

Synthesis of MMA/GMA graft and random copolymers by melt and solution copolymerization

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Abstract:

In this study Poly(MMA-g-GMA) copolymers was prepared via reactive blending of PMMA and GMA using benzoyl peroxide (BPO) and dicumyl peroxide (DCP), and Poly(MMA-ran-GMA) was synthesized by solution copolymerization of methyl methacrylate (MMA) and glycidyl methacrylate (GMA), using benzoyl peroxide (BPO), as initiator. In order to compare synthesis methods, we evaluate the effect of several items on the chemical composition including the weight percent of MMA and GMA and the initiator concentration.

Chemical compositions were determined qualitatively using FT-IR spectroscopy and quantitatively by titration by estimation of the epoxy content of GMA units. It could be concluded that the MMA/GMA copolymers have been successfully synthesized using both melt and solution copolymerization methods but with different efficiency. Accordingly the percentage of GMA comonomer units could be increased by increasing its fraction in the feed.

Keywords: Copolymerization; grafting efficiency; GMA; MMA

Introduction:

Poly methyl methacrylate (PMMA) has been used in many applications but, in general, its use is limited by its lack of functional groups. Thus, functionalization reactions have been used to increase its interfacial interactions. The grafting process is one of the methods most frequently used to modify polymers[1]. Graft polymerization by hydrogen abstraction from tertiary carbon or make free radicals with chain scission of backbone offers an effective approach to introducing some desirable properties into the polymers, but for expanding its applications we need the first method without affecting the backbone architecture[2]. Using benzoyl peroxide (BPO) or dicumyl peroxide (DCP) as initiator and GMA as monomer, the copolymerization process occurs via a free-radical mechanism, through the scission of the double bond in the GMA. The detailed mechanism of GMA grafting in a saturated polymer using BPO as initiator was described elsewhere (before)[3]. It was observed that grafting does not modify the epoxy ring of the GMA, maintaining its reactivity in the final product. Some authors have used this reactivity to attach molecules with specified properties. This process clearly make some reactions possible (e.g. ring opening epoxide with carboxyl, amine...)[4]. These stabilizers were attached to the GMA epoxy groups protecting the polymer from most of the UV irradiation (improving degradation stability).[5]

The aim of this work was the functionalization of poly methyl methacrylate by a process of free radical grafting with glycidyl methacrylate using benzoyl peroxide and dicumyl peroxide as initiator in an internal mixer and it occur in other method i.e. solution polymerization. We studied some factors involved in the grafting process such as initiator and copolymerization method, then evaluated the reactivity of the GMA epoxy group after its grafting onto PMMA.

Experimental:

Material:

Pellets of PMMA (Acrylic EG920, supplied by LG Co., Korea) dried at 70°C for 12 hours and kept in vacuum. Glycidyl methacrylate (GMA, Sigma-Aldrich), methyl methacrylate (MMA, Merck) and the initiator benzoyl peroxide (BPO, Merck) and dicumyl peroxide (DCP, Merck) and solvents i.e. methanol, 1,4 dioxane (Merck) were used as received.

Grafting process:

First of all copolymerization process was occurred in solution copolymerization it would be resulted a random copolymer i.e. Poly (MMA-ran-GMA) using 0.5ml GMA, 4.5 ml MMA and 0.5 g BPO dissolved in 50 ml 1,4 dioxane then mixed heated at 90°C by a heater-stirrer for 2 hour.

The copolymer was precipitated by addition of methanol as a non-solvent. After that the products was tested by FT-IR and titration and normalized the height of peak to measuring the grafting percentage for the other samples by the PGMA that was synthesized by this method and pure GMA and BPO as an initiator that was dissolved in 1,4 dioxane. Grafting GMA onto PMMA in melt mixing and characterization is the next step. Grafting was occurred in internal mixer for 10min at 185°C and 60 rpm for 10wt% and 6wt% of GMA and 1g BPO and 1g DCP separately. In the following step the productions was washed in 1,4dioxane and methanol to extraction of extra monomer and was dried at 50°C for 24 hour under vacuum. Then the productions was characterized by FT-IR. Samples' information are shown in Table1.

Table1. Samples Information

Sample	GMA wt. %	PMMA(MMA) wt. %	Initiator	(Co)polymerization method
PMMA	0	100	-	-
PGMA	100	0	BPO	Solution Radical Polymerization
PGMS10	10	90	BPO	Solution Radical Copolymerization
PGMM10	10	90	BPO	Melt grafting Copolymerization
PGMMD10	10	90	DCP	Melt grafting Copolymerization
PGMM6	6	94	BPO	Melt grafting Copolymerization

Results and Discussion:

The precipitation of solution polymerization of GMA was dried in 70°C under vacuum and its weight was measured about 4g it means the conversion was 80%, then FT-IR spectroscopy's result is shown in Figure1(a), the peak of wavenumber 910 belongs to epoxy group and the peak of 1724 cm⁻¹ shows the methacrylate group in this case we should normalize other samples by 910 cm⁻¹ because 1724 cm⁻¹ is visible for both PMMA and GMA; pure PMMA (EG920) is washed as the same method and FT-IR spectroscopy's result is shown in Figure1(b).

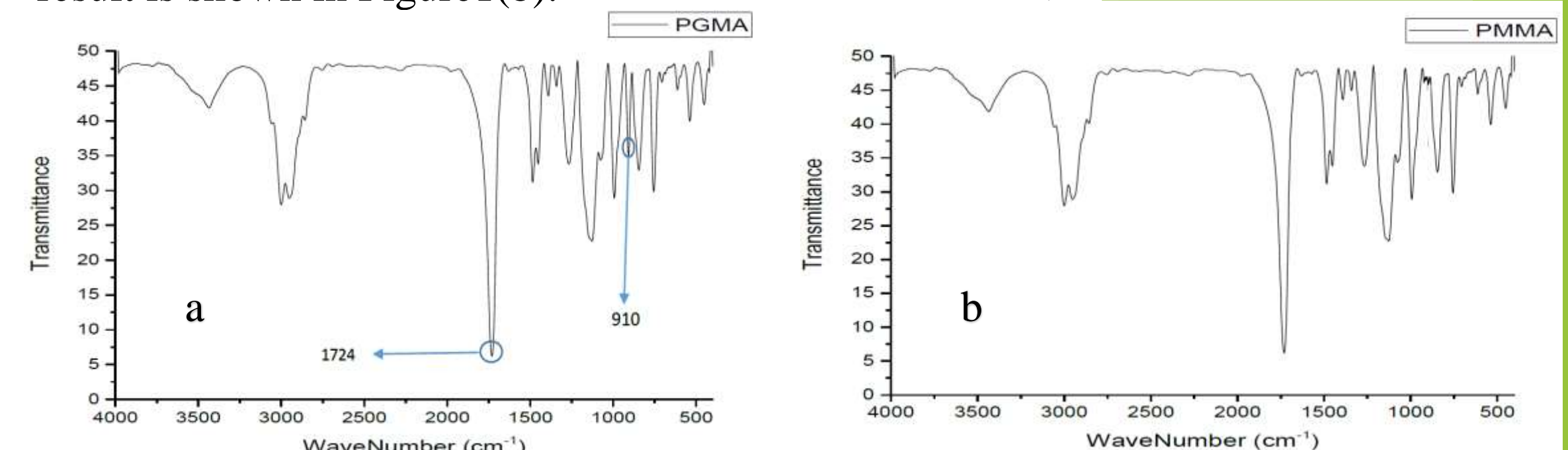


Figure1. Pure Polymers FT-IR Spectroscopy, PMMA(a), PGMA(b)

We titrated 0.5 g of PGMA and used the information for normalize other samples as 100%. Other samples tested by FT-IR Spectroscopy too.

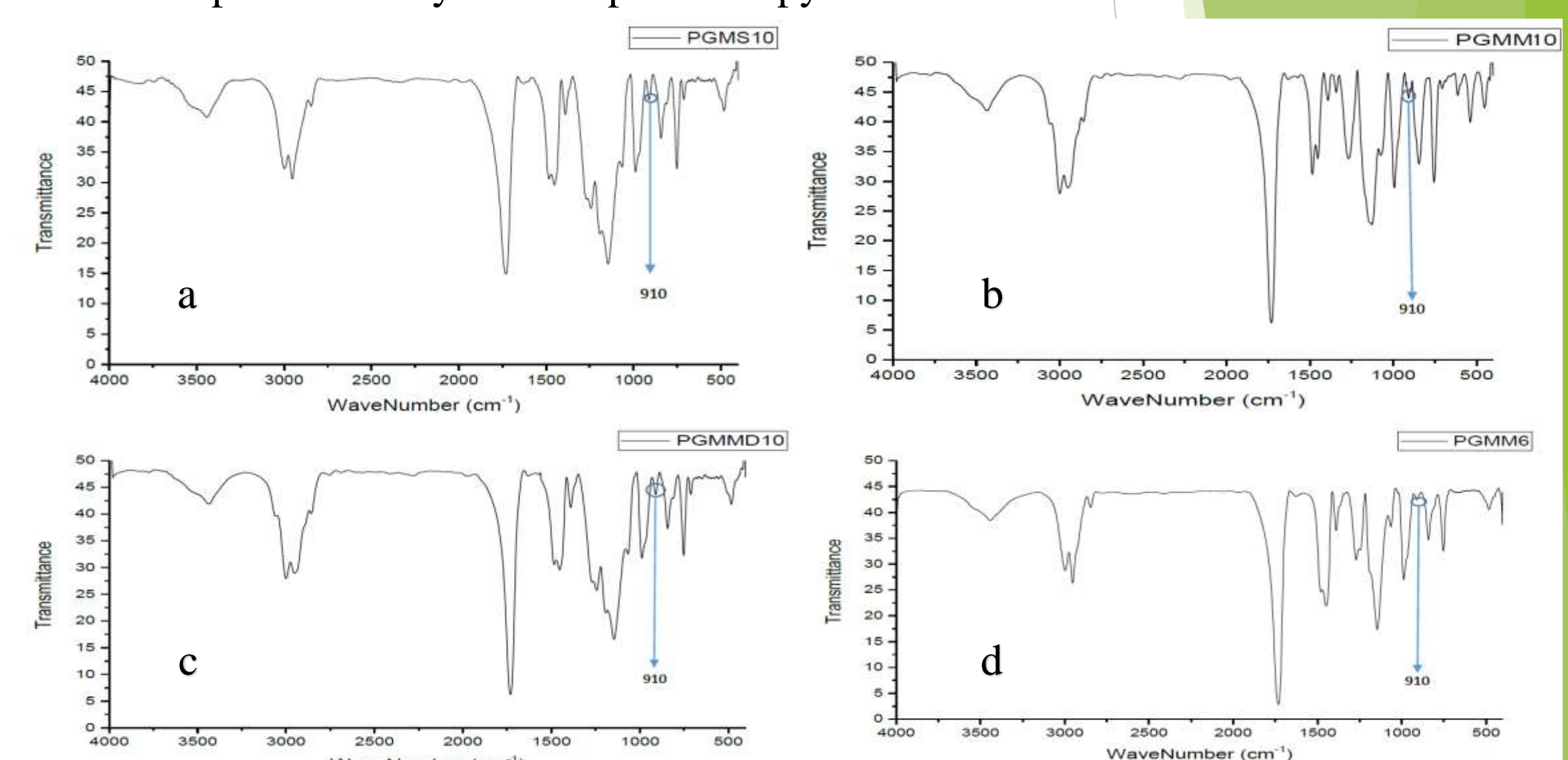


Figure2. Copolymers FT-IR Spectroscopy, 10wt.% Solution(a), 10wt.% Melt grafting with BPO(b), 10wt.% Melt grafting with DCP(c), 6wt.% Melt grafting with BPO(d)

According to these figures and titration's results we can measure grafting percentage of GMA or presence of GMA in the backbone of Poly (MMA-co-GMA), results is shown in Table2.

Table2. Efficiency of grafting

Sample	Grafting (presence)percentage	Efficiency %
PGMS10	~10	100%
PGMM10	~7.5	75%
PGMMD10	~7.8	78%
PGMM6	~4.1	69%

The efficiency increased by increasing the GMA fraction in the feed, we think the reason is the possibility of collision of GMA radicals and MMA macro-radicals together increased by increasing of GMA fraction. In melt grafting, grafting efficiency increased with changing the initiator from BPO to DCP maybe it's caused by longer half-life of DCP at 185°C under shear fields.

Conclusion:

Poly (MMA-co-GMA) was synthesized via solution radical polymerization and Poly (MMA-g-GMA) was grafted via melt mixing technique and use BPO and DCP to initiate the free radical grafting reaction. The results showed that increasing the GMA fraction increase the efficiency of grafting because of more possibility of collision of GMA radicals and MMA macro-radicals and more efficiency with increasing the half-life of initiator.

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