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Synthesis of graft copolymer by coupling reaction of living poly(methyl methacrylate) with bromomethylated polystyrene

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A novel, well-defined graft copolymer (polystyrene (PS)–g–poly(methyl methacrylate) (PMMA)) with control over the length of both the backbone and the side chain was synthesized by the coupling reaction of living PMMA with bromomethylated PS. The backbone polymer was prepared by the anionic polymerization of styrene with *n*-butyllithium followed by bromomethylation using $C_8H_{17}OCH_2Br/SnCl_4$. The living PMMA was prepared by the group transfer polymerization of MMA. Graft copolymers with a narrow molecular weight distribution, $D = 1.2 \sim 1.4$ at an $\bar{M}_n$ of around $3 \times 10^4 - 7 \times 10^4$ were obtained. The reactivity of the bromomethylated PS and the living PMMA decreased with increase in their molecular weight; the favoured reaction temperature was −20°C. Characterization of the product was performed by methods including ^1H n.m.r., g.p.c. and d.s.c.. Compared with the homopolymers PS and PMMA, the copolymer had a lower glass transition temperature.

(Keywords: anionic polymerization; group transfer polymerization; living polymer)

INTRODUCTION

Graft copolymers have generally been synthesized either by polymerizing a monomer from initiating sites on a backbone polymer, by polymerization of a macromonomer, or by linking two different polymers through polymer coupling reactions. Although many synthetic methods have been employed for the preparation of graft copolymers, living polymerization techniques are among the most effective and versatile. Living polymerizations allow the maximum amount of control of the synthesis of well-defined macromolecules[1]. For instance, Witkowski[2] synthesized macromonomers which were then copolymerized with styrene using radical methods to give polystyrene (PS)–g–poly(methyl methacrylate) (PMMA); the molecular weight of the PMMA teeth was controlled by group transfer polymerization (GTP). Hertler *et al.*[3] generated GTP initiating sites on cross-linked PS beads prepared from chloromethylated PS; MMA was successfully grafted onto the polymer support with very little formation of ungrafted PMMA.

In some studies, living polymers have been grafted with various multifunctional backbone polymers by means of nucleophilic substitution or nucleophilic addition[4,5]. A halogenomethyl group of the benzylic type is one of the functional groups that has often been used for the preparation of well-defined polymers such as star and graft polymers by means of nucleophilic substitution with living polymers. Sogah *et al.*[6] reported that the alkylation of GTP PMMA with *p*-xylylene dibromide gave a coupled PMMA with twice the original molecular weight. The purpose of the present work was to synthesize well-defined graft copolymers using a combination of living anionic polymerization and living GTP methods. The whole reaction is shown in *Figure 1*.

EXPERIMENTAL

Materials

The GTP initiator and catalyst 1-methoxy-2-methyl-1-trimethylsilyloxypropene (MTS) and tetrabutylammonium bibenzoate (TBABB) were prepared according to the literature[7,8], respectively. Inhibitor-free methyl methacrylate (MMA) of high purity was stirred with calcium hydride for 2 days, and was freshly distilled under reduced pressure before use. Tetrahydrofuran (THF) was purified by refluxing over a fresh sodium benzophenone complex (a deep purple colour indicated a moisture-free solvent). Tris(dimethylamino)sulfonium difluorotrimethylsiliconate (TASF) was obtained from Aldrich. Narrow distribution polystyrene (NDPS) was prepared by polymerization of styrene with *n*-butyllithium in benzene. Bromomethylated polystyrene (BMPS) was prepared by the reaction of NDPS with $C_8H_{17}OCH_2Br$ catalyzed by $SnCl_4$ according to a modification of the method of Warshawsky[9]. The bromine content of the backbone was found to be 20–28% by elemental analysis. The BMPS solution for the coupling reaction was prepared as follows. The weighed BMPS was dissolved in a small amount of benzene that had been distilled in the presence of sodium benzophenone. The solution was freeze-dried for 16 h, and the resulting residue was redissolved in a given volume of THF.

Group transfer polymerization and coupling reaction

A three-necked flask equipped with a stirrer, an argon inlet, a thermocouple and a syringe pump was charged with

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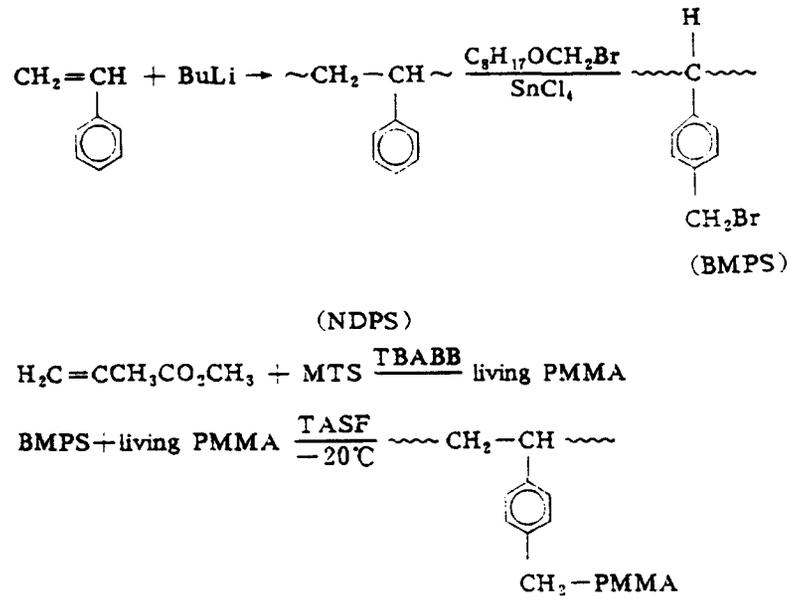

Figure 1 Preparation of PS–g–PMMA graft copolymer

MMA monomer, MTS initiator, and THF as solvent. The TBABB catalyst was then added as a solution (0.2 M) in THF, resulting in a rapid temperature rise to about 68°C during 5 min. After 30 min, a sample was removed for g.p.c analysis. The remaining mixture was cooled to − 20°C and treated with solid TASF for 1 h. BMPS was then added dropwise as a solution in THF. The mixture was stirred at − 20° for 12 h. The reaction product was poured into a tenfold excess of petroleum ether (b.p. 30–60°C) followed by filtration. We found that PMMA up to a molar mass of approximately 10 000 g mol^{-1} is soluble in methanol. Thus, the reaction mixture was then redissolved in THF and precipitated in a tenfold excess of methanol while the PMMA homopolymer remained in the mother liquor. The uncoupled BMPS was removed from the PS–g–PMMA copolymer by Soxhlet extraction with cyclohexane. The separation was confirmed by ^1H n.m.r, g.p.c. and d.s.c.

Measurements

The n.m.r. spectra were recorded on a Varian 500 MHz spectrometer for a 5% (w/v) polymer solution in $CDCl_3$ at 298 K, and tetramethylsilane was used as internal standard. The g.p.c analysis was performed on a Waters 208 instrument in THF, using PS standards for calibration. Elemental analysis was performed on a Perkin-Elmer 240B analyzer. The d.s.c measurement was carried out with a Perkin-Elmer DSC-2 using a scan speed of 10 K min^{-1}.

RESULTS AND DISCUSSION

Synthesis of NDPS

Narrow distribution polystyrene (NDPS) was synthesized by anionic initiation with *n*-C_4H_9Li initiator; the ratio of monomer to initiator controls the average molecular weight of PS. Near- monodisperse polymers were obtained. Details of the synthesis of NDPS are summarized in *Table 1*. Typically, $D = \bar{M}_w/\bar{M}_n$ from g.p.c. was about 1.05.

Preparation of BMPS

Chloromethyl-substituted polystyrenes are the most widely used intermediates in the preparation of resins for solid-phase peptide synthesis, anion-exchange resins and polymer-supported catalysts and reagents. However, for coupling with the sylyl enol ethers of living PMMA, bromomethyl-substituted polystyrenes are more active and suitable. Bromomethyl long-chain alkyl ethers should be treated with care during preparation and handling[10]. Although the BMPS obtained has randomly distributed bromomethyl groups, the percentage of bromine can be controlled by the ratio of PS to $C_8H_{17}OCH_2Br$, the $SnCl_4$ concentration and the reaction time. Typical examples of the bromomethylation of NDPS are shown in *Table 2*.

Group transfer polymerization of MMA

Living PMMA was synthesized by GTP. The living polymer thus obtained had a narrow molecular weight distribution and was still susceptible to further molecular weight increase by the addition of more monomer. The molecular weight of PMMA was controlled by the ratio of monomer MMA to initiator MTS. G.p.c. showed that the MMA polymerized apparently completely in much less than 30 min. The data and results are shown in *Table 3*.

Coupling reaction

In all coupling reactions, a control sample was removed from the living PMMA solution before the addition of the coupling agent BMPS. A comparison of the control with the coupling product enabled us to determine the extent of coupling and the average number of branches. As is shown in *Scheme 1*, the living PMMA prepared by the polymerization of MMA monomer with a ketene acetal in THF was reacted with BMPS using TASF as catalyst. This coupling

Table 1 Data for the anionic polymerization of styrene

Expt. no.	Styrene (g)	BuLi (mol)	$10^{-3}\,\bar{M}_{n,theor}$ [a]	$10^{-3}\,\bar{M}_n$ [b]	D
S-2	42.6	1.42×10^{-2}	3.0	3.21	1.04
S-3	15.3	3.06×10^{-3}	5.0	5.40	1.07
S-5	19.3	2.57×10^{-3}	7.5	7.82	1.05
S-7	38.0	38.0×10^{-3}	10	10.3	1.08
S-8	44.3	2.95×10^{-3}	15	14.7	1.07
S-9	24.0	9.60×10^{-4}	25	27.1	1.10

[a] $\bar{M}_{n,theor}$ = g styrene mol^{-1} BuLi [b] Measured by g.p.c.

Table 2 Bromomethylation of some polystyrenes[a]

Expt.	$\bar{M}_n/D$	[PS]/[$C_8H_{17}OCH_2Br$]	Product	
			%Br	$\bar{M}_n/D$
B-5	7820/1.05	0.2	8.1	9270/1.07
B-6	7280/1.05	0.3	14.8	11780/1.09
B-8	14700/1.06	0.4	21.5	20100/1.10
B-9	27100/1.10	0.4	20.7	37800/1.16

[a]Reaction time, 48 h; 30°C; 3 M solution of $C_8H_{17}OCH_2Br$ in dichloromethane; catalyst, $SnCl_4$, [$SnCl_4$]/[PS] = 0.28

Table 3 Data for the group transfer polymerization of MMA[a]

Expt.	MMA (g)	MTS (10^3 mol)	$10^{-3}\,\bar{M}_{n,theor}$	$10^{-3}\,\bar{M}_n$	D
M-1	5.6	1.87	3.0	3.14	1.08
M-2	7.7	2.57	3.0	3.25	1.06
M-3	9.5	3.17	3.0	3.32	1.12
M-4	10.5	2.63	4.0	4.39	1.08
M-5	12.4	2.06	6.0	6.62	1.19
M-6	15.4	1.93	8.0	8.70	1.16
M-7	18.3	1.83	10.0	10.75	1.26

[a][cat]/[I] = 0.8%

reaction was carried out in the presence of one equivalent of TASF catalyst to a living end of the PMMA. The coupling reaction proceeded homogeneously, and the increase in viscosity of the reaction mixture was observed unequivocally. The recovered graft copolymer was easily soluble in solvents such as THF and benzene. The results obtained under the given conditions are shown in *Table 4*.

As can be seen in *Table 4*, the graft copolymers obtained were shown to have a narrow distribution $D = \bar{M}_w/\bar{M}_n = 1.2\sim1.4$ at an $\bar{M}_n$ of around 30 000–70 000 by g.p.c. analysis. From the g.p.c. analysis of C-1, after 12 h the $\bar{M}_n$ of the copolymer increased to 28×10^4 and the dispersity to 1.3; the living PMMA content had almost completely disappeared, providing unequivocal proof that the living PMMA had coupled with the BMPS. The effect of the molecular weight of the prepolymers on the extent of coupling was investigated by keeping the mole ratio of BMPS to the living end of the PMMA, [CH_2Br]/[LE], at a constant value of 5. It was shown that the reactivity of the BMPS and the living PMMA decreases with increase of their molecular weight. The coupling reaction would indeed be affected by the resistance of chain interpenetration, which would become more pronounced with increasing chain length[11]. As the amount of living ends of PMMA is increased, the number of PMMA branches of the backbone polymer BMPS also increases, but the yield decreases. When the [CH_2Br]/[LE] mole ratio is increased, the yield of the product increased. If some losses arising from the isolation step of the graft compolymers are taken into consideration, the result is satisfactory. With regard to the reaction temperature, it has been reported that the carbanion formed from the cleavage of the silyl group from the ketene silyl acetal is unstable at high temperature, so the reaction must be carried out at -78°C[6]. Although our experiments were carried out within the range -78–50°C, we observed that the yield was high at lower temperatures, being most favourable at -20°C. The reaction yield was only 10% at 50°C when the reaction conditions were almost the same as those of experiment C-2. This supports the postulate that at low temperature, side reactions are suppressed.

Characterization of the products

The coupling reaction was carried out in homogeneous solutions in order to obtain soluble PS–g–PMMA graft copolymers. In this case, the removal of homopolymers from the graft copolymer was not so easy. We adopted a selective precipitation and conventional extraction method mentioned in Section 2.2. ^{1}H n.m.r. establishes the presence of PS and PMMA species as well as an uncoupled bromomethyl group (δ 4.4~4.5, broad). From the ratio of bromomethyl to aromatic proton before and after the reaction, the extent of the coupling reaction can also be calculated.

In order to demonstrate that the desired coupled product was obtained, the g.p.c. curves of the polymers (experiment C-3) recorded during the coupling reaction are shown in *Figure 2*. It can be seen that the elution peak of the coupled product shifts to the left compared with the initial BMPS and PMMA. The concentration of prepolymers decreases with increasing coupling reaction time. It is also important to determine whether further reaction time could allow the production of more fully developed graft copolymers without any residual living PMMA, from the g.p.c. curve.

For the characterization of the graft copolymers, the average branching functionality f must be known. The relationship

$$f = \frac{\bar{M}_{n,\text{product}} - \bar{M}_{n,\text{BMPS}}}{\bar{M}_{n,\text{living PMMA}}}$$

was used to calculate f from the g.p.c. data for the graft polymers. In the g.p.c. curves, the graft polymer and the uncoupled living PMMA or BMPS were distinguished easily owing to the great difference in their molecular weight which arose from the high degree of coupling. The results obtained from g.p.c are shown in *Table 4*.

Table 4 Coupling reaction between living PMMA and BMPS[a]

Expt.	Living PMMA solution			BMPS solution			[CH_2Br]/	Products		
	[LE] (mol l^{-1})	Vol. (ml)	$\bar{M}_n/D$	[CH_2Br] (mol l^{-1})	Vol. (ml)	$\bar{M}_n/D$	[LE]	Yield (%)	f	$\bar{M}_n/D$
C-1	0.17	9.5	3140/1.08	1.13	14.3	20100/1.10	10	92.5	2.5	28070/1.32
C-2	0.16	13.8	3250/1.06	1.2	9.2	20100/1.10	5	89.2	5.4	37800/1.37
C-3	0.15	18	3320/1.12	1.0	5.4	20100/1.0	2	64.6	7.5	45100/1.25
C-4	0.125	18.2	4390/1.08	1.25	9.1	37800/1.16	5	83.7	4.7	58430/1.31
C-5	0.067	27.1	6620/1.19	1.01	9.0	37800/1.16	5	78.1	3.8	62798/1.42
C-6	0.054	37.9	8700/1.16	0.94	9.2	37800/1.16	5	61.0	3.7	70560/1.37
C-7	0.023	72.0	10750/1.26	0.92	9.0	37800/1.16	5	50.6	3.4	74840/1.45

[a]Reaction time, 12 h; reaction temperature, -20°C; [TASF]/[LE] = 1

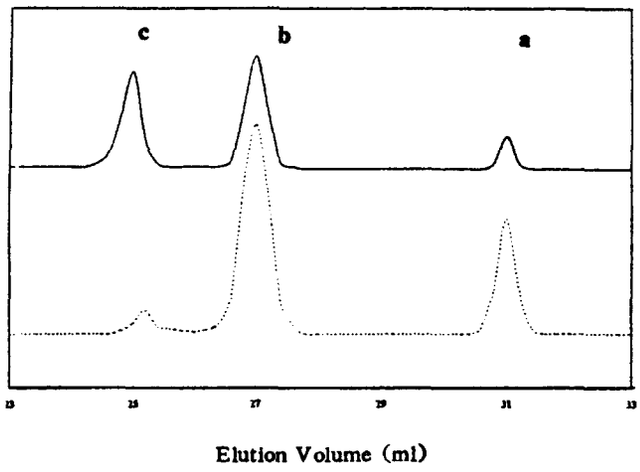

Figure 2 G.p.c. curve of the polymers obtained in experiment C-3. Peak a: PMMA, $\bar{M}_n = 3320$; peak b: BMPS, $\bar{M}_n = 20\,100$; peak c: coupled product, $\bar{M}_n = 45\,100$. Coupling reaction time: · · ·, 0.5 h; ——, 4 h

Table 5 Glass transition temperature of PS–g–PMMA and the corresponding homopolymers

Expt.	Polymer	T_g (°C)	
1	BMPS ($\bar{M}_n = 2.01 \times 10^4$, 21% Br)	76	–
2	PMMA ($\bar{M}_n = 3.14 \times 10^3$)	–	50
3	PS–g–PMMA ($\bar{M}_n = 2.8 \times 10^4$, 27.7% PMMA)	70	41
4	PS–g–PMMA ($\bar{M}_n = 3.8 \times 10^4$, 21.5% PMMA)	72	40
5	BMPS ($\bar{M}_n = 3.78 \times 10^4$, 20.7% Br)	79	–

The results obtained by d.s.c are shown in *Table 5*. It is found that the glass transition temperatures (T_g) of PS–g–PMMA and the corresponding homopolymers are lower because of lower molecular weights. On the other hand, an uncoupled bromomethyl group might also reduce the T_g of the copolymer. Both glass transition temperatures found for the graft copolymer are lower than those for the corresponding homopolymers. A similar reduction of T_g has been reported by Graham[12] for the poly(butyl methacrylate)–PS graft copolymer.

CONCLUSION

This preparative method has the advantage of yielding graft copolymers well characterized as to the length of the PS backbone, its over-all molecular weight, and the length of the side chains. By this method, a wide variety of graft copolymers composed from a polar monomer and a non-polar monomer can be prepared, with control over the length of both the backbone and the side chain.

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