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Group transfer copolymerisation of vinyl methacrylate and methyl methacrylate

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Vinyl methacrylate (VMA) was homopolymerised and copolymerised with methyl methacrylate (MMA) by group transfer polymerisation at room temperature through the methacrylolic group, resulting in linear, soluble and reactive polymethacrylates with pendant vinyl ester groups. The reactivity ratios were found to be $r_{VMA} = 105$ and $r_{MMA} = 0.0098$ by the Tidwell and Mortimer method. © 1977 Elsevier Science Ltd.

(Keywords: vinyl methacrylate; methyl methacrylate; group transfer polymerisation)

Introduction

Because of its unique characteristics, group transfer polymerisation (GTP) has several useful applications in the synthesis of novel polymers[1–6]. Of particular interest is the polymerisation of acrylic carbon–carbon double bonds to the exclusion of non-acrylic carbon–carbon double bonds, resulting in linear and soluble polyacrylates containing potentially reactive carbon–carbon double bonds. For instance, group transfer polymerisation of allyl methacrylate gives a polymer containing pendant allyl groups while the selective polymerisation of 2-methacryloyloxyethyl acrylate by GTP results in a polymer containing methacryloyl groups[1,7]. Polymer containing pendant styrene groups has also been synthesised by GTP of the bifunctional monomer *p*-vinylbenzyl methacrylate[8]

The goal of this paper is to exploit group transfer polymerisation and copolymerisation of vinyl methacrylate. Unlike allyl methacrylate or *p*-vinylbenzyl methacrylate, vinyl methacrylate has a heteroatom adjacent to the carbon–carbon double bond of the vinyl group. The reactive polymethacrylates thus obtained contain pendant vinyl ester groups and may be useful for the synthesis of novel polymer networks.

Experimental

Materials. Methyl trimethylsilyl dimethylketene acetal (MTS) (Aldrich) was used as received. Methyl methacrylate (MMA) (Fluka) and vinyl methacrylate (VMA) (Tokyo Chemical Industry) were redistilled under reduced pressure, dried and stored over molecular sieves prior to polymerisation. Tetrahydrofuran (THF) was refluxed over sodium and freshly distilled under nitrogen before use. Tris(dimethylamino)sulfonium bifluoride used was a 0.1 M solution in acetonitrile. All other reagents were used as received. All polymerisations were carried out at ambient temperature (30–32°C) under nitrogen in a round-bottomed flask equipped with a water condenser and a thermometer. The whole system was flame-dried under nitrogen and then cooled to room temperature before any reagents were added. All glassware and syringes were dried at 120°C for several hours before use.

Average molecular weights and polydispersities were determined by gel permeation chromatography (g.p.c.) with a Waters system consisting of a 600E pump, an external column oven of LC-100 set at 28°C, and a Waters 410 Differential Refractometer. There was a guard column of the same packing material of dimensions 50 mm × 7.80 mm placed before the two mixed-bed columns of length 300 mm × 7.80 mm (Phenogel 10). The whole system was operated at a flow rate of 0.8 ml min^{-1} by using THF as solvent. A calibration line was constructed with polystyrene standards. Glass transition temperatures (T_g) were determined on a DuPont 910 differential scanning calorimeter at a heating rate of 20°C min^{-1}. The 90 and 300 MHz ^{1}H n.m.r. spectra were obtained with a JEOL FX90Q and a Bruker ACF300Q spectrometer, respectively, in $CDCl_3$ with tetramethylsilane (TMS) as internal standard.

Polymerisation of VMA. MTS (0.05 ml, 0.25 mmol) was added to a magnetically stirred solution of tris(dimethylamino)sulfonium bifluoride (0.020 ml, 0.1 M, in acetonitrile) and VMA (4.0 ml, 22.5 mmol) in 10 ml THF under nitrogen. The temperature rose rapidly to 50°C, and the solution became viscous. After stirring for 3 h, 2 ml methanol was added to quench the reaction. Then the solution was poured into hexane to precipitate polymer, which was purified by further precipitation from acetone solution into hexane and dried *in vacuo* for 24 h at room temperature, to give 3.30 g of poly(vinyl methacrylate) (PMVA) (88.1%). G.p.c.: $M_n = 1.23 \times 10^4$ (theoretical $M_n = 1.50 \times 10^4$), $M_w = 2.23 \times 10^4$, $M_w/M_n = 1.81$. I.r. (KBr, ν cm^{-1}): 1748 (C=O), 1647 (C=C). ^{1}H n.m.r. ($CDCl_3$, δ ppm): 4.5–4.7 (d, =CH *trans* to methacryloyl), 4.8–5.0 (d, =CH *cis* to methacryloyl), 7.0–7.2 (t, -OCH=).

Copolymerisation of VMA and MMA. In a typical procedure, MTS (0.1 ml, 0.5 mmol) was added to a magnetically stirred mixture of tris(dimethylamino)sulfonium bifluoride (0.020 ml, 0.1 M, in acetonitrile), VMA (1.0 ml, 8.38 mmol) and MMA (3.0 ml, 28.0 mmol) in 10 ml THF under nitrogen. The temperature rose rapidly to 35°C. The mixture was stirred for 3 h and then quenched by 2 ml of methanol. The solution was poured into hexane and the copolymer thus obtained was purified by further precipitation from acetone solution into hexane and dried *in vacuo*

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Table 1 Synthesis and characterisation of PVMA and VMA/MMA copolymers

No.	(mol l^{-1})			Yield (%)	Theoretical	Experimental		VMA (mol%)		T_g (°C)
	VMA	MMA	MTS		$M_n \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	Charge	Polymer	
1	0.30	2.34	0.036	17.7	7.49	3.61	1.70	11.3	80.9	79
2	0.60	2.00	0.036	32.4	7.50	4.42	1.98	23.0	87.5	79
3	0.90	1.67	0.036	41.3	7.50	4.83	1.72	35.0	93.0	77
4	1.20	1.34	0.036	44.3	7.50	6.28	1.82	47.3	95.3	77
5	1.50	1.00	0.036	47.3	7.51	6.37	1.83	59.9	95.6	77
6	1.80	0.67	0.036	62.1	7.51	6.88	1.98	72.9	98.1	76
7	2.10	0.33	0.036	70.9	7.52	8.14	1.90	86.2	98.6	76
8	2.67	0	0.036	86.5	7.52	7.75	1.61	100	100	76
9	2.67	0	0.018	88.1	15.0	12.3	1.81	100	100	76

for 24 h, to give 1.22 g of copolymer (32.4%). G.p.c.: $M_n = 4.42 \times 10^3$, $M_w = 8.77 \times 10^3$, $M_w/M_n = 1.98$. The copolymer composition was determined by calculating the ratio of the signal at 3.6 ppm ($-OCH_3$) to the signal at 4.6–5.0 ppm ($=CH_2$) in the ^1H n.m.r. spectrum. For determination of the reactivity ratios of VMA and MMA, the mixture was stirred for 60–180 s and then quenched by 2 ml of methanol so that the conversion yields of the copolymerisation would be less than 10%.

Table 2 Data for determination of reactivity of VMA (1) and MMA (2)

No.	1	2	3	4	5
f_1	0.114	0.230	0.350	0.473	0.599
F_1	0.936	0.954	0.964	0.970	0.983

f_1, mole fraction in monomer mixture; F_1, mole fraction in copolymer

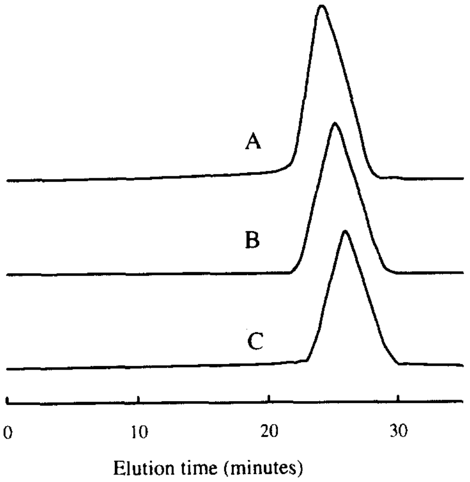

Figure 1 G.p.c. chromatograms of poly(vinyl methacrylate) (curve A for sample 9 and curve B for sample 8) and vinyl methacrylate/methyl methacrylate copolymer sample 2 (curve C)

Results and discussion

Vinyl methacrylate was homopolymerised and copolymerised with methyl methacrylate for mole fractions of vinyl methacrylate ranging from 0.113 to 0.862. The results of the preparation and characterisation of polymers of vinyl methacrylate, as well as its copolymers with methyl methacrylate, are shown in *Table 1*.

It is noted that the homopolymerisation of vinyl methacrylate takes place very rapidly and the yield is considerably good, showing that vinyl methacrylate may be one of the most active monomers in group transfer polymerisation. This was further confirmed by its copolymerisation with methyl methacrylate. As shown in *Table 1*, regardless of the feed composition, vinyl methacrylate is easier to incorporate into polymers than methyl methacrylate. For example, even though there was only 11.3 mol% of vinyl methacrylate in the initial monomer mixture, the copolymer had 80.9 mol% vinyl methacrylate units. Moreover, when the vinyl methacrylate content in the initial monomer mixture was 70% or more, the copolymers contained so many vinyl methacrylate units that they almost became the homopolymer of vinyl methacrylate. These results demonstrate well that vinyl methacrylate is much more active than methyl methacrylate in group transfer polymerisation. Quantitatively, the conversion of each monomer can be calculated by using the yield and composition of the copolymer. For instance, the conversions are 84.7% for vinyl methacrylate and 3.7% for methyl methacrylate in the copolymer when equal amounts of vinyl methacrylate and methyl methacrylate monomers are used (sample 4 in *Table 1*).

Table 2 shows the charges and copolymer compositions of five samples obtained at low conversion. It has been suggested that the best method to calculate reactivity ratios is that of Tidwell and Mortimer[9]. The reactivity ratios of vinyl methacrylate and methyl methacrylate calculated by the Tidwell and Mortimer method[10] are $r_{VMA} = 105$ and $r_{MMA} = 0.0098$. These values of reactivity ratio show that vinyl methacrylate greatly prefers homopolymerisation to copolymerisation with methyl methacrylate. In comparison, the reactivity ratios of allyl methacrylate (AMA) and methyl methacrylate have been found to be $r_{AMA} = 1.62 \pm 0.34$ and $r_{MMA} = 0.65 \pm 0.11$ by Oncul-Koc and Catalgil-Giz[11]. Obviously allyl methacrylate also shows similar preference for homopolymerisation but its tendency is much smaller than that of vinyl methacrylate in group transfer polymerisation with methyl methacrylate.

The yields of the copolymer of vinyl methacrylate and methyl methacrylate increased steadily with increasing vinyl methacrylate content in the feed as shown in *Table 1*, demonstrating that the copolymerisation is dominated by the highly active monomer, vinyl methacrylate.

Although the molecular weights of vinyl methacrylate polymers depend upon the ratios of monomers and initiator as in other group transfer polymerisations, the molecular weight polydispersities were found to be broad in both the homopolymerisation and copolymerisation of vinyl methacrylate because of its high reactivity at room temperature.

The g.p.c. chromatograms of PVMA and a copolymer are shown in *Figure 1*. Each polymer has a single peak, showing that the broad molecular weight polydispersities are not caused by side reaction of vinyl groups and that no crosslinking takes place in the group transfer polymerisation of vinyl methacrylate. The results demonstrate that the vinyl ester group was not affected under the polymerisation conditions used. It is important to note that PVMA and all the copolymers are completely soluble in tetrahydrofuran, chloroform, acetone, etc., and can be further polymerised or functionalised through the unreacted vinyl groups. Thermal analysis showed that the poly(vinyl methacrylate) has a T_g of 76°C, which is about 40°C lower than that of poly(methyl methacrylate). The glass transition temperatures of the copolymers increase slightly with increasing methyl methacrylate content in the copolymer.

Conclusions

Vinyl methacrylate was homopolymerised and copolymerised with methyl methacrylate by group transfer polymerisation. Vinyl methacrylate has high activity in group transfer polymerisation. Its activity is much higher than that of methyl methacrylate. In the copolymerisation of vinyl methacrylate and methyl methacrylate, the reactivity ratios determined by the Tidwell and Mortimer method are $r_{\mathrm{VMA}} = 105$ and $r_{\mathrm{MMA}} = 0.0098$. Group transfer polymerisation and copolymerisation of vinyl methacrylate give linear polymethacrylates with pendant vinyl ester groups which could be useful in further functionalisation.

Acknowledgements

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