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Modification of styrene polymer by attaching suitable groups as side chain

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Abstract: Chemical modification of inexpensive commercial polymers, such as styrene, is a safe methodology to obtain new copolymers. The 4-chloromethyl styrene (CMS) was copolymerized with styrene (in various mole ratios) by free radical polymerization method at 70 ºC using α,α-azobis(isobutyronitrile) (AIBN) as an initiator. The azide ion was covalently attached to the obtained copolymers with replacement of all the chlorine atoms in CMS units. The 1,3-dipolar click cycloaddition reaction between azido polymers and dimethyl acetylene dicarboxylate (DMAD) yielded polymers with 1,2,3-triazoles in side chain. The polymers, obtained in quantitative yields, were characterized by FT-IR and ^{1}H NMR spectroscopy; thermogravimetric analysis (TGA) and GPC studies. The thermogravimetric analysis (TGA) indicated that the thermal stability of copolymers increases with incorporation of 1,2,3-triazole groups in side chains of copolymers.

Keywords: 4-chloromethyl styrene, azides, 1,2,3-triazole, dipolar click cycloaddition reactions.

Introduction

4-Chloromethylstyrene (CMS), also called p-vinyl benzyl chloride (VBC), is a monomer that can be reacted with a series of reagents to produce polymer with functional groups [1, 2]. This monomer can polymerize or copolymerize before or after the functional groups reaction with benzyl chloride. The mobility of benzyl chloride bonds in poly(4-chloromethylstyrene) (PMS) and related copolymers allows their reaction with various nucleophilic reagents. Also functionalized PCMS and related copolymers have been widely used in different processes such as bactericide polymers [3], photosensitizers [4], solar energy storage [5], photoresist [6], nonlinear optics [7], and prodrugs in biochemical application [8].

One of the modifications of PCMS and related copolymers is achieved by nucleophilic substitutions of the chlorine atom, by attaching suitable groups as a side chain.

Azides are considered very important compounds due to both their industrial as well as biological applications. Azide derivatives have been used in rubber vulcanization, polymer crosslinking, dyes, tire cored adhesives, foaming of plastics, pharmaceuticals, pesticides and herbicides [9]. Many azide compounds show mutagenic activities [10-12].

The chemistry of azides has thus attracted the attention of many chemists, since many of these compounds play an important role in organic chemistry [13-15]. One of the more useful synthetic applications of azides is the preparation of 1,2,3-triazoles via 1,3-dipolar cycloaddition click reactions of azides with substituted acetylene compounds [16-19].

The chemistry of 1,2,3-triazoles has also received much attention because of their wide range of applications. They have been used as fungicides, herbicides, light stabilizers, fluorescent whiteners, optical brightening agents, and corrosion retardants [20, 21]. Moreover 1,2,3-triazole derivatives show significant antimicrobial, cytostatic, virostatic, and anti-inflamatory activities.

In this work, we report the synthesis and properties of 4-chloromethyl styrene (CMS) polymers modified with aromatic 1,2,3-triazole groups. We first synthesized the copolymer of 4-chloromethyl styrene with styrene by radical polymerization. The initial strategy involved replacing the –Cl on the side-chain of PMS with a –N3 group. Then 1,2,3-triazole groups were linked to the resulted copolymers by click cycloaddition reaction between azide and dimethyl acetylenedicarboxylate (DMAD). The thermogravimetric analysis (TGA) indicated that the thermal stability of copolymers increases with incorporation of aromatic 1,2,3-triazole groups in side chains of polymers and these polymers are thermally stable up to 400 ºC.

Results and Discussion

The resulting copolymers are white solids and soluble in chloroform, THF, N,N-dimethylformamide, and dimethylsulfoxide but insoluble in n-hexane, methanol, ethanol, and water.

In ^{1}H NMR spectra, with replacement of chlorine atoms with azide group, the peak around 4.5 ppm corresponding to two methylene protons of benzyl chloride disappeared and two new peaks at 4.2 ppm corresponding to two methylene protons attached to azide group appeared (Figure 1).

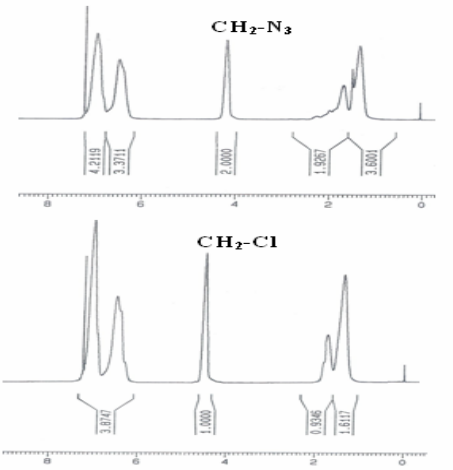


Fig. 1. ^{1}H NMR spectrum of PCSS and PASS in $CDCl_3$.

The copolymer compositions were calculated from the ^{1}H-NMR spectra data. In the past few decades ^{1}H-NMR spectroscopic analysis has been established as a powerful tool for the determination of copolymer compositions because of its simplicity, rapidity and sensitivity [22]. Spectrum of copolymer PCSS1 in CDCl3 is shown in Figure 2. The molar compositions of CMS and styrene in copolymer P1 were calculated from the ratio integrated intensities of the peaks around 4.5 ppm, corresponding to two methylene protons of benzyl chloride in CMS units to the total area between 1-1.8 ppm, which were attributed to six protons marked by (#) in CMS and (*) in styrene. The molar compositions of CMS and styrene were calculated from Eqs. (1) and (2) where x and y were the mole fractions of CMS and styrene, respectively.

$$\frac{\text{Area at } 4.5}{\text{Area at } 1-1.8} = \frac{2x}{3x+3y} \qquad (1)$$

$$x + y = 1 \qquad (2)$$

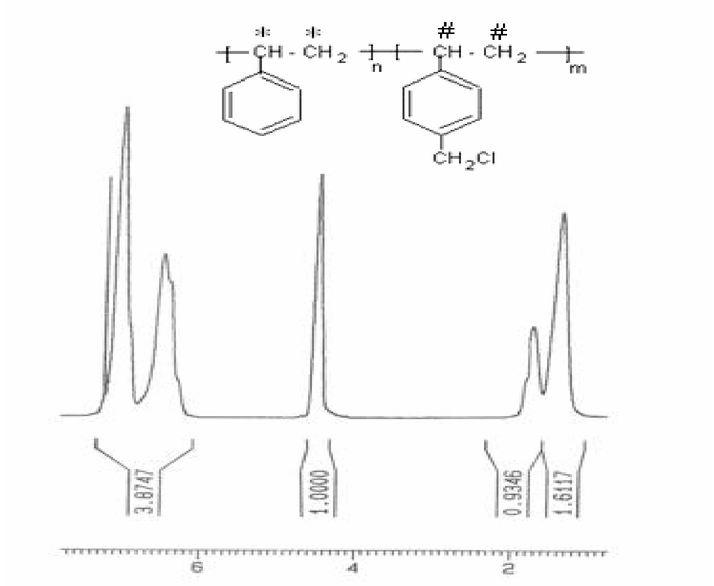


Fig. 2. ^{1}H NMR spectrum of PCSS1 in $CDCl_3$.

A similar method was used to calculate the molar compositions of monomers in copolymers PCSS2 and PCSS3. The compositions of copolymers are presented in Table 1.

Tab. 1. Molar composition and GPC data of copolymers

Copolymer	Molar composition of monomers in the feed (%)	Calculated from the ^{1}H-NMR		M_w	M_n	M_w/M_n
		(% mole) m	(% mole) n			
PCSS1: $(CMS)_m$ $(styrene)_n$	43.5%: 56.5%	42	58	16490	8500	1.94
PCSS2: $(CMS)_m$ $(styrene)_n$	30%: 70%	30	70	22344	11413	1.96
PCSS3: $(CMS)_m$ $(styrene)_n$	21%:79%	22	78	26122	13425	1.95

Thermal Behaviour

The thermal behavior of polymer is important in relation to its properties. Differential scanning calorimetry (DSC) and thermal gravimetry (TGA) for the network polymers were evaluated. The thermal properties of the polymers are summarized in Table 2 and 3. T_g values of copolymers showed that the presence of the 1,2,3-triazoles group in the side chain increased the rigidity of polymers, and the T_g value subsequently increased.

Tab. 2. DSC data of copolymers.

Copolymer	Tg(º C)
P1	95
P2	101
P3	102
P4	67
P5	77
P6	77
P7	160
P8	175
P9	175

Several factors affect the T_g: decreased mobility of polymer chains, increased chain rigidity, and a resulting high T_g. Materials characterized as having high T_g have high degrees of crystallinity, crosslinking, or rigid chains and yield high strength and low elongation. High elongation flexible side groups increase chain separation, and the T_g decreases. Cyclic monomers tend to exhibit high T_g values. The rigidity of polymer chains is especially high when there are cyclic structures in the main polymer chains. Table 3 including initial decomposition temperature of the polymer (IDT), temperature of 10% weight loss of the polymer (PDT) and also the temperature at which the maximum decomposition rate occurred for the polymer (PDTmax). The thermogravimetric analysis (TGA) indicated that the thermal stability of copolymers increases with incorporation of 1,2,3-triazole groups in side chains of polymers and these polymers are thermally stable up to 400 ºC.

Tab. 3. TGA data of copolymers.

Copolymer	IDT (º C)	PDT	PDTmax (ºC)
P7	280	340	430
P8	300	330	420
P9	310	325	420

Conclusions

The copolymers PCSS1-3 were synthesized by free radical solution polymerization. The molar compositions of the obtained copolymers were calculated by the ^1H NMR spectral method. The azide groups as side chains were linked to copolymers from the reaction between sodium azide and benzyl chloride bonds to obtain the three new modified copolymers containing azide substituents. The ^1H NMR spectra data showed that azide groups were attached to phenyl rings via methylene spacers with replacement of all chlorine atoms. The 1,3-dipolar cycloaddition reaction between azido polymers and dimethyl acetylene dicarboxylate (DMAD) yielded polymers with 1,2,3-triazoles in side chain. The thermogravimetric analysis (TGA) indicated that the thermal stability of copolymers increases with incorporation of 1,2,3-triazole groups in side chains of polymers and these polymers are thermally stable up to 400 ºC. In this way, the presence of the heterocyclic rings on the polymer gives some extra stability.

Experimental

Measurements

Infrared spectra were recorded with a 4600 Unicam FT-IR spectrophotometer as KBr pellets. ^{1}HNMR spectra were run on a **Bruker** 400 MHz spectrometer at room temperature using $CDCl_3$ as a solvent. The molecular weights (M_W and M_n) were determined using a Waters 501-gel permeation chromatograph (GPC) fitted with 102 and 103 nm Waters styragel columns. THF was used as an elution solvent at a flow rate of 1 mL/min, and polystyrene standard was employed for calibration. The differential scanning calorimetry (DSC) curves were obtained on a TGA/SDTA 851 calorimeter at heating and cooling rates of 10 °C/min under N_2.

Materials

CMS (Aldrich, 90%), styrene and DMAD (Merck) were distilled under reduced pressure to remove inhibitors, before use. The initiator α,α-azobis (isobutyronitrile) (AIBN) (Merck) was purified by crystallization from methanol.

Copolymerization of 4-chloromethylstyrene with styrene: PCSS

For preparing of copolymers (PCSS1, PCSS2, and PCSS3), a mixture of 4-chloromethylstyrene with different amounts of styrene with molar ratios of 1:1.3, 1:2.3 and 1:3.8, respectively, was dissolved in 15 mL of dioxane and was mixed with AIBN (1% molar) as a radical initiator, in a pyrex glass ampoule. The ampoule was degassed, sealed under vacuum, and maintained at 70 ± 1 ºC in a water bath, with stirring for about 48 h. Then the solutions were poured from ampoules into cooled methanol. The precipitates were collected and washed with methanol and dried under vacuum to yield (approximately 85%) of copolymers. For PCSS1, PCSS2, and PCSS3: ^{1}H NMR ($CDCl_3$, ppm) 1–1.8 (CH_2-CH), 4.5 (CH_2-Cl), 6.2–7.2 (Ar-H). FT-IR (KBr, cm^{-1}): 3024 (aromatic C-H), 2921-2860 (aliphatic C-H), 1490–1600 (aromatic C=C).

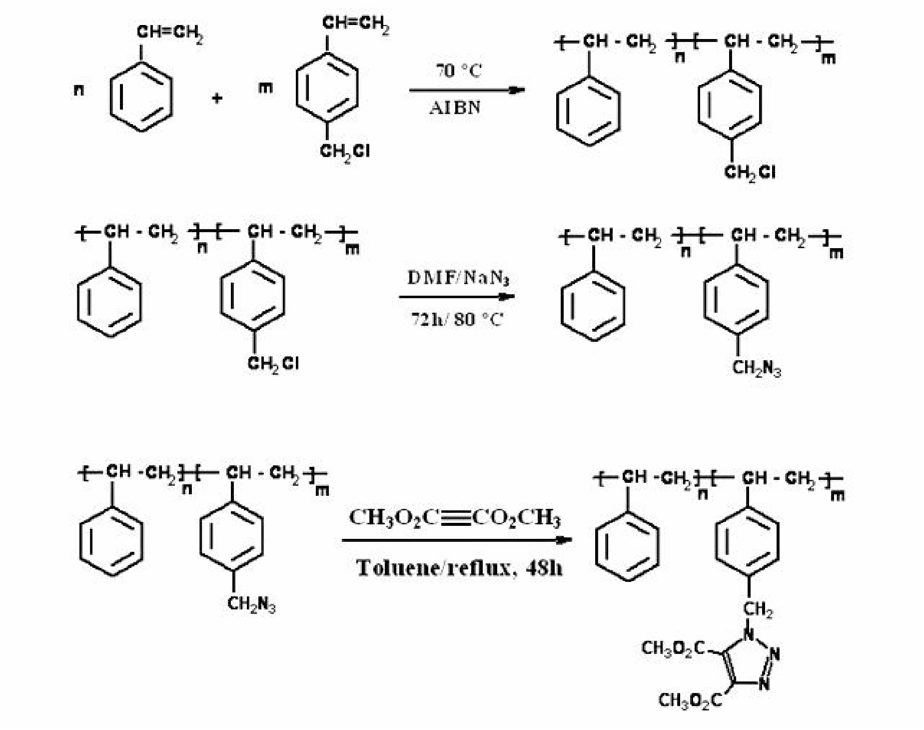
Attaching azide groups to copolymers: PASS

To a solution of copolymers (1 g) in anhydrous DMF was added excess amount of NaN_3 (0.5 g). The reaction was heated at 80 ºC for 48 hours. After addition of ethyl ether, the precipitated azide polymers was collected, washed with cold water and dried in vacuum to yield (around 95%), (Scheme 1). ^{1}H NMR ($CDCl_3$, ppm): 1–1.8 (CH_2-CH), 4.2 (CH_2-N_3), 6.2–7.2 (Ar-H). FT-IR (KBr, cm^{-1}): 3026 (aromatic C-H), 2921-2860 (aliphatic C-H), 2094 (azide N_3), 1490–1600 (aromatic C=C).

1, 3-cycloaddition of PASS with DMAD: PTAS

A solution of PASS (1 g) and dimethyl acetylenedicarboxylate (3 g) in toluene (40 ml) was heated at reflux. After 24 h, a further quantity of DMAD (1 g) was added, and the mixture heated at reflux for a further 24 h. After addition of ethyl ether, the precipitated polymers was collected, washed with cold methanol and dried in vacuum to yield (around 80%). ^{1}H NMR ($CDCl_3$, ppm): 1.2–1.8 (CH_2-CH), 3.6-4.2 (COO-CH_3), 5.6 (Ar-CH_2), 6.2–7.2 (Ar-H).

FT-IR (KBr, cm^{-1}): 3026 (aromatic C-H), 2921-2860 (aliphatic C-H), 1735 (ester C=O), 1490–1600 (aromatic C=C).



Scheme 1. Preparation of styrene type polymers containing 1,2,3-triazoles groups.

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