the second heating cycle. 200 MHz ^{1}H-NMR spectra were recorded on a Varian XL-200 spectrometer in CDCl$_3$ solutions with TMS as internal standard.

B. Synthesis of p-Vinylbenzyl Methacrylate (VBM)

The potassium salt of methacrylic acid was made by titrating a solution of methacrylic acid (25 ml, 0.29 mol) in methanol (400 ml) by 1.5 M KOH in methanol (216 ml, 0.32 mol) using phenolpthalein as indicator. This was then poured into diethyl ether and the precipitate filtered and dried. p-Chloromethylstyrene (20 ml, app. 0.13 mol) was then added to an ice-cooled solution of potassium methacrylate (18g, 0.14 mol) and tetrabutylammonium hydrogen sulfate (TBAH) (4.2g, 12.4 mmol) in THF (300

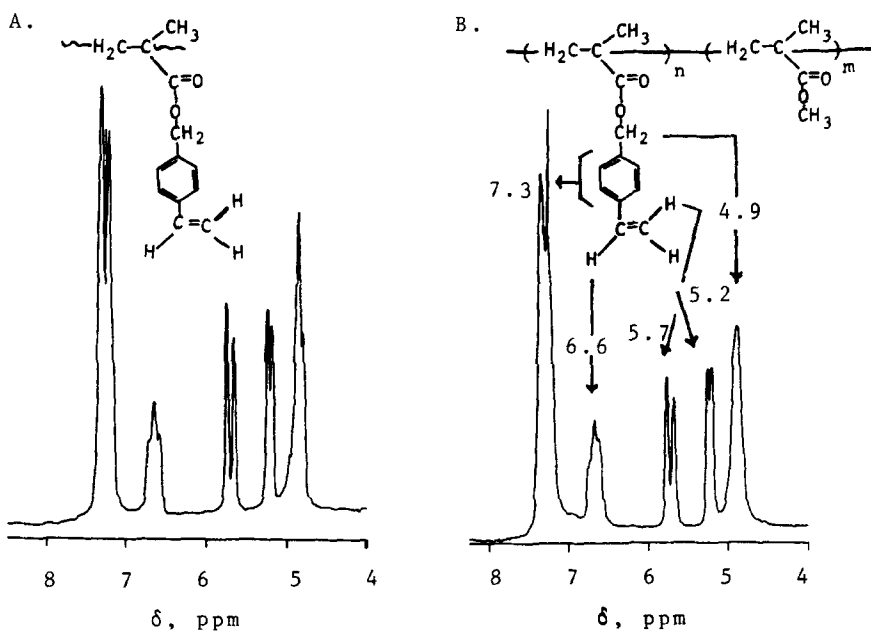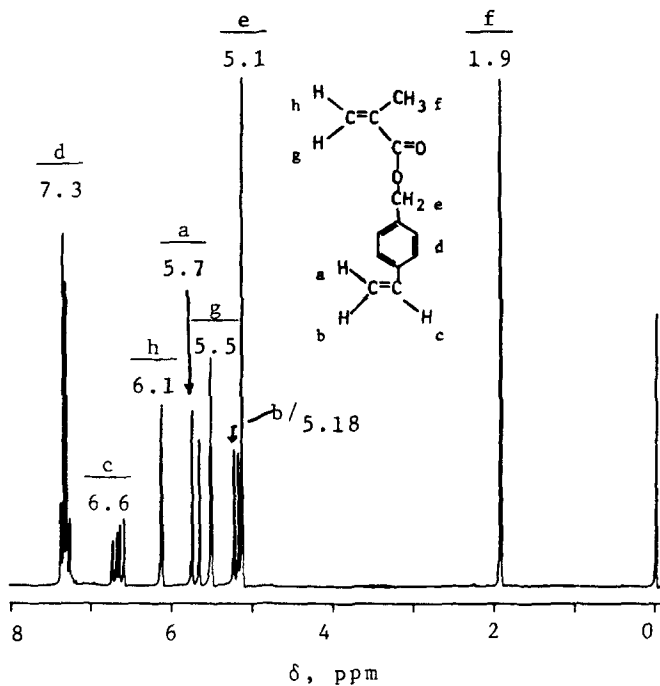Figure 1. 200 MHz ^{1}H-NMR spectrum of VBM (CHCl$_3$, d$_1$, TMS).

Figure 2. Aromatic and olefinic region of the 200 MHz ^{1}H-NMR spectra of (A) PVBM, and (B) MMA/VBM=2.5 copolymer (CHCl$_3$, d$_1$, TMS).

ml) and DMSO (50 ml), and stirred at 60°C 20 hrs. The resulting orange solution was poured into water and stirred until an orange liquid separated, which was extracted with chloroform, washed several times with water, and dried over sodium sulfate overnight. After filtration, chloroform was removed on a rotovapor at room temperature, and the product was dissolved in anhydrous diethyl ether. This was then dried and purified prior to each polymerization by passage through a column of sodium sulfate sandwiched between basic activated alumina, and the solvent removed by rotary evaporation. ^{1}H-NMR (CHCL$_3$, d$_1$, δ, ppm): 1.9 (s, -CH$_3$), 5.1 (s, -OCH$_2$), 5.15-5.2 (d, =CH trans to benzyl), 5.5 (s, =CH trans to CH$_3$), 5.65-5.75 (d, =CH cis to benzyl), 6.1 (s, =CH cis to CH$_3$), 6.55-6.75 (d, =CH α to benzyl) 7.2-7.4 (m, 4 aromatic protons). The 200 MHz ^{1}H-NMR spectrum is presented in Figure 1.

C. Polymerization of VBM

Tris(dimethylamino)sulfonium bifluoride (approximately 0.1 mol% relative to initiator) was added to an ice-cooled solution of VBM (1.0g, 4.9 mmol) and dimethylketene methyl trimethylsilyl acetal (0.1 ml, 0.34 mmol) in THF (5 ml) under argon. The reaction mixture was stirred 1.5 hrs., and then poured into methanol. The obtained polymer was purified by precipitation from THF solution into methanol, to give 0.55g PVBM (55%). GPC: $\overline{M}w$ =30961, $\overline{M}n$ = 3722, (theoretical $\overline{M}n$ = 2979), $\overline{M}w/\overline{M}n$=8.3. ^{1}H-NMR (CHCl$_3$, d$_1$, δ, ppm): 0.5-1.5 (m, -CH$_2$), 1.5-2.3 (d, methacryloyl -CH$_2$), 4.9 (s, -OCH$_2$), 5.15-5.25 (d, =CH trans to benzyl), 5.65-5.75 (d, =CH cis to benzyl), 6.5-6.8 (m, =CH α to benzyl), 7.2-7.4 (m, 4 aromatic protons). The 200 MHz ^{1}H-NMR spectrum is presented in Figure 2a.

D. Copolymerization of VBM and MMA

In a typical procedure, tris(dimethylamino)sulfonium bifluoride (approximately 0.1 mol% relative to initiator) was added to an ice-cooled solution of VBM (0.53g, 2.2 mmol), MMA (0.58g, 5.8 mmol), and dimethylketene methyl trimethylsilyl acetal (0.15 ml, 0.50 mmol) in THF (3.7 ml) under argon. The reaction mixture was stirred 1.5 hrs., and then poured into methanol. The obtained polymer was purified by precipitation from THF solution into methanol, to give 0.36g copolymer (46%). GPC: $\overline{M}w$ = 21320, $\overline{M}n$ = 8331, $\overline{M}w/\overline{M}n$=2.6. ^{1}H-NMR (CHCl$_3$, d$_1$, δ, ppm): 0.75-0.95 (m, -CH$_2$), 1.75-1.9 (d, methacryloyl -CH$_2$), 3.5 (s, -OCH$_3$), 4.9 (s, -OCH$_2$), 5.15-5.25 (d, =CH trans to benzyl), 5.65-5.75 (d, =CH cis to benzyl), 6.5-6.8 (m, =CH α to benzyl), 7.2-7.4 (m, 4 aromatic protons). The 200 MHz ^{1}H-NMR spectrum is presented in Figure 2b. The copolymer composition was determined by calculating the ratio of the area of the signal at 3.5 ppm (-OCH$_3$) and the area of the signal at 4.9 ppm (-OCH$_2$). In this case, the ratio was calculated to be 3.3, indicating a different copolymer composition from the initial monomer composition. The extent of unreacted styrenic double bonds can be determined by calculating the ratio of the area of the peaks from 5.15 to 5.65 ppm (=CH$_2$) and the area of the

Table 1. Synthesis and Characterization of PVBM and VBM/MMA Copolymers.

No.	VBM (mol/l)	MMA (mol/l)	Initiator*	Yield %	$\overline{Mn}$ (x10³) theor.	$\overline{Mn}$ (x10³) GPC	$\overline{Mw}$ (x10³) GPC	$\overline{Mw}/\overline{Mn}$	MMA/VBM (mol/mol) charge	MMA/VBM (mol/mol) copolymer	Tg (°C) 1st scan	Tg (°C) 2nd scan
1[a,e]	0.987	0	0.067	55	2.98	3.72	30.9	8.3	0	0	56	---
2[a,e]	0.705	0.692	0.135	46	1.55	61.11	172.3	2.8	0.98	1.1	74	---
3[c,d]	0.540	1.439	0.076	61	3.34	8.33	21.3	2.6	2.7	3.3	75	---
4[b,f]	0.274	1.387	0.085	38	2.27	5.08	6.2	1.2	5.1	3.6	88	---
5[b,e]	0.376	2.510	0.068	81	4.81	16.99	18.0	1.1	6.7	4.3	114	134
6[b,f]	0.203	2.406	0.068	80	4.16	11.72	13.0	1.1	11.8	8.7	113	132
7[a,d]	0.196	2.683	0.076	40	4.09	8.04	12.4	1.6	13.7	11.6	112	131

*dimethylketene methyl trimethylsilyl acetal
a = polymerization time 1.5 hr; b = polymerization time 2.0 hr; c = polymerization time
2.5 hr; d = ambient reaction temperature; e = reaction flask immersed in ice-water;
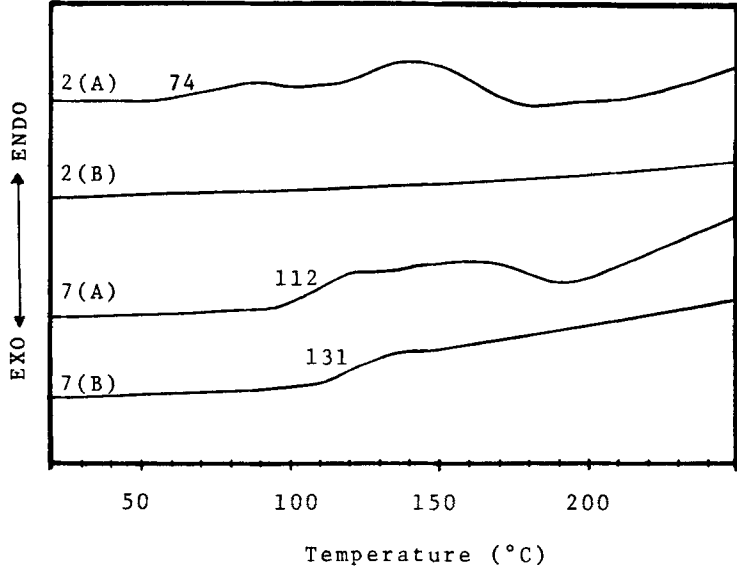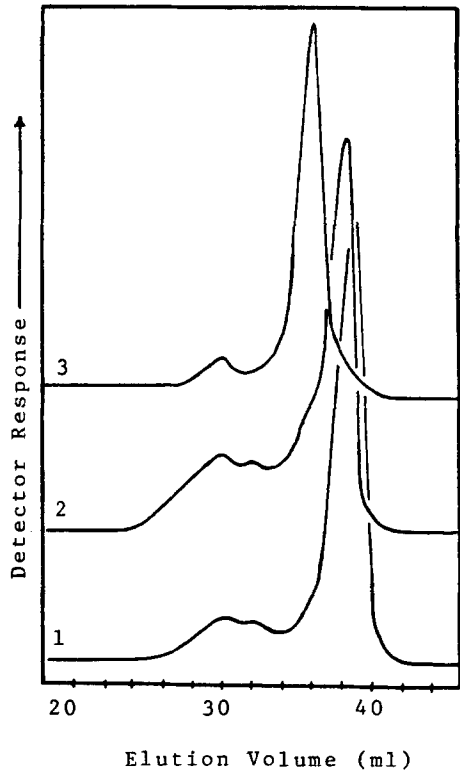f = reaction flask immersed in dry-ice/acetone.

Figure 3. DSC traces of
entries 2 and 7 from
Table 1:
  (A) first heating
  (B) second heating

Figure 4. GPC traces of
PVBM and some typical
copolymers of VBM and
MMA. (Numbers corres-
pond to those in Table 1.)

peak at 4.9 ppm ($-OCH_2$). This ratio must be 1.0 or less in all cases.

RESULTS AND DISCUSSION

VBM was homopolymerized or copolymerized with MMA in ratios of MMA to VBM of 0.98 to 13.7. The results of the synthesis and characterization of PVBM and its copolymers with MMA are shown in Table 1. Some of the yields are low, probably due to the low molecular weights involved, which may be partially soluble in methanol used to isolate these polymers. The copolymer compositions (as determined by comparison of $-OCH_2$ to $-OCH_3$) and initial monomer concentration can also be found in Table 1. There is slightly less MMA in the copolymer than in the initial monomer composition as determined by NMR in all cases.

Although comparison of Figure 2 with Figure 1 demonstrates that GTP of VBM polymerizes the methacrylate double bond to the exclusion of the styrenic double bond, the wide molecular weight distributions seen in Table 1 indicate that this is not necessarily true. This is further elucidated by the typical gel permeation chromatographs presented in Figure 4, in which there is a small peak at high molecular weight in addition to the large, very narrow peak at low molecular weight. Apparently, a minor amount of styrenic double bonds polymerize due to the heat of polymerization. The best indication of unreacted styrenic double bonds seem to be a very narrow molecular weight distribution, and the absence of a second peak at higher molecular weight, both of which are true for entries 4-6 in Table 1. These entries show that it is necessary to copolymerize with another monomer (in order to decrease the proximity of styrenic double bonds), and to use subambient temperatures in order to completely prevent any thermal reaction of the styrenic double bonds of VBM by GTP. However, comparison of entries 4-6 in Table 1 demonstrate that only ice-cooled conditions (approximately 0°C) are required.

Further evidence of unreacted styrenic double bonds in all polymers presented in Table 1 is their thermal behavior. In the first DSC heating scan, we see both a glass transition and an exotherm due to reaction of the vinylbenzyl groups. Heating after this curing process shows either no glass transition temperature nor exotherm, or only a glass transition temperature at a higher temperature if enough MMA is used to allow segmental motions between crosslinks. Examples of both behaviors are presented in Figure 3. It is also important to note that all the polymers of this study are completely soluble in THF, chloroform, etc., even if some branching has taken place. Therefore, they can be further processed, polymerized, and copolymerized through the unreacted vinylbenzyl groups as desired.

ACKNOWLEDGEMENTS

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