

A STUDY ON STYRENE MALEIC ANHYDRIDE MODIFICATION BY BENZOIC ACID DERIVATIVES AND DIMETHYL SULFOXIDE

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ABSTRACT: Poly(Styrene co-maleic anhydride) (SMA) is a synthetic copolymer with interesting chemical and biological properties. The anhydride group can also easily react with hydroxyl and amine containing compounds *viz* aminobenzoic acid in DMF at 90°C to obtained modified SMA polymer in P1 and P2 with high yield. It was found that the dissolution of copolymer in dimethyl sulfoxide leads to its charge transfer interaction with dimethyl sulfoxide and subsequent Pummerer rearrangement. The T_g of the polymer were higher than that of SMA due to H-bonding interaction between the polymer chains. The detailed structural study of polymer complexes by using method of molecular spectroscopy.

KEYWORDS: Styrene-co-maleic anhydride, O-Hydroxy benzoic acid, Esterification, Amidation

INTRODUCTION

The copolymerization of styrene and maleic anhydride has been studied extremely over many years. Copolymers of maleic anhydride with styrene, vinylic chloride, and ethylene are available commercially. Copolymerization of maleic anhydride (MA) and Styrene provides a copolymer with strong electron accepting ability. On the other hand, it is known that DMSO is not only widely used as a solvent but it can act as an electron-donor during complex formation with different agents^[1]. When SMA mixed with Dimethyl sulfoxide in (1:2) it forms a polyelectrolytic (intermediate) unstable complex^[2]. On the basis of dielectric relaxation spectroscopic measurements a charge-transfer complex formation between DMSO and diethyl sulfoxide (DESO) with carbon tetrachloride has been suggested. To date very little articles were published on the charge transfer interaction of DMSO with anhydride. Modified SMA-DMSO complex behave as a p^H lowering polymer as well as it has antibacterial activity against *E-Coli*^[3]. The etheric oxygen (-O-) of maleic anhydride is very reactive for pure DMSO, these etheric oxygen also helps in the formation of SMA derivatives with amines^[4], hydroxy compounds aminophenol conjugates^[5] and aliphatic alcohols by half esterification reaction^[6], all were studied earlier. This modified SMA-DMSO (P1,P2) complex has some antimicrobial activity.

In the current study we are taking 4-aminobenzoic acid (ABA) and 4-Hydroxybenzoic acid(HBA) as a modifier

of SMA, the characterization of copolymer complex P1,P2 was study by using method of molecular spectroscopy.

EXPERIMENTAL

Styrene (99%) was purchased from Aldrich and washed with aqueous Sodium hydroxide solution then distilled water followed by drying over anhydrous calcium chloride and finally distilled under vacuum for further use. Maleic anhydride (99%) purchased from S.d.fine and purified before use by recrystallization from anhydrous benzene and sublimation in vacuum. ABA(99%), HBA(99%), Dimethylformamide (DMF,99%) Pure DMSO(d₆) also purchased from S.d.fine, was used for the synthesis, all the chemicals were purchased as analytical grade from S.d.fine. Infrared spectra of complex polymer were recorded on Perkin-Elmer Spectrum RX1 FTIR in range of 4000-450cm⁻¹, pellets were prepared by mixing of complex with KBr while ¹H NMR Spectra of the polymer complex was recorded on 500 MHz-FT NMR spectrometer. Differential scanning calorimetry (DSC) experiment was performed using a calorimeter.

SYNTHESIS

Synthesis of copolymer with different compositions, were carried out in a 250 ml round bottom flask with 70 ml. of DMF as solvent and (1.6 mole %) of AIBN as an initiator and it mixed with 15.6g (0.149 mole) of styrene and 14.7g (0.149mole) of maleic anhydride. The mixture was

heated at 60-70⁰ C and stirred for 12 hrs. in nitrogen atmosphere. A part of the reaction mixture was withdrawn, cooled to room temperature, Cooled mixture was poured in to a large volume of diethyl ether to precipitate the polymer product were in white powder form, which were dried under vacuum at 50⁰C in vacuo overnight to constant weight. The yield was about 95% and the calculated molecular wt. was 22000 Daltones. The molecular weight of poly (maleic anhydride-co-styrene) was calculated from the single point viscosity of its acetone solution at 25⁰C using the following equation^[7].

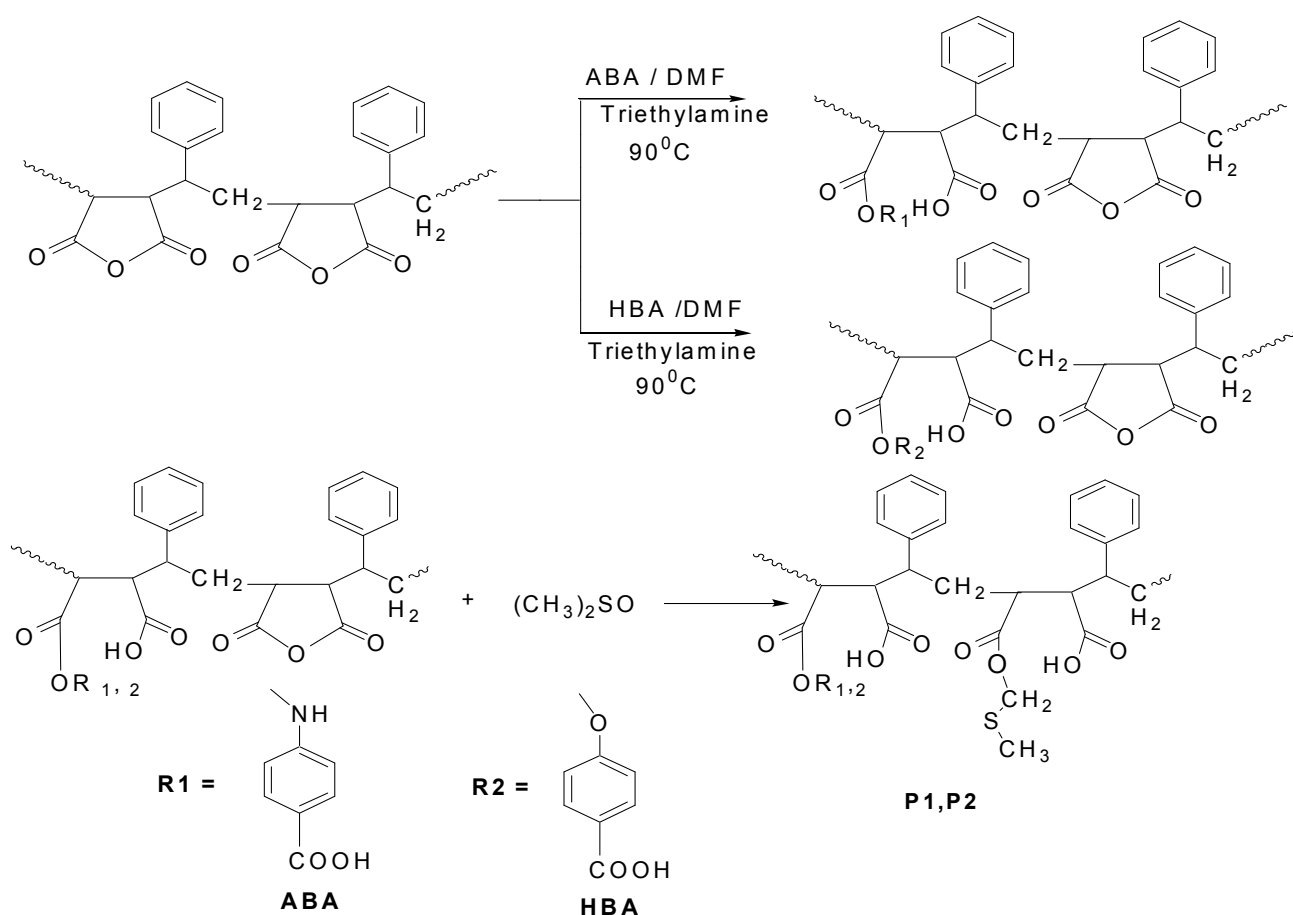
$$[\eta = 8.69 \times 10^{-5} M_n^{0.74}] \quad \eta = \frac{\eta_{sp}}{1 + 0.28 \chi \eta_{sp}}$$

Synthesis of Styrene-co-maleic anhydride with benzoic acid derivatives ABA,HBA compounds

One part of the synthesized SMA was withdrawn and added to a solution of ABA in anhydrous DMF, followed by the addition of triethylamine. The calculated molar ratio of the succinic anhydride unit, ABA, and triethylamine was approximately 1:1, 5:2. The mixture was heated at about 90⁰C for 48hrs. under a nitrogen atmosphere, cooled to room temperature, and finally precipitated into tetrahydrofuran. The precipitate was redissolved in DMF, and precipitated in to tetrahydrofuran to obtain P1. The remaining reaction mixture was also reacted with HBA at 90⁰C for 24 hrs. under a nitrogen atmosphere to obtain P2.

Now copolymer powder was mixed with DMSO in the 1:2 at room temperature and kept in desiccator with P₂O₅ for 15 days. DMSO was removed by vacuum evaporation.

Scheme-1



RESULTS AND DISSCUSION

The prepared polymer complex was in white appearance, the extent of amidation and esterification between SMA and ABA and HBA was attempted to be estimated by elemental analysis for carbon, hydrogen, nitrogen and sulfur of P1,P2 were conducted: (P1): C-63.34, H- 5.41, N-2.23, S-5.13%, (P2): C- 64.89, H- 6.24, S-5.23% respectively. The less amount of carbon indicates that the esterification of with HBA was not completed. The FTIR spectrum of P2 indicated the remaining peaks more clearly. This result is probably due to the shorter reaction time because HBA reacted for only 24 hrs. while ABA for 48hrs. For identification of polymer complex the FTIR, ^1H NMR, ^{13}C NMR, spectra were registered.

FTIR spectra was investigated for copolymer complex P1, P2. To obtain spectra with better signal to noise ratio, especially for weak bands, the measurements in the transition mode was performed as well, the following absorption peaks registered as (Figure.1). The FTIR Spectrum of SMA showed the two peaks at about 1850 and 1780 cm^{-1} as shown in fig.1, corresponding to the stretching vibrations of the anhydride moiety. The peaks within a range of 3100-3000 cm^{-1} were due to aromatic stretching vibrations. Absorption peak at 1742 cm^{-1} which are characteristic absorption of C=O (stre.) of ester group. In the FTIR Spectrum of the copolymer complex peak shows the higher conversion of anhydride to ester group (1750-1735 cm^{-1}) after the reaction of anhydride with DMSO by ring opening, an other peak at 1665 cm^{-1} clear seen in spectra it represents enolic form of ester while peak at 1021 cm^{-1} due to C-O (stre.) are also seen it is generally present in all type of the esters. In this case copolymer chain becomes less rigid and it proved that the ester group is formed after the ring opening. Peaks at 1461 cm^{-1} are indicative of C=C(stre.) of the aromatic ring, 1561 cm^{-1} represents carboxylate ion, the absorption peak at 3020 cm^{-1} (=C-H stretching for aromatic fragments). 1423,762 cm^{-1} shows that (-CH₂) and mono substituted aromatic ring respectively. In FTIR spectra clearly indicated that the absorption peaks of the anhydride carbonyl groups at about 1850 and 1780 cm^{-1} disappeared and instead new carboxyl group peaks appeared with in a range from 1694 -1727 cm^{-1} . it has been previously reported that carboxylic acid groups exhibit peaks at 1727 when they are H-bonded to ether oxygen and at 1710-1700 cm^{-1} when they exist as H-bond. Thus the peak at 1709 cm^{-1} indicates that H-bonded carboxylic acid pairs were present in P1. The peak at 1665 cm^{-1} is probably due to amide carbonyl groups.(Fig.1)

In contrast interestingly, there were two absorption peaks at 1727 and 1694 cm^{-1} in P2. The peaks at 1727 cm^{-1} may have been due to carboxyl groups, H-bonded to the ester groups, and the other peak at 1694 cm^{-1} due to carboxyl groups which are existing as H-bonded pairs. The ester groups may have also been H-bonded with some of the carboxyl groups as mentioned above, thereby shifting their absorption peaks to a lower frequency region.

It is well known that styrene and maleic anhydride can form alternating copolymers with in a wide range of feed ratios due to the donor/acceptor interaction or rapid cross-propagation reactions. To avoid an overlapping of the polymer and solvent proton peak, SMA was reacted with d₆DMSO. The resulting polymers did not include any unreacted succinic anhydride units, thereby indicating that the ring opening reaction of the succinic anhydride units with dimethyl sulfoxide was almost complete. The integral ratio of phenyl (5H) to the methylene group (2H) bonded directly to the oxygen atom of the ester bond was 2.5:1, as shown in figure 2. This result partially supports the fact that SMA is an alternating copolymer since even random copolymers can have the same overall composition. Beside the ^{13}C NMR spectrum of the modified polymer complex showed peaks at 204 ppm. due to carbonyl carbon of maleic anhydride, peak at 125,126,128,129,137,139 ppm. due to aromatic carbon of styrene and 13,21,33,34,44ppm due to aliphatic carbon respectively.(Fig.2)

The thermal transition of SMA, SMA+ABA and SMA, SMA+HBA studied using DSC, and the results shown in (fig.3). The glass transition temperature (T_g) of SMA was measured to be about 202 °C, which is very close to a previously reported value (M_n 83000; T_g 201°C). In contrast, the T_g of SMA+ABA and SMA+HBA was 251 and 253°C, respectively. The increased T_g of the new polymers probably resulted from enhanced molecular interactions due to H-bonding, as mentioned above.(Fig.3)

SMA began to decompose at about 300°C. In contrast, the two new polymers were decomposed with two steps. The initial weight loss in P1 and P2 at temperature near 250°C was 6.7 and 9.8% respectively. The calculated weight of water to be formed via formation of an anhydride from two carboxylic groups in P1 and P2 were 9.1 and 10.4%, which are somewhat close to the calculated value. In the case of P1, the dehydration can also occur via imidation between an amide group and neighboring carboxyl group as the imidation is well known to occur on heating SMA with primary amine. In order to prove this hypothesis, the polymers were heated at about 300 °C for 1hr. under the identical conditions as above.

CONCLUSION

P1 and P2 were synthesis successfully by reacting SMA-ABA-DMSO and SMA-HBA-DMSO, respectively. The T_gs of the polymers were higher than that of SMA because of H-Bonding interaction between the polymer chains. The polymers became cross linked and insoluble in organic solvents on heating at about 300 °C. For the SMA-DMSO interaction is more efficient in pure DMSO, and probably further transformation of charge-transfer complexes takes place. The sulfur (S) moiety of pure DMSO is highly reactive. When styrene maleic anhydride (SMA) is mixed with this particular form of DMSO the sulphur moiety of DMSO interacts with the etheric oxygen (-O-) of the maleic anhydride moiety of

the SMA thereby leading to the formation of an intermediate unstable complex of SMA and DMSO. The carbonyl oxygen of SMA being resonance stabilized, is not affected. FTIR studies proved that reality of the reaction between modified (SMA) and DMSO as it follows from above scheme1, the reaction results in the

increase of the local concentration of COO^- group in unit of transformed polymer, Hence the relative intensity at 1644cm^{-1} increases, and the intensities of the peaks at 1777cm^{-1} and 1709cm^{-1} due to $\text{C=O}(\text{str.})$ decrease. We believe that the results obtained fully agree with the mechanism.

Figure : 1, FTIR spectra of SMA, P1 and P2

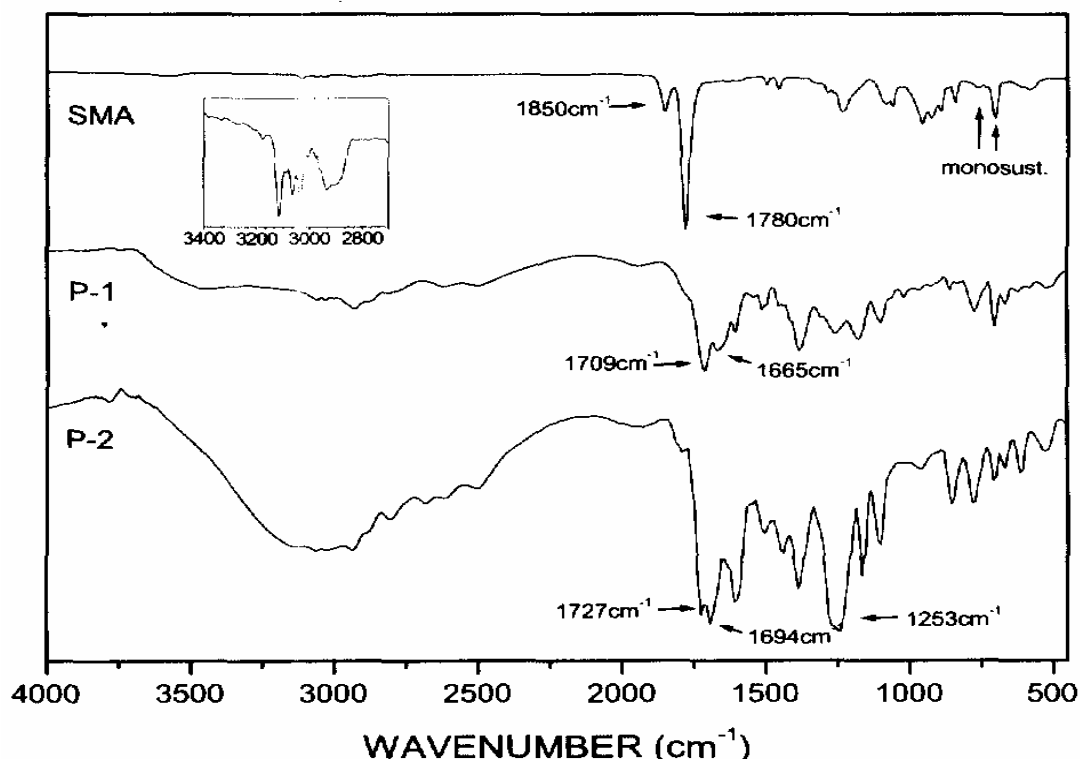


Figure : 2 ^1H - NMR spectra of SMA modified with in DMSO-d_6

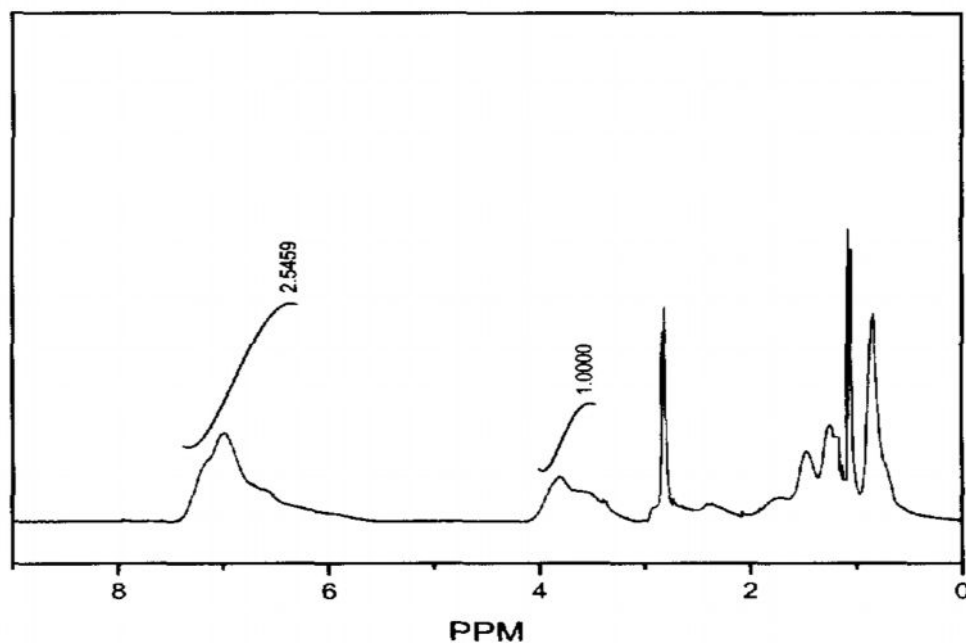
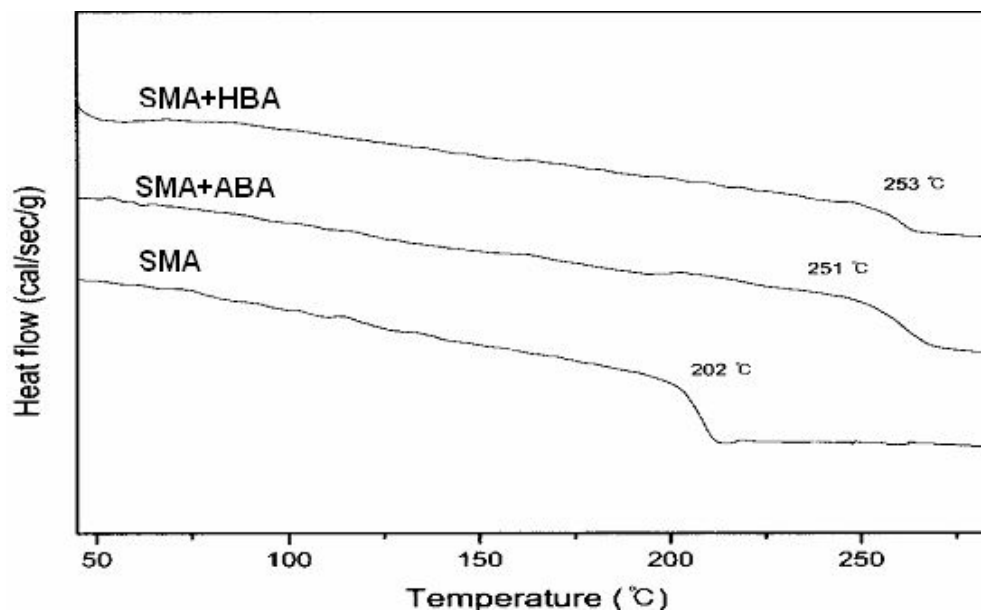


Figure : 3 DSC Thermograms of SMA, P1 and P2



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