Grafting of Carboxyl Terminated Polymethylmethacrylate onto Polystyrene-hydroxyethylmethacrylate Copolymer Backbone

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Summary: Carboxyl terminated polymethylmethacrylate (PMMA) polymers were grafted onto polystyrene-hydroxyethylmethacrylate (Sty-HEMA) copolymer backbone by condensation reaction between the hydroxyl groups bearing copolymers backbone and the carboxyl terminated PMMA polymer chain. Grafted products were characterized by the Gel Permeation Chromatography (GPC) using UV and RI detectors, Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared (FTIR) spectroscopy.

Introduction

Interest in the graft copolymers has increased over the years owing to their diverse applications as adhesives, surface coating agents, surface modifying agents, stabilizers, dispersants, emulsifiers and compatibilizers in polymer blends [1-3].

A number of methods are reported in the literature for the synthesis of graft copolymers [4-8]. In these methods the grafts on the backbones were introduced either by polymerizing a monomer on the already existing active sites or by generating these sites. The disadvantages of these methods are the contamination of graft copolymer with homo-polymers and the difficulties involved in characterisation of the newly synthesised product [8].

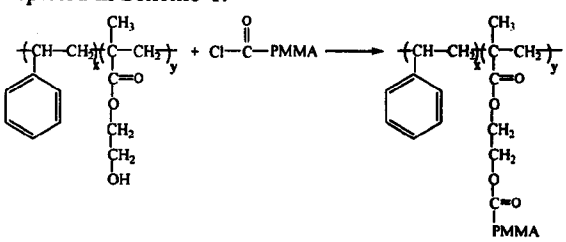
The aim of this work was to develop a method for the preparation of graft copolymers to avoid such difficulties. It was considered worthwhile to synthesise carboxyl terminated PMMA prepolymer separately and condense onto a Sty-HEMA copolymer backbone bearing pendant hydroxyl groups. A major advantage of this method is that the two reactants a backbone and the side chain can be synthesised and characterized separately prior to grafting reaction, which facilitates considerably the analytical identification of the grafted products.

Methylmethacrylate (MMA) was chosen to synthesise carboxyl terminated prepolymer. Thompson & Waite [9] reported the preparation polymer chain bearing a single carboxyl group by a technique in which a solution polymerization of a monomer was performed using matched initiator and chain transfer agent. PMMA prepolymer was selected since MMA radical chain polymerization terminates by disproportionation, so that the matched chain transfer method produced chain close to 100 % mono-functionality [10].

Styrene (Sty) and HEMA were used to prepare copolymer backbone because, the monomer reactivity ratios of styrene (0.68) and HEMA (0.64) in 2-ethoxyethanol at 60 °C have been reported [11]. Since monomer reactivity ratios of both monomers are ≤1, this shows that each radical has a preference to react with the other monomer rather than its own, therefore the copolymer composition should not vary far from the monomer feed composition.

Results and Discussion

The grafting of acid chloride terminated PMMA onto a poly (Sty-HEMA) backbone is depicted in Scheme-1.



Scheme-1: Preparation of poly (Sty-HEMA)-g-PMMA copolymer.

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Gel Permeation Chromatography (GPC) was used for the comparison of chromatograms of precursor, Sty-HEMA copolymers and grafted products and for the determination of molar masses of the Sty-HEMA copolymer and graft copolymers. GPC was performed at room temperature with THF as eluent using dual RI and UV detectors attached to the GPC system. The UV response of UV detector is only due to Sty units while the HEMA and MMA units are transparent to UV. Comparison of typical chromatograms of precursor copolymer and graft copolymer is given in Fig. 1.

The upper traces represent a UV response and lower traces represent a RI response in terms of concentration of copolymers respectively. The shift of chromatogram towards low elution volume (retention volume) of a graft copolymer compared to Sty-HEMA copolymer indicates a change in the molar mass of the graft copolymer. The reduction in peak heights of UV and RI responses in the graft copolymer compared to the precursor Sty-HEMA copolymer can also be observed and can be used qualitatively to judge graft copolymer formation. The decrease in UV peak height is expected from the incorporation of non-UV absorbing methacrylate units onto a backbone consisting mainly of styrene units which are UV absorbing. There are reports [12, 13] in which GPC equipped with UV and RI detectors in series have been used to confirm the success of grafting reactions. From the chromatogram in Fig. 1 it is observed that the peak height ratio defined as a UV/RI ratio decreases by graft copolymer formation, and so values of ratio can provide guideline to the extent of grafting. The molar masses of the graft copolymers are presented in Table-1. The increase in molar mass of the graft copolymers compared to the precursor and decrease in the UV/RI ratio support the success of grafting reaction. The molar masses of the graft copolymers are polystyrene equivalents and are obtained from a calibration curve based on linear polystyrene standards. Graft copolymers have a branch structure, and as a result their hydrodynamic volume will be smaller than for linear polymer with the same molar mass which will affect their GPC elution behavior. GPC separates on the basis of hydrodynamic volume and the molar masses of the graft copolymer obtained could be lower than the actual values. Drott and Mendelson [14] have compared the calibration curves of several branched polystyrene samples with linear polystyrene samples and obtained a similar calibration curve for both types of samples. They concluded that the branching effect becomes significant only at higher molar masses (above 10^4 g mol^{-1}). The graft copolymers prepared here are within the range of these molar masses and it is quite possible that in a GPC column the branching effect is

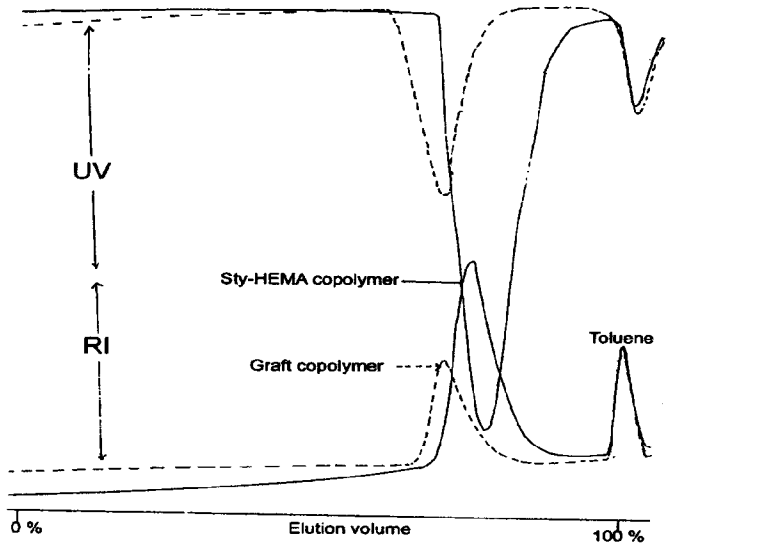

Fig. 1: Comparison of chromatogram of a typical poly (Sty-HEMA)-g PMMA with Sty-HEMA copolymer.

Table-1: Comparison of molar masses & UV/RI peak ratios of precursor Sty-HEMA copolymers and poly (Sty-HEMA)-g-PMMA copolymer obtained by GPC.

Sample code	Mn (PMMA) end group	Mn (Sty-HEMA) copolymer GPC	UV/RI (Sty-HEMA) copolymer	Mn (Graft copolymer) GPC	UV/RI (Graft copolymer)
SH1	1500	8200	2.05	40000	1.5
SH2	2000	8200	2.05	37000	1.7
SH3	3000	8200	2.05	29000	1.8
SH4	4400	8200	2.05	33000	1.8

less significant for these copolymers. Therefore, the molar masses obtained are likely to be close to the actual values.

The IR spectrum of the graft copolymer is given in Fig. 2. It shows a band at 1730 cm^{-1} due to carbonyl esters present in HEMA and MMA units. The two bands of a monosubstituted benzene ring appeared at 750-650 cm^{-1}. The C-H stretching due to HEMA and MMA units appeared at the same region 2960-2850 cm^{-1} and is difficult to differentiate. However disappearance of the significant broad band at 3300-3600 cm^{-1} due to O-H groups strongly indicates the replacement of these groups by PMMA side chains.

The NMR spectrum of a graft copolymer is presented in Fig. 3, which shows significant chemical shifts due to Sty-HEMA copolymer and PMMA side chains. The chemical shift due to five aromatic protons (a) in Sty. units appeared at δ = 6.5 ppm, the methyl ester $-COOCH_3$ protons (b) resonate at δ = 3.5 ppm, $-(CH_2)-$ protons (c) in Sty. units and HEMA units resonate at δ = 1.5 ppm, while $-(CH_2)-$ protons(d) in MMA units appeared at lower value of δ 1.2 ppm., $-CH_3$ protons (e) in MMA appeared at δ = 1.1 ppm and $-(CH_2)-$ protons (f) in HEMA appeared at δ = 1.0 ppm. These important chemical shifts of the copolymers together with the changes in the molar massed found by GPC suggest a graft copolymer structure of Sty-HEMA backbone and PMMA side chains. The composition of the graft copolymer was determined by comparing the integration height of five aromatic protons in Sty with the integration heights of the total protons present in the spectrum, and hence moles of MMA units in graft copolymer were determined. The graft copolymer compositions determined are shown in Table-2. The mole fraction of MMA and % grafting indicates a level of graft incorporated in the product.

Graft copolymers were synthesized by the coupling reaction between acid chloride terminated prepolymer and hydroxyl containing copolymer backbone. It is possible that this condensation reaction produces graft copolymers of a different architecture; for $-COOCH_3$ groups to undergo a transesterification reaction. It has been presumed that carboxyl terminated prepolymers have been converted to acid chlorides which are far more reactive than ester groups and therefore, the side reactions are minimum. However, these transesterification reactions are catalysed by acid media and it could be possible for the HCl, eliminated during the coupling reaction may have catalysed such reactions.

The chromatograms of the resultant product for confirming the possibility of any side reaction of MMA (Fig. 4) did not show any change in

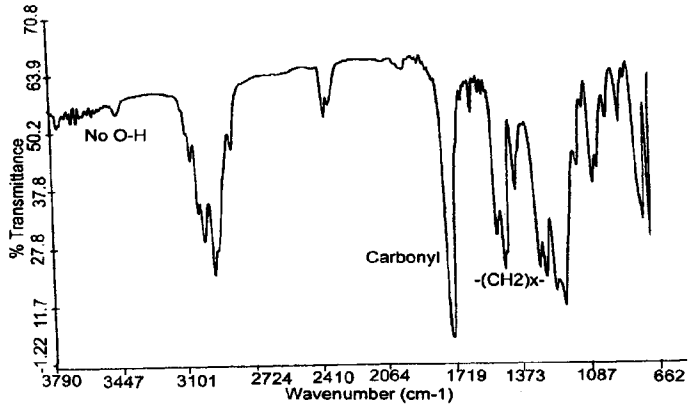

Fig. 2: A typical IR spectrum of poly (Sty-HEMA)-g-PMMA copolymer.

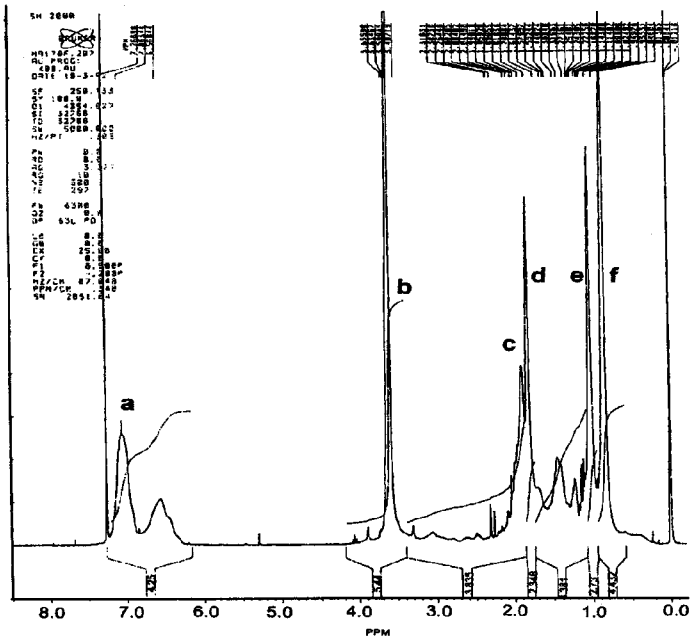

Fig. 3: A typical ^1H NMR spectrum of poly (Sty-HEMA)-g-PMMA copolymer.

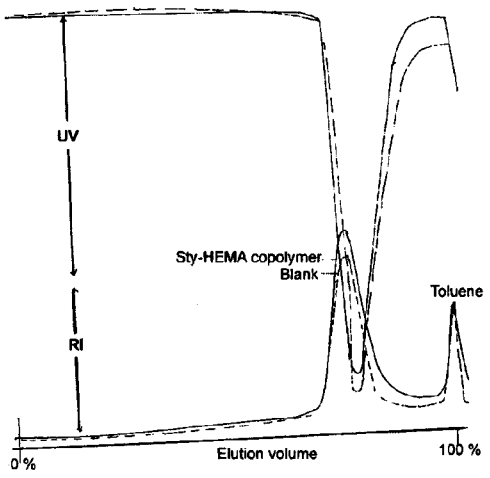

Fig. 4: Comparison of chromatograms of Sty-HEMA copolymer and a reaction product of butanethiol terminated PMMA with Sty-HEMA copolymers.

UV/RI ratio and in molar mass, which suggested that the change in the molar masses and UV/RI ratio are not due to any such side reactions but in fact due to coupling reactions between acid chloride terminated PMMA and hydroxyl groups on the Sty-HEMA copolymer backbone.

Table-2: Composition of poly (Sty-HEMA)-g-PMMA copolymer and grafting %.

Sample code	Mol. Fraction (Sty) in Graft copolymer (NMR)	Mol. Fraction (HEMA) in Graft copolymer by (NMR)	Mol. Fraction of (MMA) in Graft copolymer by (NMR)	% Grafting
SH1	0.735	0.10	0.165	61
SH2	0.77	0.105	0.125	41
SH3	0.835	0.11	0.55	32
SH4	0.835	0.115	0.050	43

Experimental

Materials

2-ethoxyethanol, 99 % pure, was used as supplied by Aldrich Chemical company Ltd. 4,4-azobis (isobutyronitrile) (AIBN) was used as supplied, 4,4-azobis (cyanovaleric acid) (ACVA) was used as supplied by Aldrich. Butanethiol, was used as supplied by Aldrich, 2-hydroxyethyl methacrylate (HEMA) was supplied by Aldrich, was inhibited with 300 ppm hydroquinone monoethyl ether dried over anhydrous magnesium sulphate before it was used. Methyl methacrylate (MMA) was obtained from

Aldrich, 99 % pure and inhibited with 100 ppm hydroquinone monoethyl ether, purified by vacuum distillation at room temperature before use. Oxalyl chloride, 98 % pure was supplied by Aldrich and was used as supplied. Styrene was obtained from Aldrich, 99 % pure, inhibited with 10-15 ppm 4-ter-butyl catechol, purified by vacuum distillation at room temperature before use. Mercaptoacetic acid, (thioglycollic acid) (TGA), 95 % pure was used as supplied by Aldrich.

Procedure

Carboxyl terminated prepolymer of PMMA was synthesised by solution radical polymerization. In order to prepare a carboxyl terminated prepolymer of Mn 1500 g mol^{-1} (determined by end group analysis), the reaction scheme was followed as. In a three necked round bottom flask (250 ml) containing nitrogen inlet and reflux condenser, monomer (3.96 mol/lit) mixed with TGA (0.59 mol) in (100ml) ethyl acetate as polymerization solvent. After purging with nitrogen for 15 minutes ACVA (0.028 mol/lit) was added and the flask was transferred to a thermostated water bath maintained at 80 °C. The polymerization time was 2 hrs. The polymer was isolated by evaporating the ethyl acetate solution. Impure polymer was dissolved in a minimum amount of methanol and was precipitated in an excess of distilled water. PMMA was precipitated as a white viscous material. Further purification was carried out by redissolving polymer in a minimum quantity of hot methanol and reprecipitation in distilled water which was repeated two further times. Finally, all the purified polymers were dried in a vacuum oven, initially at 100 °C for 2-3 hrs to remove traces of water, and then at 60 °C overnight. Carboxyl terminated prepolymer were converted to acid chloride by reaction with oxalyl chloride. The prepolymer (equal to the mol. of HEMA present in the Sty-HEMA copolymer backbone) as a (5 % w/v) solution in dry toluene was placed in a three necked round bottom flask (100 ml), equipped with a silica-gel drying tube. The oxalyl chloride twice the required molar concentration of the polymer was added. The solution was first cooled in an ice bath followed by stirring at room temperature for 24 hrs. The unreacted oxalyl chloride was distilled off under vacuum at room temperature. The conversion of carboxyl group to acid chloride was confirmed by IR spectroscopy.

Sty-HEMA copolymer backbones having hydroxyl groups were synthesised by copolymerising styrene and HEMA monomers. The monomer feed ratio was determined from the copolymer equation as reported [15-19]. The monomers Sty and HEMA were copolymerized in 2-ethoxyethanol using AIBN as initiator. In a three necked round bottom flask (250ml) equipped with nitrogen inlet and reflux condenser, the monomers were mixed and added to the polymerising solvent 2-ethyoxyethanol. The nitrogen purge was for five minutes, and the flask was transferred to a thermostated water bath maintained at 60 °C. The polymerisation was allowed to proceed for 6 hrs. After the polymerisation the reaction was cooled and poured into chilled petroleum ether (40:60). The copolymer was isolated as a viscous liquid which settled at the bottom of the flask. The petroleum ether was decanted off. The copolymer was purified by dissolution in a minimum amount of toluene and precipitated in chilled cyclohexane. Further purification was performed by redissolving copolymer in a minimum amount of chloroform and reprecipitating in chilled methanol. This procedure was repeated three times. Finally, the pure copolymer was dried in a vacuum oven at 60 °C overnight.

Sty-HEMA Graft Copolymer

A (5 % w/v) solution of PMMA acid chloride in dry toluene was placed in three necked round bottom flask (250 ml) fitted with reflux condenser and silica gel drying tube. A (2 % w/v) solution of St-HEMA copolymer in dry toluene was added to the PMMA acid chloride solution with a dropping funnel. The mixture was allowed to reflux for 24 hrs at 110 °C under constant stream of nitrogen; the conditions of high temperature and nitrogen stream through out the reaction mixture are recommended for HCl removal to complete the reaction [20]. After the reaction the mixture was cooled and impure graft copolymer was isolated by pouring into chilled n-hexane. The unreacted PMMA was removed by dissolving impure graft copolymer in a minimum quantity of chloroform and precipitating in chilled methanol. This redissolution/ precipitation procedure was repeated five times. The purified graft copolymer was dried in a vacuum oven at 60 °C for 24 hrs.

For studying the possibility of side reactions, MMA was polymerised in the presence of

initiator (AIBN) along with butanethiol. This PMMA was reacted to the St-HEMA copolymer backbone under the similar conditions in the presence of organic acid catalyst p-toluene sulphonic acid. The resultant product was analysed by GPC.

Conclusions

Synthesis of graft copolymers by onto process can be achieved by the use of a matched chain transfer method to synthesise a prepolymer chain with terminal functional groups and by condensing with copolymer backbone having hydroxyl groups. Dual detector RI and UV attached with GPC can be used to establish the success of a grafting reaction by comparing the UV/RI peak ratios.

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