e-Polymers **2007**, no. 096

http://www.e-polymers.org
ISSN 1618-7229

Synthesis and characterization of poly(ethylene-vinyl alcohol)-g-poly(phenyl ethyl methacrylate) copolymers by a grafting onto method

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(Received: 25 May, 2007; published: 5 September, 2007)

Abstract: Graft copolymers of poly(ethylene-vinyl alcohol)-g-poly(phenyl ethyl methacrylate) copolymers were prepared by a grafting onto method in two steps. In the first step carboxyl terminated poly(phenyl ethyl methacrylate) (PPHETMA) were prepared by solution radical polymerization using 4,4-azobis(cyanovaleric acid) (ACVA) as initiator and thioglycolic acid (TGA) as matched chain transfer agent and then converting carboxyl groups into acid chloride terminated prepolymer by reacting with oxalyl chloride. In the second step acid chloride terminated prepolymers were reacted to the ethylene-vinyl alcohol (EVOH) backbone. Grafting was confirmed by Size Exclusion Chromatography (SEC), Fourier Transfer Infrared spectroscopy (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopy. Thermal properties of the graft copolymers were studied by Differential Scanning Calorimetery (DSC) and Dynamic Mechanical Thermal Analysis (DMTA).

Introduction

Graft copolymers are important polymeric materials due to many applications as adhesives, surface coating agents, surface modifying agents, stabilizers, dispersants, emulsifiers and compatibilizers in polymer blends [1-3]. This class of copolymers has backbone and side chain of different chemical nature which is bonded by a covalent bond [4].

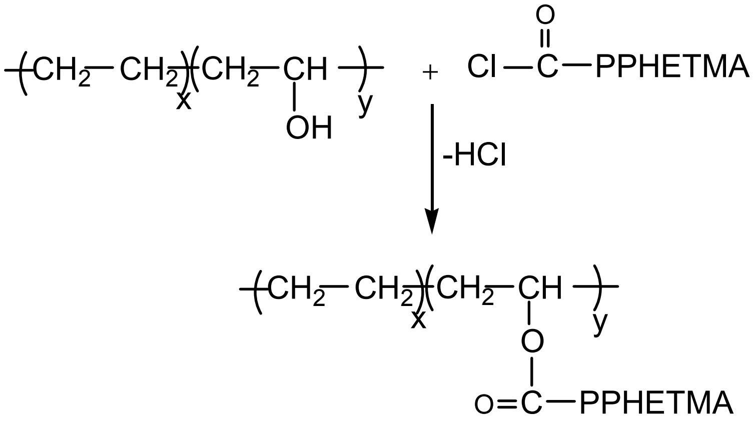
A number of methods have been reported in the literature for the synthesis of graft copolymers [5]. Two of these are grafting-from and grafting-through methods which involves chain reaction polymerization of a monomer or in the presence of a macromonomer capable of copolymerization with the monomer. The most controlled grafting-from process is exemplified by the formation of active sites on a polysaccharide chain by oxidation with a transition metal compound [6]. Copolymerization with macromonomers as a grafting-through process is considered to be effective for the preparation of well defined comb copolymers [7, 8].

The third process defined as grafting-onto involves a reaction between two polymers; one is a backbone containing functional groups together with a terminal reactive group on a polymer which will form the grafted chain. A major advantage of a grafting-onto process is that the polymeric reactants can be characterized separately prior to grafting, which facilitates considerably the analytical identification of the grafted products. Ethylene-vinyl alcohol copolymer (EVOH) has invoked particular interest. There are examples of modification of EVOH by conventional esterification to produce a polyethylene chain backbone with attached carboxyl groups [9], phthalate derivatives [10] and side chains of stearly groups [11], methyl methacrylate [12], lactic acid [13] and caprolactone [14, 15].

The aim of this work was to investigate modification of EVOH by reaction with a linear prepolymer having a terminal functional group. Monofunctional prepolymers based on polystyrene have been grafted onto various chain backbones [16, 17]. Addition prepolymers comprising a terminal group participating in a grafting-onto process may be prepared by a chain reaction polymerization with functionalized initiator and chain transfer agent [18, 19]. In this work PPHETMA was chosen since PPHETMA in radical chain polymerization terminates by disproportionation, so that the matched chain transfer method produced chains close to 100 % functionality.

Results and discussion

The EVOH copolymers resulting from hydrolysis of Ethylene-vinyl acetate (EVA) precursors were characterized by IR spectroscopy. Complete hydrolysis was established by observing the complete disappearance of the absorption band for carbonyl at 1743 cm^{-1} (absent in EVOH) and the appearance of the band for hydroxyl at 3350-3500 cm^{-1}. For partial hydrolysis of EVA to produce a terpolymer of ethylene-vinyl acetate-vinyl alcohol, the composition was established by quantitative IR calibrated at 1743 cm^{-1} for the concentration dependence of absorbance with homopolymers of poly(vinyl acetate), which also served to confirm the vinyl acetate (VA) contents of EVA precursors. The grafting of acid chloride terminated PPHETMA onto a EVOH backbone is depicted in scheme 1.



Scheme. 1. Preparation of poly(ethylene-vinyl alcohol)-g-PPHETMA.

GPC was used to establish the change in the molar masses of graft copolymer products with respect to the precursor samples. The parent EVA samples were use for comparison. The EVA was preferred to EVOH, because ester based segments in the precursor and product both are in good solvent environment in hot o-dichlorobenzene and so both copolymer types should exhibit size exclusion separation behaviour with little or no adsorption onto polystyrene gel in a GPC column. EVOH is a much more polar polymer and its retention may depend on interaction effect involving pendant hydroxyl groups with the column gel. It has been established that the separation of small molecules by GPC can be perturbed by an interaction mechanism involving polar groups such as –OH [20]. It is possible that polymers bearing –OH groups in some solvents might separate by both size exclusion and adsorption mechanisms. Consequently, it appeared unsatisfactory to use GPC of EVOH samples to establish molar mass changes for grafted products. It was preferred for the comparison to use GPC data of precursor EVA samples since samples of EVA in o-dichlorobenzene or trichlorobenzene separate in GPC at high temperature by size exclusion with minimum adsorption problem, as confirmed by the validity of the universal calibration principle in GPC for EVA [21]. It is therefore assumed that the grafted product will also separate in GPC by size exclusion with o-dichlorobenzene at 140 ^{0}C.

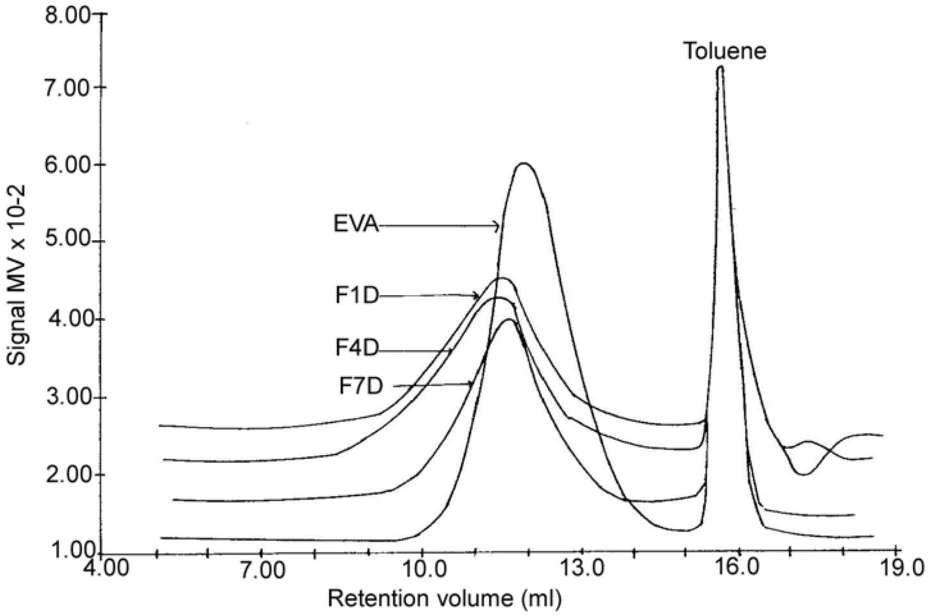


Fig. 1. Comparison of IR chromatograms of EVA precursor with series of Poly(ethylene-vinyl alcohol)-g-PPHETMA.

Tab. 1. Comparison of number average molar masses of precursors and graft copolymers.

Sample code	Mn PPHETMA end group	Mn EVA GPC	Mn EVOH GPC	Mn graft copolymer GPC
F1D	1800	18000	12000	55000
F4D	3000	18000	12000	42000
F7D	4000	18000	12000	44000
F2D	1800	17000	10000	82000
F5D	3000	17000	10000	65000
F8D	4000	17000	10000	51000
F3AD	1800	17000	15000	51000
F6D	3000	17000	15000	45000
F9D	4000	17000	15000	52000

Comparison of chromatograms of EVA copolymers and graft copolymers are given in Fig.1. in which chromatograms of a series of graft copolymers prepared from PPHETMA of molar masses ranging from 1800-4000 g mol^{-1} and an EVA sample with VA content of 9.8 mol % are shown. In these chromatograms the clear shift of the main peak towards low retention volume indicates high molar mass of the products compared with the precursor EVA samples and suggests successful grafting reactions. This shift in GPC towards lower retentions time of the product has been reported to confirm the success of grafting reactions [22, 23]. The results of the molar masses obtained are presented in Table 1 which indicates significant change in the molar masses of the graft copolymers compared with the precursor EVA copolymer. These molar masses are polystyrene equivalents and were obtained with the polystyrene calibration curve. Since graft product has a branch architecture, calibration with polystyrene standards will not provide absolute molar masses [24, 25]. However, it is possible that the level of branches and level of methacrylate incorporation will not necessarily be the same over the whole range of chain size, so products could have branching and composition distributions as well as a molar mass distribution. In these circumstances it will be extremely difficult to provide an accurate GPC calibration curve. Therefore, a polystyrene calibration was used to provide a relative comparison between molar masses of EVA precursors and the graft copolymers.

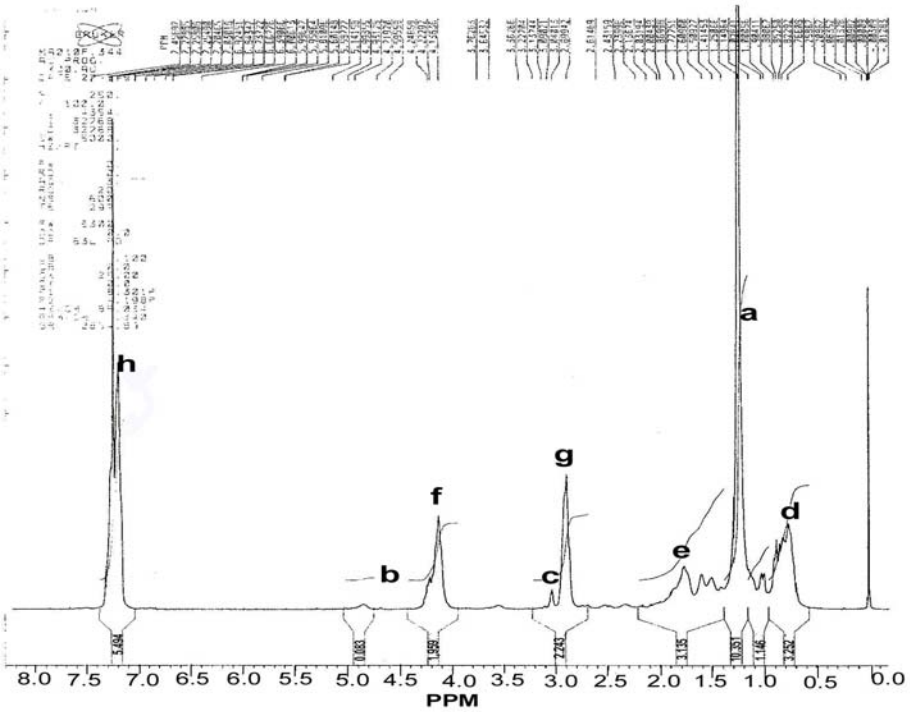
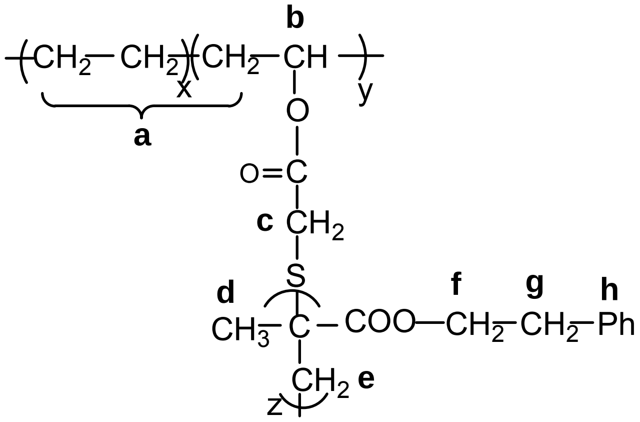


Fig. 2. ^{1}H NMR spectrum of a typical poly(ethylene-vinyl alcohol)-g-PPHETMA copolymer sample.

A ^{1}H NMR spectrum of a purified graft copolymer is shown in Fig. 2, and chemical shifts due to various protons are assigned in Table 2. The EVOH and EVA copolymers were not soluble in chloroform. However, published NMR spectra of these copolymers [26, 27] indicate two important chemical shifts due to methylene – $(CH_2)_n$- protons and methine –(CH)- protons which provide important structural information. All methylene –(CH_2)- protons in ethylene, vinyl acetate and vinyl alcohol resonate at δ = 1.2 ppm due to a similar structural environment.

Tab. 2. Assignment of chemical shifts in ^{1}H NMR spectrum of poly(ethylene-vinyl alcohol)-g-PPHETMA copolymer.

Chemical Shift δ ppm	Assignment	Label
1.2	$-(CH_2)_n-$	**a**
4.8	$-\underset{\mid}{CH}-$	**b**
3.1	$-CH_2-S-$	**c**
0.9	CH_3-	**d**
1.8	$-(CH_2-C)-$	**e**
4.2	$-COO-CH_2-$	**f**
3.0	$-CH_2-Ph$	**g**
7.2	$-Ph$	**h**



The methine –(CH)- protons in EVA and EVOH are reported [27], to resonate at δ = 4.8 ppm. The ester protons in EVA copolymers resonate at a δ = 2.0 ppm value. From the NMR spectrum of the graft copolymer shown in Fig. 2, two important chemical shifts at δ = 1.2 ppm due methylene –(CH_2)- protons and at δ = 4.8 ppm due to methane -(CH)- protons indicate the presence of a backbone in the graft copolymer consisting of polyethylene. The PPHETMA side chain generates a significant chemical shift due to methylene –COO-(CH_2)-CH_2-Ph protons (g) adjacent to an aromatic ring resonating at δ = 3.0 ppm and methylene protons (f) adjacent to an ester group resonating at a higher value of δ = 4.2 ppm. The other chemical shifts due to α-methyl protons (d) resonating at δ = 0.9 ppm and methylene –CH_2-S- protons (c) resonating at δ = 3.1 ppm were also detected. All these chemical shifts suggest the structural features of a graft copolymer with a polyethylene backbone and PPHETMA side chains. The compositions of the graft copolymers were determined by calculating the moles of PPHETMA units per gram of copolymer. The methylene – $(CH_2)_n$- protons of the backbone and the five aromatic protons in the side chains resonate separately form the rest of the spectrum, and from the integrated heights of these chemical shifts composition can be determined. The results are given in Table 3 and are compared with the theoretical values from which the % of grafting is calculated. It is concluded that a high level of graft incorporation was achieved.

Tab. 3. Comparison of moles of PHETMA determined by NMR, IR & theoretical values and grafting % by NMR & IR in poly(ethylene-vinyl alcohol)-g-PPHETMA copolymers.

Sample code	Mol. of PHETMA g^{-1} of graft copolymer (Theoretical) 10^{-3}	Mol. of PHETMA g^{-1} of graft copolym. (NMR) 10^{-3}	Mol. of PHETMA g^{-1} of graft copolym. (IR) 10^{-3}	Grafting % (NMR)	Grafting % (IR)
F1D	4.40	3.0	2.75	68	62
F4D	4.70	3.8	3.0	80	63
F7D	4.84	4.1	3.0	84	62
F2D	4.74	3.2	3.4	68	71
F5D	4.90	3.9	3.0	79	61
F8D	5.0	4.0	3.2	80	64
F3AD	4.14	3.8	--	91	--
F6D	4.53	4.0	--	88	--
F9D	4.69	4.0	--	85	--

N.B: Samples F3AD, F6D & F9D, were prepared from terpolymer backbone in which the PHEMA & VA units contribute to carbonyl absorbance which makes it difficult to determine PHEMA conc. by IR.

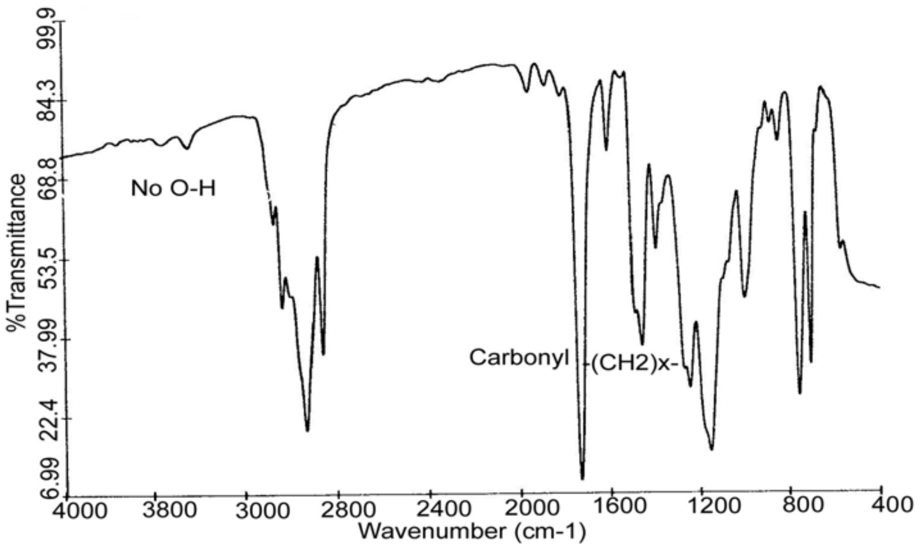


Fig. 3. IR spectrum of a typical poly(ethylene-vinyl alcohol)-g-PPHETMA graft copolymer.

An IR spectrum of a graft copolymer is given in Fig. 3. The important band due to –(CH_2)- of the polyethylene backbone at 1465 cm^{-1} is prominent. The band due to a carbonyl ester of the PPHETMA side chain appears at 1732 cm^{-1}. The appearance of these two significant bands of the backbone and the side chain and the disappearance of a broad band at 3300-3500 cm^{-1} due to O-H groups suggest the structural features of a graft copolymer with polyethylene backbone and PPHETMA side chains.

Since the carboxyl terminated PPHETMA prepolymers have –$COOCH_2$-CH_2-Ph it may be possible for a backbone polymer chain having –OH groups to interact with a prepolymer chain having an ester group in a common solvent at high temperature (xylene b.p. 140 ^{o}C) to undergo transesterification reactions and to produce graft copolymers of different architectures. Since carboxyl terminated prepolymers were converted to acid chloride terminated prepolymers, in the presence of ester groups and acid chloride, there will be a competition among these groups to react with hydroxyl groups, but since acid chloride groups are more reactive than esters the possibility of such side reaction to occur should be minimal. However, such transesterification reactions are catalysed by acidic media. It could be possible that acid chloride terminated prepolymer after several coupling reactions eliminated HCl which catalyse such reactions.

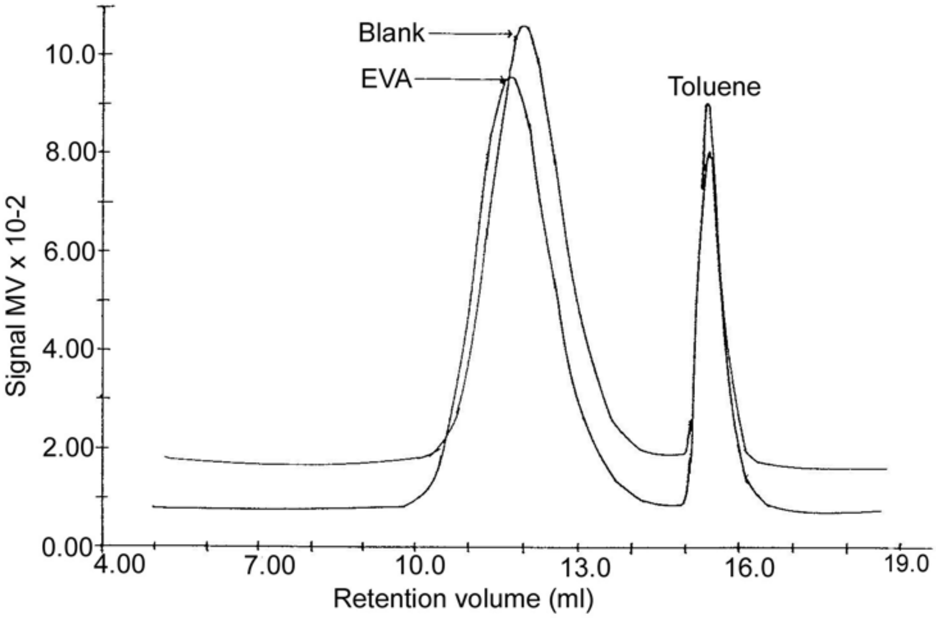


Fig. 4. Comparison of IR chromatograms of EVA copolymer with product after reaction of PPHETMA prepolymer without carboxyl end group with EVOH.

In order to study the possibility of any transesterification reaction and to establish that the change in molar mass of the products was because of coupling reactions between acid chloride functional groups at the ends of prepolymer chains and the hydroxyl groups on the backbone, a series of reaction were performed. For this purpose prepolymer of PPHETMA with no carboxyl acid end groups were prepared by free-radical solution polymerization of phenyl ethyl methacrylate (PHETMA) in the presence of initiator 4-4-azobisisobutyronitrile (AIBN) and chain transfer agent butanethiol. This was chosen because prepolymer with no carboxyl functional groups only have ester groups and if this prepolymer was allowed to react with a backbone having hydroxyl groups in acid media, then only a transesterification reaction is possible. This low molar mass prepolymer was reacted with EVOH copolymer backbone with a VOH content 9.8 mol % and a VOH content of 21 mol % using p-toluene sulphonic acid catalyst in xylene under similar conditions used for the grafting reaction. The products isolated as a result of these reactions were analysed by GPC under similar experimental conditions. The GPC chromatogram of the product obtained from this experiment is presented in Fig. 4. In this Fig. no shift in the retention volume peak towards lower value indicates no change in the molar mass of the product and suggests no transesterification reaction. The compositions of the copolymers were determined from the carbonyl absorption of PPHETMA prepolymer units at 1732 cm^{-1} for solutions of graft copolymer in $CHCl_3$. A calibration curve of IR absorbance versus [PPHETMA] was established with PPHETMA samples with no carboxyl end group in $CHCl_3$, by preparing these calibration samples by using butanethiol as the transfer agent and AIBN as initiator in the polymerization. From results for [PPHETMA] the IR compositions given in Table 3 are calculated. The IR compositions are in reasonable agreement with data obtained by NMR, confirming a high level of % grafting.

Thermal properties of graft copolymers

DSC thermograms of typical graft copolymers are presented in Fig. 5. The DSC traces presented in this Fig. do not show any melting peak. The EVOH copolymer is highly crystalline (Fig. 6) and after grafting reaction onto it the resultant graft copolymer shows no melting peak indicating an amorphous behaviour.

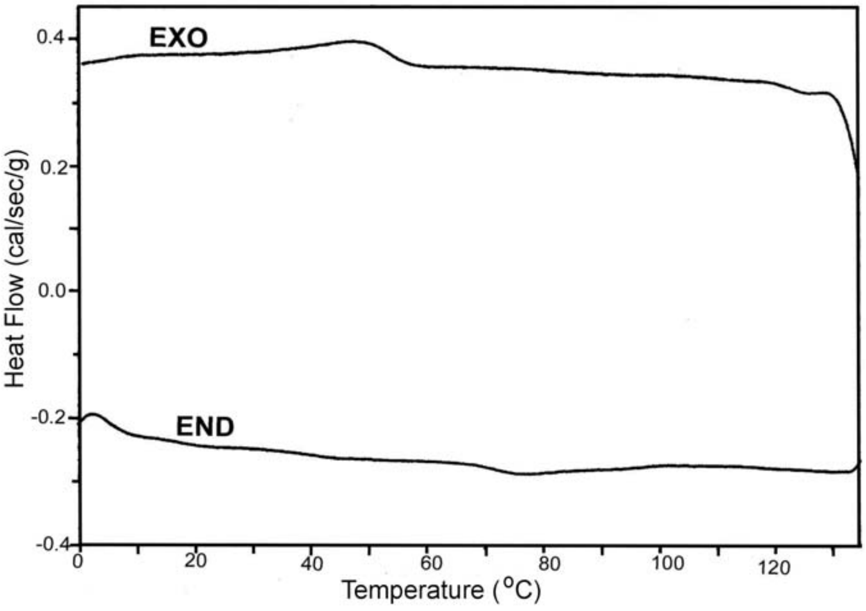


Fig. 5. DSC traces of a typical poly(ethylene-vinyl alcohol)-g-PPHETMA sample.

The replacement of small -OH groups with PPHETMA chains has disturbed the crystallinity of EVOH copolymer. Okui [28], Yao [29] and Moraes [30] in their studies observed the same behaviour of the crystalline backbone after the introduction of uncrystallizable side chain. Cole and Holmes [31] studied the effect of length of side chain on the intermolecular crystallinity and observed that intermolecular crystallinity decreases with the increase in the size of the side chain. Hence prepolymers are chains with 14-31 monomer units in the graft copolymer. Thus it would be extremely difficult for the ethylene units to establish crystallinity and as a result the product showed an amorphous behaviour.

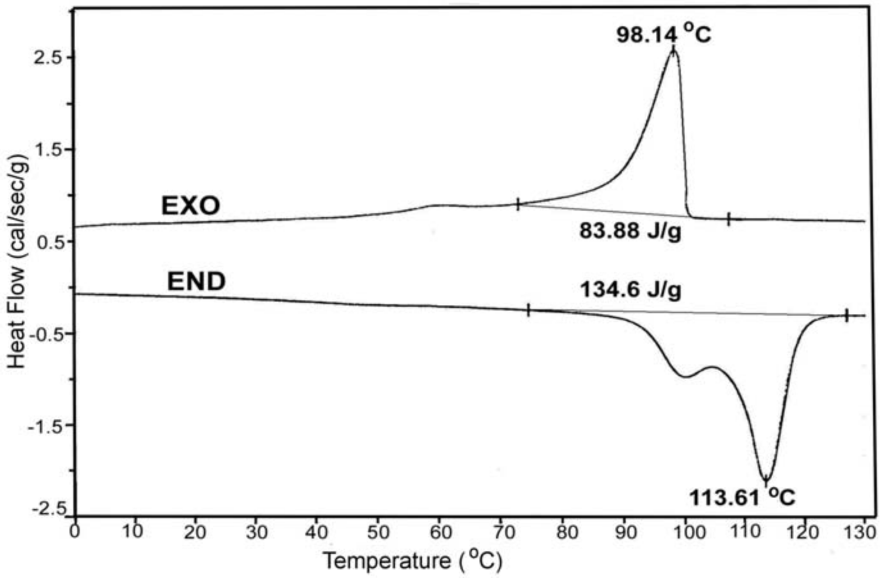


Fig. 6. DSC traces of ethylene-vinyl alcohol (EVA) copolymer.

Tab. 4. Comparison of glass transition temperatures of EVA precursor, PPHETMA prepolymer and graft copolymers by DMTA.

Sample code	T_g PPETMA ^{0}C	T_g EVA ^{0}C	T_g graft copolymer ^{0}C
F1D	33	92	37
F4D	60	92	51
F7D	60	92	59
F2D	33	77	33
F5D	33	77	47
F8D	60	77	56
F3AD	33	77	42
F6D	60	77	50
F9D	60	77	53

Glass transition temperatures (T_g) obtained by DMTA are shown in Table 4 for EVA, PPHETMA precursors and graft copolymer. The resultant graft copolymers have a single tan δ peak. The resultant values of T_g are close to the corresponding prepolymers, indicating that the graft copolymers have a transition mainly due to side chains and no transition due to backbone. These graft copolymers have a polyethylene backbone which is non-polar and PPHETMA side chains which are polar. The backbone and the side chain components are of a different chemical nature and they are insoluble in each other which may enhance microphase separation in the graft copolymer. However, DMTA analysis did not indicate such microphase separation as only a single T_g value was obtained.

Conclusions

Synthesis of graft copolymers by a onto process can be achieved by the use of a matched chain transfer method to synthesise a prepolymer chain with a terminal carboxyl functional group and then reacting this prepolymer with a polymer backbone having hydroxyl functional groups distributed randomly along the backbone chain. GPC can be used to establish the success of a grafting reaction by comparing the retention volume of the precursor and the grafted product. The crystalline behaviour of the EVOH is disrupted remarkably after the grafting of amorphous branches

Experimental part

Materials

Commercial-grade Phenyl ethyl metharylate (PHETMA) (obtained from Polyscience Inc) was inhibited with 200 ppm hydroquinone monoethyl ether, and purified by passing through a column packed with inhibitor removal (supplied by Aldrich Chemical Company Ltd). 4,4-Azobis(4-cyanovaleric acid) (ACVA) used as supplied by Fluka Chemie Ltd. Thioglycolic acid (TGA) was used as supplied by Aldrich Chemical Company Ltd; toluene, SLR grade, was supplied by Carless solvents and was dried over CaH_2 before used. Xylene, AR grade supplied by Fisons plc was dried over sodium wires before use.

Procedures

Carboxyl terminated prepolymer PPHETMA was synthesized by radical solution polymerization. ACVA and TGA were used as matched free-radical initiator and chain transfer agent, respectively. To exemplify this polymerization, the preparation of a carboxyl terminated prepolymer of number average molar mass M_n 1600 g.mol^{-1} (determined by end group analysis) is described. In a three necked round bottom flask (250 ml) containing nitrogen inlet and reflux condenser, monomer (1.86 mol/lit) was mixed with TGA (0.42 mol/lit) in ethyl acetate (100 ml) as polymerization solvent. After purging with nitrogen for 15 minutes ACVA (0.025 mol/lit) was added and the flask was transferred to a thermostated water bath maintained at 80 ^{0}C. The polymerization time was 4 hours. The polymer was isolated by evaporating the ethyl acetate solution. Impure polymer was dissolved in a minimum amount of chloroform and was precipitated in chilled methanol. Redissolution/reprecipitation steps were repeated two further times. The purified polymer was dried in a vacuum oven initially at 100 ^{o}C for 3 hours to remove traces of water, and then at 60 ^{0}C overnight. Carboxyl terminated prepolymers were converted to acid chloride by reaction with oxalyl chloride. The prepolymer (equal to the mol. of VOH repeat units present in EVOH copolymer backbone) as a 5 %(w/w) solution in dry toluene was placed in a three necked round bottom flask (100ml), equipped with a silica-gel drying tube. Oxalyl chloride with 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 hours. 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.

Synthesis of ethylene-vinyl alcohol (EVOH) copolymer backbone

Two different grades of commercial ethylene-vinyl acetate (EVA) copolymers supplied by Dr. D.E. Higgins, ICI Petrochemicals and Polymer Division were used. EVA copolymer with vinyl acetate (VA) contents of 9.8 mol % and 21 mol % were hydrolysed to EVOH. A solution of EVA copolymer in xylene (20 % w/v) was prepared. The required amounts of EVA and xylene were placed in a three necked round bottom flask (500ml) fitted with a reflux condenser and nitrogen inlet. The flask was placed on an oil bath having a magnetic stirrer. The mixture was allowed to reflux for 2-3 hours with constant stirring, so that EVA copolymer completely dissolved in xylene. In a separate flask, KOH was dissolved in ethanol by reflux. An excess of three to four times the stiochiometric amount of KOH was used for complete hydrolysis of EVA copolymers. The required amount of KOH was dissolved by refluxing in ethanol in the ratio of 1:3 by volume of xylene used for the EVA solution. The EVA solution temperature was maintained at 65 ^{0}C. The KOH solution was added slowly by dropping funnel to an EVA solution with vigorous stirring. After the addition of the KOH solution has been completed the reaction mixture was allowed to reflux for 24 hours. It was removed from the oil bath and allowed to cool to room temperature. The product was isolated by pouring the reaction mixture into excess methanol. The copolymer was precipitated as a whitish powder and sedimented at the bottom of a beaker after allowing the mixture to stand for several hours. The methanol was decanted and the remaining methanol was removed by filtration. The product was washed with methanol several times to remove the remaining traces of xylene, followed by washing with acetone. The inorganic salts were removed from the product by washing thoroughly with distilled water. Finally, the product was washed with methanol and acetone. The purified copolymer product obtained was dried in a vacuum oven at 60 ^{0}C for 24 hours. The EVA copolymer containing 21 mol % VA was partially hydrolysed to a terpolymer of ethylene-vinyl acetate-vinyl alcohol. The required amount of EVA and KOH were dissolved in xylene and ethanol, respectively by the same procedure as described above. For partial hydrolysis of EVA, the KOH was used as half the molar amount of VA present in EVA. The EVA solution (2% w/v) was placed in a round bottom flask (500ml) fitted with reflux condenser and nitrogen inlet. It was stirred on an oil bath and the temperature was maintained at 65 ^{0}C. The KOH solution was added to the EVA solution slowly with vigorous stirring. After the addition of KOH solution has been completed the reaction mixture was allowed to reflux for 24 hours. The isolation of product was same as described above.

PPHETMA samples having molar masses ranging from 1800-4000 g mol^{-1} were grafted either onto EVOH copolymer backbone with a VOH contents 9.8 mol % and 21 mol % or onto the terpolymer of ethylene-vinyl acetate-vinyl alcohol with a VOH content 8.0 mol %. For the condensation reactions, mol. of acid chloride terminated prepolymer equal to the mol. of VOH (repeat units present in the EVOH copolymer) were used. A solution of EVOH copolymer in dry xylene (2 % w/v) was prepared. The required amount of EVOH was placed in a three necked round bottom flask with reflux condenser and nitrogen inlet. Dry xylene was added to the EVOH copolymer and the mixture was allowed to reflux at 140 ^{0}C for one hour under nitrogen. A solution of acid chloride terminated prepolymer in dry xylene (10% w/v) was prepared separately and then added to the EVOH solution slowly with a dropping funnel. The mixture was allowed to reflux at 140 ^{0}C for 24 hours under constant stream of nitrogen; the conditions of high temperature and nitrogen stream through the reaction mixture are recommended for HCl removal to complete the reaction [32]. On completion of the reaction, the mixture was cooled down to room temperature. First, the unreacted polymer backbone was removed by precipitation from xylene at room temperature and then filtering the reaction mixture. Second, the resulting filtrate was added to excess methanol in order to precipitate the graft copolymer produced with unreacted prepolymer remaining dissolved. Further purification was carried out by redissolving the graft product in chloroform and precipitating in methanol. After at least six redissolution/reprecipitation steps, the methanol filtrate was poured into n-hexane to check any traces of unreacted prepolymer present in the methanol solution. At each purification/filtration step the methanol solution was evaporated off and the product was analyzed by GPC to check the effectiveness of the purification step for removing unreacted prepolymer.

Characterization

The characterisation of carboxyl terminated PPHETMA prepolymers was performed with a GPC system containing two columns (60 cm and 30 cm in length) containing crosslinked polystyrene beads (particle diameter 10 μm in diameter with nominal pore sizes 50 nm and 10 nm respectively). Filtered solutions (0.155 w/v) in tetrahydrofuran (HPLC Grade) containing toluene as internal marker were injected through a 50 μl loop at a flow rate of 1 ml/min with a Knauer HPLC pump at room temperature. Chromatograms were obtained with an on-line Knauer differential refractometer. The characterization of graft copolymers was performed with a high temperature GPC system with o-dichlorobenzene as solvent (flow rate 1.0 ml/min) operating at 140 ^{0}C. The column (60cm in length) contained mixed gel crosslinked polystyrene beads (particle diameter10 μm). A solution of copolymer (0.20ml at concentration 0.10% w/v) was injected onto the column and chromatograms were obtained with an IR detector at wavelength 3.42 micron. All columns were calibrated with polystyrene standards and chromatograms were analysed with a computer program to calculate molar mass distributions and number average molar masses for prepolymers and graft copolymers.

A Nicolet 20 Dx FTIR spectrometer was used for the analysis of synthesised polymers. Spectra for carboxyl terminated prepolymers, acid chloride terminated prepolymers, and graft copolymers were obtained for polymer films cast on a sodium chloride disc. Typically, 20 scans over the range of 4000-600 cm^{-1} at resolution 2 cm^{-1} were performed.

A Bruker 250 MHz NMR spectrometer was used for analyses of synthesised polymers. The analysis was performed by dissolving 20 mg of sample in 1ml of deuterated $CHCl_3$ with tetra methyl silane (TMS) as internal reference. Typically, 500 scans for each sample were recorded for the range of 0-10 δ value.

The thermal behaviour of EVA, EVOH and graft copolymers were studied with a Du Pont 2000 DSC fitted with cooling and computing accessories. A sample was scanned under a nitrogen atmosphere over the temperature range of 0-130°C. Cooling and heating rates of 10°C per minute were used.

The dynamic mechanical behaviour was analysed with a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA). The samples were prepared as an impregnated filter paper by pressing the polymer between filter paper on a hydraulic press at 120 ^{0}C for few minutes at a pressure of 200 p.s.i. Samples were cooled to room temperature and left in a vacuum oven at 60 ^{0}C for 24 hours. The stability of the filter paper as an inert support was checked by analyzing a blank filter paper under the same conditions and blank did not show any significant behaviour over the temperature range studied. Samples with known thickness and breadth were clamped onto the clamping frame, which was cooled to -50 ^{0}C by pouring liquid nitrogen into the cooling coil of the DMTA head. A heating rate of 5 ^{0}C per minute and frequency of 1 Hz were used. The samples were analysed in the temperature range of -50 ^{0}C to 130 ^{0}C.

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