

Synthesis and Characterization of Acrylic Copolymers of 4-Chloromethyl Styrene with Incorporation of Phthalimide Groups and Amination of Resulted Polymers

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ABSTRACT: 4-Chloromethyl Styrene (CMS) was copolymerized with different monomers such as Methyl MethAcrylate (MMA), Methyl Acrylate (MA), 2-EthylHexyl Acrylate (EHA) by free radical polymerization method at $70 \pm 1^\circ\text{C}$ using α, α' -Azobis(IsoButyrylNitrile) (AIBN) as an initiator. The copolymer compositions were obtained using related $^1\text{HNMR}$ spectra and the polydispersity of the copolymers were determined using Gel Permeation Chromatography (GPC). The amino copolymers were prepared by treating 4-chloromethyl styrene copolymers with sodium phthalimide and then with hydrazine monohydrate. The polymers were characterized by $^1\text{HNMR}$ and FT-IR spectroscopic techniques. The glass transition temperature (T_g) of all copolymers was determined by Dynamic Mechanical Thermal Analysis (DMTA). Study of DMTA analysis showed that chemical modification of 4-chloromethyl styrene copolymers with phthalimide substituent leads to an increase in the rigidity and glass transition temperature of polymers.

KEY WORDS: 4-Chloromethyl styrene, Phthalimide, Glass transition temperature, Aminated polymers.

INTRODUCTION

4-Chloromethyl Styrene (CMS) is one of the most important functional monomers. Due to the benzylic chlorine, a great number of nucleophilic substitution are made possible, leaving the double bond undamaged and providing new monomers that can be polymerized or copolymerized when the experimental conditions are well chosen [1-2]. CMS has been copolymerized with many

different comonomers by the radical polymerization method and the resulting copolymers could provide new products by nucleophilic substitution reaction of the chlorine atom. Some of articles and patents deal with the numerous physical and chemical properties of the chloromethyl styrene polymers and their applications [3]. 4-Chloromethyl styrene monomers and the resulting

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polymers with various functional groups have wide potential application, such as for ion exchange resins, polymer supports of catalysts and resins for microlithography [4-6]. Functionalized Poly(ChloroMethyl Styrene) (PCMS) or related copolymers have been widely used in different processes as bactericide polymers[4], photo-sensitizers[5], solar energy storages[6], photo-resists [7], non-linear optics [8], cholesterol trapping of human serum [9] and prodrugs in biomedical applications [10]. N-Substituted phthalimide copolymers may be used as activated drug binding materials [11]. In this research work, CMS was first copolymerized with MMA, MA, EHA by free radical polymerization method. Then phthalimide groups were linked to the resulted copolymers by nucleophilic substitution reaction. The hydrolysis of those polymers gave Poly(4-AminoMethyl Styrene) (PAMS). We report the synthesis, characterization and thermal behavior of styrenic copolymers of CMS without and within phthalimide groups and NH_2 groups. The DMTA analysis showed that the incorporation of phthalimide groups as side chains decrease the free volume of the polymers and therefore, the rigidity and the T_g are increased. This could be explained by inter or intramolecular hydrogen bonding [12].

EXPERIMENTAL SECTION

Materials

Phthalimide (Merck), CMS (Acros, 90%), MMA, MA, EHA (Merck) were distilled under reduced pressure to remove inhibitors before using. Toluene was stirred over calcium hydride for 24 h and distilled in argon atmosphere. Initiator of AIBN (Merck) was purified by crystallization from methanol. DMF was dried over anhydrous MgSO_4 for 2 days and later with phosphoric anhydride overnight. After drying, DMF was distilled under reduced pressure.

Instruments

The infrared spectra were recorded on Bruker spectrometer scientific 500 IR. ^1H NMR spectra were run on a Bruker 250 MHz spectrometer at room temperature using chloroform-d and dimethyl sulfoxide-d₆ as solvent. DMTA was characterized by Triton (Tritec 2000 DMA) with rate $5^\circ\text{C}/\text{min}$. The molecular weights (M_w and M_n) were determined using a Waters 501 Gel Permeation Chromatograph (GPC) fitted with 10^2 and 10^3 nm Waters Styragel columns.

Copolymerization and modification of CMS with different monomers:

Poly(CMS-co-MMA) (I), Poly (CMS-co-MA) (II), Poly (CMS-co-EHA) (III) was separately prepared as follows. In a Pyrex polymerization tube, 1.56 g (10 mmol) of CMS and 0.065 g (0.4 mmol) of AIBN were dissolved in 15 mL of toluene. Then 3g (30 mmol) of MMA or 2.58 g (30 mmol) of MA and 5.52 g (30 mmol) of EHA was added to tube and the mixture was flushed with argon for 20 min. Each tube was sealed under vacuum and immersed in a thermo stated water bath maintained at $70 \pm 1^\circ\text{C}$ and shaken vigorously by the shaker for about 30h. Pouring the solution into excess cooled methanol precipitated the polymer. The precipitated polymer was filtered off, washed with methanol and purified by reprecipitation. Finally, the obtained polymer was dried under vacuum in room temperature for 24 h. Then Poly (CMS-co-MMA) containing phthalimide group (I-pht), Poly (CMS-co-MA) containing phthalimide group (II-pht), Poly (CMS-co-EHA) containing phthalimide group (III-pht) were prepared as follows. In a 100 mL two-necked flask equipped with a dropping funnel and a reflux condenser, 0.5 g of each copolymer (I-III) was dissolved in 15 mL of DMF and system maintained under a slight pressure of dry argon. A solution of phthalimide salt in about 20 mL of DMF was prepared, transformed into dropping funnel under argon and added drop wise with stirring to each solution of copolymers in to flask at 60°C . After the addition of phthalimide salt was completed, reaction mixture refluxed for about 4h. Then, the solution was poured into an excess methanol and the precipitate washed with 150 mL NaOH 0.2 N and 150 mL H_2O . The obtained copolymer containing phthalimide substituent in the side chain were finally collected and dried under vacuum at room temperature. Then a mixture of resulted copolymers (0.5g) and 1 mL of pure hydrazine monohydrate (80%) refluxed in 20 mL of ethanol. The solution was heated under reflux for 20 h. The mixture was evacuated to remove the volatile components, to which residue conc. During that time a white solid formed. The reaction mixture was filtered, and the filtrates were concentrated by rotary evaporation and precipitated into water. The mixture was kept at 0°C overnight. Filtration following day yielded the amino polymer (Fig. 2).

Table 1: Molecular Weights and Mole Fractions of the Synthesized Copolymers I–III.

Copolymer	MW $\times 10^{-3}$	Mn $\times 10^{-3}$	MW/Mn	CMS (%)	co-monomer (%)
I	37.2	24.8	1.5	33	67
II	26	15.7	1.6	29	71
III	22	16	1.35	69	31

RESULTS AND DISCUSSION

Characterization of copolymers

The resulted copolymers (I–III) are white solid and soluble in chloroform, dichloromethane, benzene, toluene, xylene, THF, DMF and DMSO and insoluble in n-hexane, methanol, ethanol and water.

The FT-IR spectra of copolymers (I–III) showed a peak around 3024 cm^{-1} due to C-H stretching of the aromatic ring. The peaks around 2854 and 2925 cm^{-1} were attributed to the asymmetrical and symmetrical C-H stretching of methylene and methyl groups. The ester carbonyl stretching of ester group was observed around 1726 cm^{-1} . The ring stretching vibrations of the aromatic nuclei were observed at 1600 and 1485 cm^{-1} . The asymmetrical and symmetrical bending vibrations of methyl groups are seen at 1453 and 1380 cm^{-1} , respectively. The peaks at 1273 and 1165 cm^{-1} were due to C-O stretching. The C-H out-of-plane bending vibrations due to the aromatic nuclei were observed at 883 , 750 and 690 cm^{-1} .

In the ^1H NMR spectra of the copolymers (I–III), two methylene protons of benzyl chloride appeared at 4.5 ppm . The proton signals of the aryl groups were seen between 6.7 and 7.2 ppm . The resonance signal at 3.9 ppm was attributed to two methylene protons of $-\text{COOCH}_2$ in copolymer III and signal at 3.7 was attributed to three methyl protons of $-\text{COOCH}_3$ in copolymer I, II. The broad signal at 0.9 – 2.6 ppm was due to the methylene groups of backbone and other alkyl groups (Fig. 1a).

The number and weight-average molecular weights of synthesized copolymers were determined by GPC and are presented in Table 1.

The average composition of the copolymer samples was determined from the corresponding ^1H NMR spectra. In the past few decades ^1H NMR spectroscopic analysis has been established as a powerful tool for the determination of copolymer compositions because of its simplicity, rapidity and sensitivity [13,14]. The assignment of the resonance

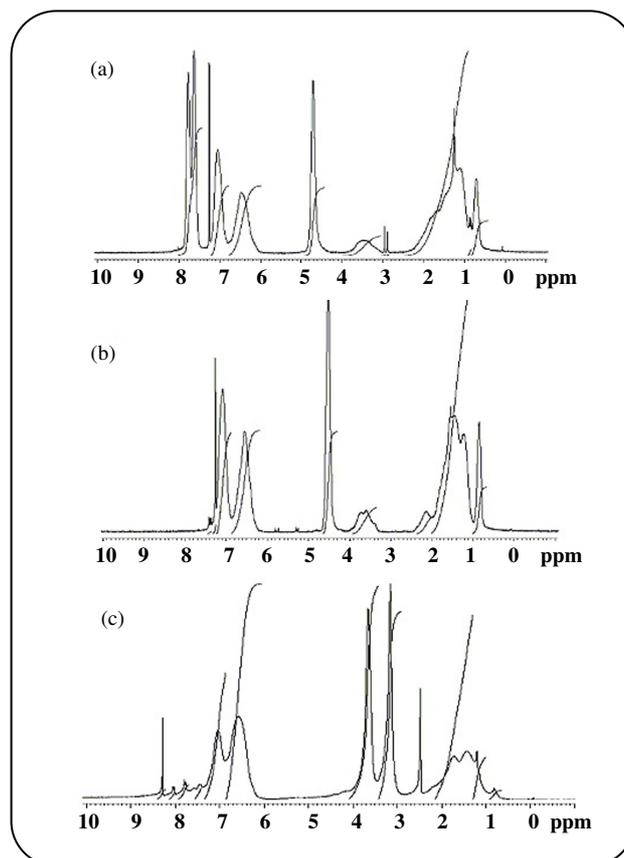


Fig 1: ^1H NMR spectra of (a) copolymer III and (b) III-pht and (c) III-NH₂. The solvents were (a), (b) CDCl_3 and (c) DMSO-d_6 .

peaks in the ^1H NMR spectrum leads to the accurate evaluation of the content of each kind of monomeric unit incorporated into the copolymer chains. Thus, the mol fraction of CMS in the copolymer chain was calculated from measuring the integrated peak areas of aromatic protons of the CMS unit and aliphatic protons of the CMS and other monomer units. The following expression is used to determine the composition of copolymer III. Let m_1 be the mol fraction of CMS and $1-m_1$ is that of EHA monomer. The CMS contains 4 aromatic protons and 5 aliphatic protons and EHA contains 20 aliphatic protons:

$$B = \frac{\text{Integrated peaks areas of aromatic protons}}{\text{Integrated peaks areas of aliphatic protons}} = \frac{4m_1}{5m_1 + 20(1 - m_1)} \quad (1)$$

This on simplification gives:

$$m_1 = \frac{20B}{15B + 4} \quad (2)$$

Therefore, the mol fraction of CMS in the copolymer III was determined from Eq. (2). A similar method was used to calculate of the mol compositions of the other copolymers. Table 1 gives the mol fractions of CMS and related co-monomer in the copolymers.

The T_g value of the copolymers (I-III) was determined by DMTA and the data are presented in Table 2. All the synthesized copolymers show a single T_g , showing the absence of formation of a mixture of homopolymer or the formation of a block copolymer.

Characterization of poly (*p*-vinylbenzylphthalimide) copolymers (PVBP)

The FT-IR spectra of these products showed two peaks at 1771-1713 cm^{-1} and one peak at 719 cm^{-1} indicates quantitative conversion of the chloromethyl styrene into its phthalimide derivative.

The replacement of chlorine atom by phthalimide group is easily followed by $^1\text{HNMR}$. The peak around 4.5 ppm corresponding to two protons of methylene of benzyl chloride in CMS disappeared and a new peak corresponding to two methylene protons attached to phthalimide group at 4.7 ppm and two peak of phenyl of phthalimide groups appeared at 7.2-7.8 ppm (Fig. 1).

The DMTA scans showed that the presence of bulky phthalimide groups lead to an increase in the T_g from 88.9 °C for copolymer I to 143.6 °C for copolymer (I-pht), from 75 °C for copolymer II to 115 °C for copolymer (II-pht) and from 81.7 °C for copolymer III to 140 °C for copolymer (III-pht) (Fig. 3). Study of DMTA curves clearly showed that incorporating of phthalimide substituent in copolymer side chains increased the glass transition temperature as expected. It was observed that there is only one glass transition temperature for each polymer; i.e. the polymerization did not result in a block copolymer. This implies that the monomer reactivity was likely random and that there was no phase separation.

Table 2: Comparison of observed T_g values of copolymers I-III.

Copolymer	T_g (°C)
Poly(CMS-co- MMA)	89
Poly(VBP-co- MMA)	143
Poly(AMS-co- MMA)	127
Poly(CMS-co- MA)	75
Poly(VBP-co- MA)	115
Poly(AMS-co- MA)	104
Poly(CMS-co- EHA)	82
Poly(VBP-co- EHA)	140
Poly(AMS-co- EHA)	130

The π -stacking and ring structure of the aromatic groups increases the rigidity of the polymer. This reduces the flexibility of polymer chains and hence more energy has to be induced in order to overcome the interactions. The presence of a number of carbonyl groups also adds to the rigidity of the polymer. Because the bulky group is pendant and not a part of the polymer backbone, the rise in T_g was slight; however, it is important that T_g 's of the polymers are high enough to withstand semiconductor processing [15]. Consequently with incorporation of highly sterically hindered phthalimide groups in polymer side chains, a series of novel modified polymers containing new properties is obtained.

Characterization of PAMS copolymers

FT-IR spectra of these products showed two peaks at 3400-3380 cm^{-1} and one peak at 1728 cm^{-1} indicates confirming the formation of the primary amine.

The $^1\text{HNMR}$ of these products indicates quantitative conversion of the phthalimide groups into primary amine groups. The peak around 4.7 ppm corresponding to two methylene protons attached to phthalimide group and two peaks of phenyl of phthalimide groups at 7.2-7.8 ppm disappeared and a broad peak corresponding to the mobile protons of the amino groups appeared at 3.6 ppm (Fig. 3c).

The T_g values of I-NH₂, III-NH₂, III-NH₂ are 127.3, 104, 130.2 °C respectively, (Fig. 3).

CONCLUSIONS

The reason for this was the first of several amino groups in the chain can be produced with different ratios.

Table 3: Solubility of aminated copolymers in various solvent.

Compound	I-NH ₂	II-NH ₂	III-NH ₂
DMF	++	++	++
Toluene	++	++	++
CHCl ₃	++	++	++
Ethanol	--	--	--
DMSO	++	++	++
H ₂ O	--	--	--

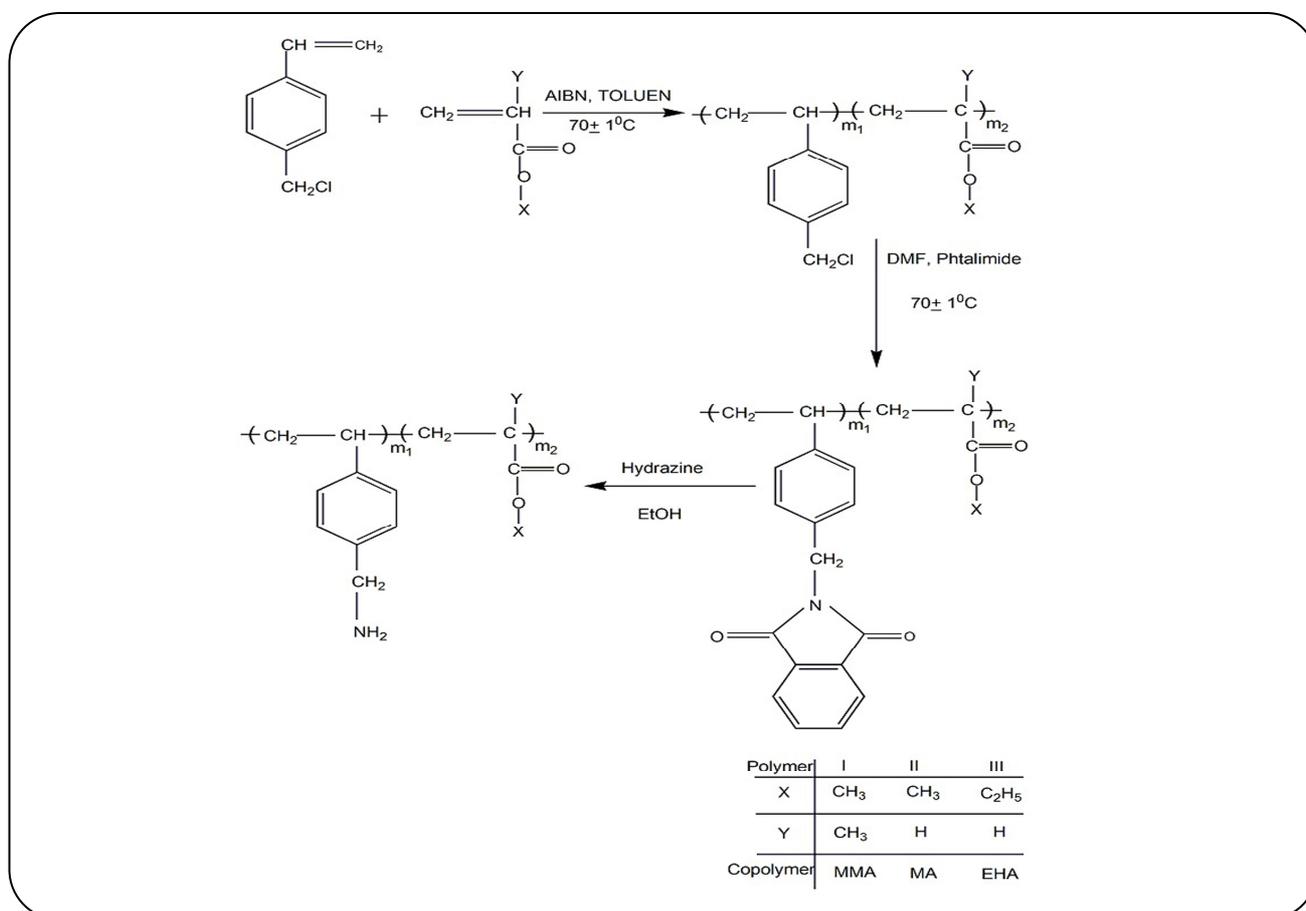


Fig. 2: Synthesis of poly (4-aminomethyl styrene) copolymers.

Secondly, the solution was prepared by changing the percentage was somewhat functional groups. Eventually it became clear how much of the functional groups on the polymer chain is greater than the solubility of the solventte goal of this research was to prepare polymers with amine groups can be used copolymers conductive

polymer can be synthesized from the copolymers prepared to be a classical conductor.

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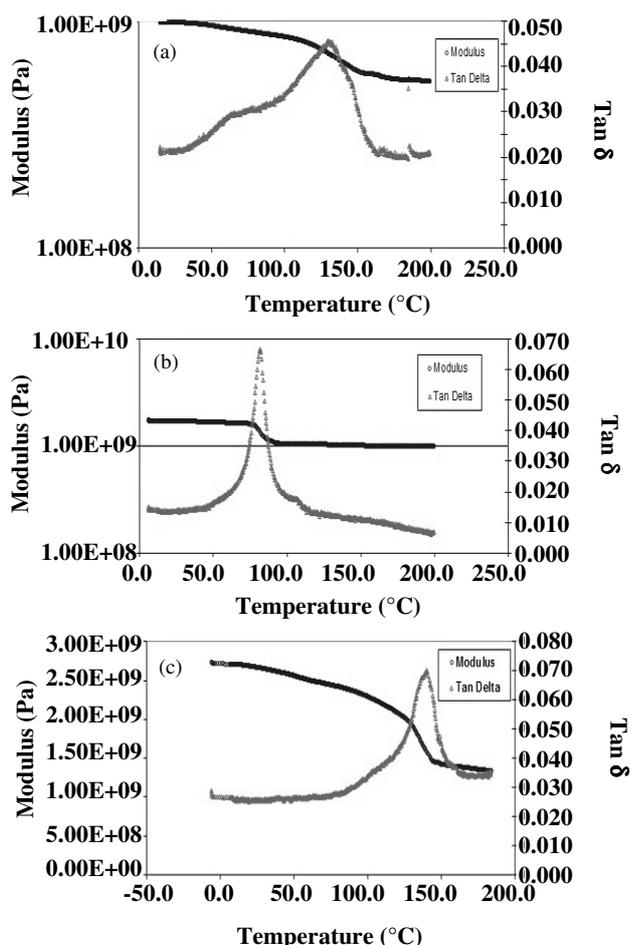


Fig. 3: DMTA Curves of (a) copolymer III and (b) III-pht and (c) III-NH₂.

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