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Synthesis and Characterization of Grafted Polystyrene with Acrylonitrile using Gamma-Irradiation

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Abstract: Polystyrene grafted with acrylonitrile using gamma-irradiation technique was successfully synthesized. This process was carried out at various gamma dose (0.2-1.5 Mrad). The new grafted polymer was characterized and its properties were investigated. The results indicate that best grafting percentage ratio could be revealed when the concentration of the catalyst Ferrous Ammonium Sulphate (FAS) is about 2% and the monomer concentration is 90%, at 1.25 Mrad dose. The new grafted polymer was proved by FTIR, TGA and Viscosity techniques, which was analyzed and studied with a suggested presented mechanism. The adding of acrylonitrile to polystyrene improved the physical properties of polystyrene.

Key words: Polystyrene, acrylonitrile, FAS, gamma-irradiation, grafted polymer

INTRODUCTION

The uses of ionizing radiation to graft the macromolecules with monomeric molecules were the subject of several early studies. Special concern was paid by other studies to those macromolecules which have industrial applications such as polyethylene, polypropylene, polystyrene, cellulose and others. Some times used gamma irradiation in grafting process in the presence of atmospheric oxygen using different parameters i.e., temperature, solvents and catalyst variations, it was suggested that the degree of grafting of monomer increases with the increasing of the dose and the concentration of the monomer to certain limits. It is well known that physico chemical properties of some polymers can be verified to accommodate certain industrial and other applied demands (Kurilenk, 1980; Imai, 1982; Dole, 1973; Dongming *et al.*, 2009; Fydelor, 1971; Chapiro, 1962; Nicholas, 1997).

The study of polystyrene (PS)/acrylonitrile-butadiene-styrene (ABS) grafted copolymer/cyclohexanone or methylene chloride system compatibility both in concentrated solutions and solid state has been carried out by phase separation, viscosimetric measurements and thermal behavior (Cornelia *et al.*, 1981).

It is possible to graft vinyl monomers, such as acrylonitrile, on to polystyrene via anionic processes but not by a radical process. Both homopolymerization of the added acrylonitrile and graft copolymerization in which

acrylonitrile units are added to the para position on the benzene ring in styrene occur; the conversion of acrylonitrile into polymer depends upon the time and temperature of the reaction and on the concentration of the anionic initiator, butyllithium. A constant 15-20% of the acrylonitrile is converted to graft copolymer while the remainder is homopolymerized (Thomas and Wilkie, 1997).

Poly (styrene-co-acrylonitrile)-graft-poly (propylene oxide), the stabilizer formed *in situ* in the dispersion polymerization of styrene, acrylonitrile and macromonomer was separated from ungrafted copolymer by liquid chromatography. After the determination of the separation conditions by thin-layer chromatography, the effective separation of the graft polymer from copolymer was achieved by liquid column chromatography. The graft efficiency and the composition of the graft polymer was determined by UV and ¹H NMR (Guo *et al.*, 2001).

Gamma radiation-induced graft copolymerization of styrene onto poly (ethylene terephthalate) films was studied using simultaneous irradiation technique. The effects of grafting conditions on the degree of grafting were investigated. The grafting conditions include monomer concentration, irradiation dose, dose rate and the type of solvent (Mohamed, 2000).

The effects of γ irradiation on polymers used in food packaging have been studied by NMR. In order to assess the presence of a threshold dose for an observable effect, the whole range of 1-100 KGy was investigated. Polystyrene, poly-butadiene, styrene-acrylonitrile, high-impact polystyrene and acrylonitrile-butadiene-

tyrene were studied before and after the γ irradiation treatment and in the presence or in the absence of antioxidants and stabilizers (Pentimalli *et al.*, 2000).

The gamma radiation-induced surface graft copolymerizations of styrene-acrylonitrile and styrene-methyl acrylate to Teflon were studied. It was observed that the compositions of the various grafted copolymers are richer in the more polar monomer. These results were interpreted in terms of a preferential solvation of the relatively immobile growing graft polymer free radicals by the polar monomers (George *et al.*, 2003).

An evaluation of the flory-huggins interaction parameter was determined of poly (styrene-co-acrylonitrile) and poly (methyl-methacrylate) blend from the thermodynamic properties as enthalpy of mixing measurements to make a comparison for each temperature in accordance with the behavior of these mixtures (Frezzotti and Ravanetti, 1994).

In the present study a polystyrene polymer was grafted by acrylonitrile using gamma-irradiation, with chloroform as a solvent and FAS as a catalyst. The new grafted polymer obtained was investigated and characterized.

MATERIALS AND METHODS

Chemicals and materials: Polystyrene (Sigma Aldrich, Germany, 2009). Acrylonitrile a commercial form was purchased from Merck, Germany 2009 and used without any laboratory interferences.

Dimethyl formamide DMF (BDH Limited Poole England). Ferrous ammonium Sulphate FAS a grade of Fluka-Garantic was used. Chloroform and Ethanol (Scharlau).

Techniques

Gamma irradiation technique: Irradiation procedure was carried out by introducing polystyrene in a pyrex tubes with acrylonitrile as monomer using chloroform as solvent and FAS as a catalyst. The irradiation performed in the presence of atmospheric air. The resulting of grafted polymer was dissolved in DMF solvent, precipitated by ethanol then filtered using funnel. Precipitation process was repeated three times and then the yield was kept under reduced pressure in order to ensure complete removal of solvent. The gamma-irradiation was obtained with dosing rate 1.1 Mrad h⁻¹ using gamma cell 220 of Co⁶⁰ Canadian type. Figure 1 show the distribution of the dose in the gamma cell (Belchior *et al.*, 2008).

FTIR technique: The FTIR spectra were obtained from the perkin elmer FTIR 1650 spectrophotometer at room temperature using KBr disc method for characterizing the

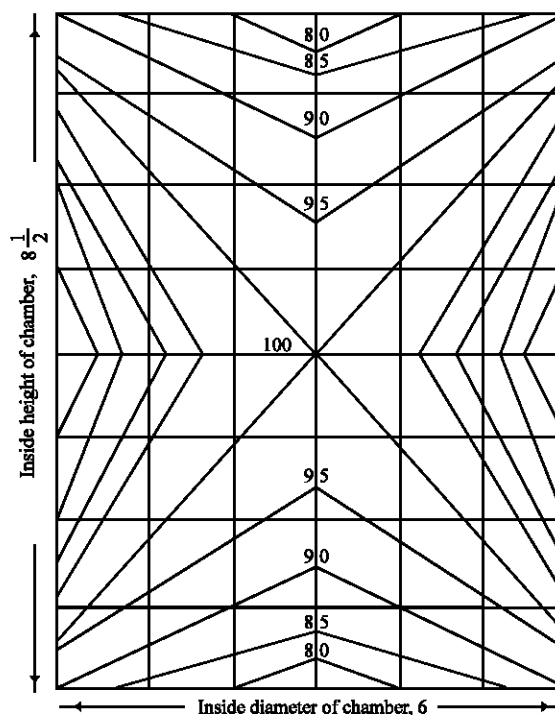


Fig. 1: The isodose distribution in the irradiation chamber

polymer. To prepare the disc method, the sample was dried and grounded with the KBr powder until they were in a well mixed, powdered form. The powder was then pressed at 8 tons for 1 min to produce the disc. The sample was scanned at 16 scans at wavenumber range of 4000-400 cm⁻¹.

Viscosity technique: Viscometry measurement of viscosity was performed by a viscometer. The grafted polymer was dissolved by DMF solvent, the reduced viscosity values (η_{red}) were calculated and plotted versus concentrations to give a straight line in accordance with Flory-Huggins equation (Ovejero *et al.*, 2007; Huggins, 1942; Fabio *et al.*, 2006).

$$\eta_{red} = \frac{t - t_0}{t_0 C}$$

Where:

- t_0 : Time flow of the solvent
- t : Time flow of the solution
- C : Concentration in g 100 mL⁻¹
- η_{red} : Reduce viscosity

Quantitative determination of grafting yield

$$\text{Grafting yield (\%)} = \frac{W_2 - W_1}{W_1} \times 100$$

Where:

W_1 : Film weight of polystyrene before grafting

W_2 : Film weight of polystyrene after grafting

TGA and DTGA techniques: The TG and DTG analysis using perkin elmer model TGA 7 thermalgravimetry analyzer was used to measure the weight loss of the samples. The samples were heated from 30-600°C with the heating rate of 10°C min⁻¹ under nitrogen atmosphere with a nitrogen flow rate of 20 mL min⁻¹.

RESULTS

Synthesis of polystyrene grafted with acrylonitrile using gamma-irradiation was proved by many identification methods:

- **FTIR methods:** Table 1 shows the assignment of the polystyrene, acrylonitrile and new grafted polymer (polystyrene grafted with acrylonitrile) as illustrate with the three spectra of FTIR in (Fig. 2)
- **Grafting study:** Figure 3-5 show the relationship between the percentage of grafting (w/w%) with gamma dose (Mrad), catalyst percentage (FAS w/w%) and monomer percentage (acrylonitrile w/w%), respectively
- **Viscosity study:** Figure 6 shows the viscosity relationship with grafted percentage for three different grafting percent samples to produce the intrinsic viscosity from intercept of linear relationship

Table 1: FTIR Assignment of Grafted Polystyrene, Polystyrene and Acrylonitrile

Assignment	Acrylonitrile	Polystyrene	Grafted polymer
CH ₂	3130(w)	Nd	Nd
CH ₂	Nd	Nd	3120(m)
CH	3075(m)	3025(s)	3025 (s)
CH	Nd	2920(s)	2920(s)
CH ₂	Nd	Nd	2925(s)
C=N	2230(s)	Nd	2245(s)
C=C	1940(m)	1945(m)	1950(m)
C=C	Nd	1740(m)	1740(m)
CH	1600(m)	1600(m)	1600(m)
C=N	1615(w)	Nd	Nd
CH-ring	Nd	1490(v.s.)	1490(v.s.)
C=C ring	Nd	1450(s)	1450(s)
CH-ring	Nd	1360(s)	1360(s)
-CH	Nd	Nd	1220(s)
CH	1090(w)	1070(s)	1070(s)
C=C ring	Nd	1030(s)	1030(s)
C=CH ₂	965	Nd	Nd
C=C-H	Nd	910(m)	910(w)
CH- ring	Nd	750(v.s)	750(v.s)
CH	690(v.s.)	690(v.s)	690(v.s)
CH- ring	Nd	540(s)	540(s)

s: Strong, m: Medium, w: Weak and v: Very

- **Thermal degradation properties (TGA and DTG):** Figure 7 is the TGA thermograms curve for polystyrene only and polystyrene grafted with

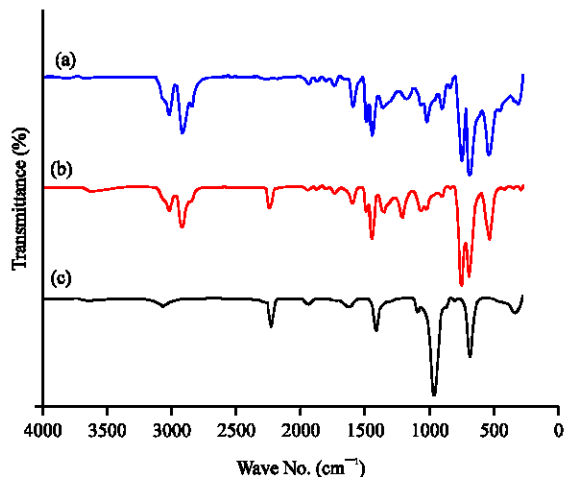


Fig. 2: FTIR spectra of (a) polystyrene, (b) grafted polymer and (c) acrylonitrile

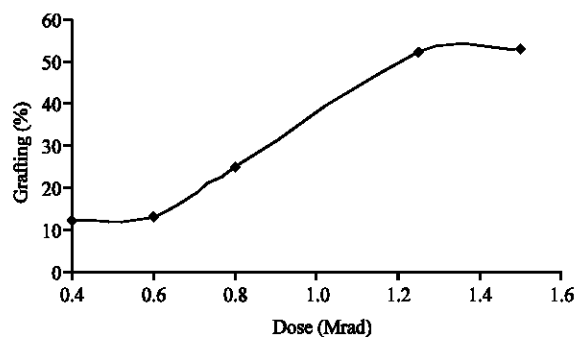


Fig. 3: Variation of grafting percent (w/w%) as a function of gamma dose of constant FAS concentration 2% (w/w%) and monomer concentration 90% (w/w%)

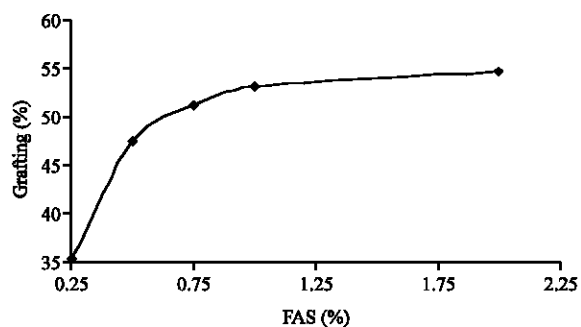


Fig. 4: Variation of grafting percent (w/w%) as a function of FAS concentration (w/w%) of constant dose 1.25 Mrad and monomer concentration 90% (w/w%)

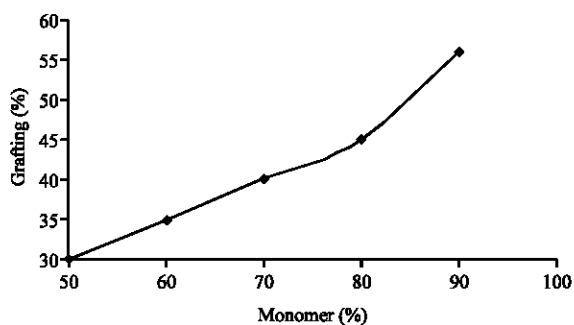


Fig. 5: Variation of grafting percent (w/w%) as a function of monomer concentration of constant dose 1.25 Mrad and FAS concentration 2% (w/w%)

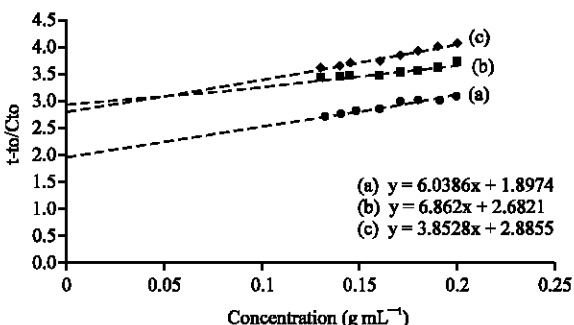


Fig. 6: Variation of reduced viscosities (mL g^{-1}) of grafted polymer as function of concentration (g mL^{-1}) of grafted polymer in different grafted percentage (a) grafted polymer (%) = 21.68 (b) grafted polymer (%) = 42 and (c) grafted polymer (%) = 54.1

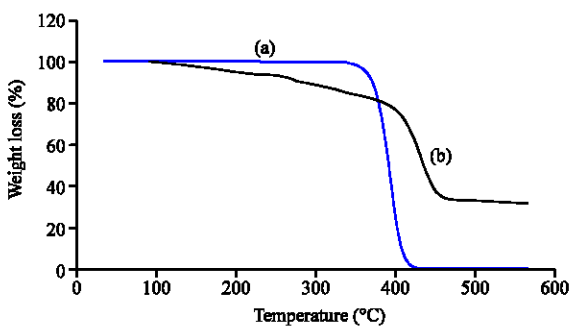


Fig. 7: TGA thermograms curve for (a) Polystyrene and (b) Grafted polymer

acrylonitrile. Figure 8a and b of DTG for polystyrene only and polystyrene grafted with acrylonitrile, respectively

The concentration of the catalyst (FAS) is 2% and the monomer concentration is 90%, at 1.25 Mrad dose.

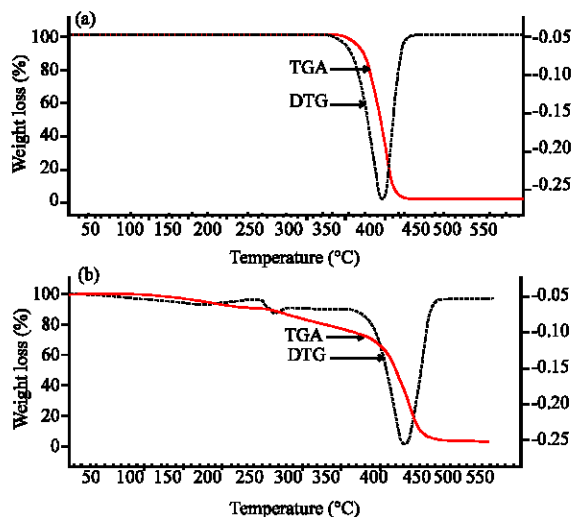


Fig. 8: (a) TGA and DTG thermogram curves for Polystyrene at a heating rate of $10^{\circ}\text{C min}^{-1}$, (b) TGA and DTG thermogram curves for Grafted Polymer at a heating rate of $10^{\circ}\text{C min}^{-1}$

These results designate that best grafting percentage ratio could be exposed. The new grafted polymer was proved by FTIR, TGA and Viscosity techniques, which was analyzed and studied with a suggested presented mechanism.

The above results confirm that the adding of acrylonitrile to polystyrene was successfully grafted.

DISCUSSION

FTIR study: Figure 2 shows the FTIR spectra that grafting occur of the acrylonitrile on to the polystyrene specially when the spectrum of polystyrene alone has no indication of (-CN) absorption band, this band 2230 cm^{-1} appears in the grafted polymer at 2245 cm^{-1} for CN. Moreover, the band of C=N appeared at 1615 cm^{-1} corresponding to the resonance of the nitrile group when it was in the acrylonitrile form. However, it disappears when the group is grafted with polystyrene. Moreover, a strong band appears at 1220 cm^{-1} for -CN of grafted polymer only. Then the very strong broad band appears in the spectrum of acrylonitrile at 965 cm^{-1} which indicating that C=C-H₂ of the carbon closed to C=C group was disappeared in the grafted polymer and polystyrene which proved this band is for acrylonitril only. The detailed information of FTIR spectra are shown in Table 1 (Radhi and EL-Bermami, 1990; Colthup *et al.*, 1975).

Grafting study: It was found that the percent of grafting increased with the dose of gamma irradiation throughout the dose range from 0.4-1.5 Mrad as show in Fig. 3. It

explain the type of variation when keeping the concentration of the catalyst FAS and the monomer at 2 and 90% (w/w%), respectively. It was also found that the percent of grafting in it's higher value is occur when the concentration of the catalyst FAS is about 2% (Fig. 4), although that at constant gamma dose (1.25 Mrad) and monomer concentration (90%) the grafting percent was in high value. Another study was the effect of monomer concentration on grafting percent which is found at 90% as in Fig. 5.

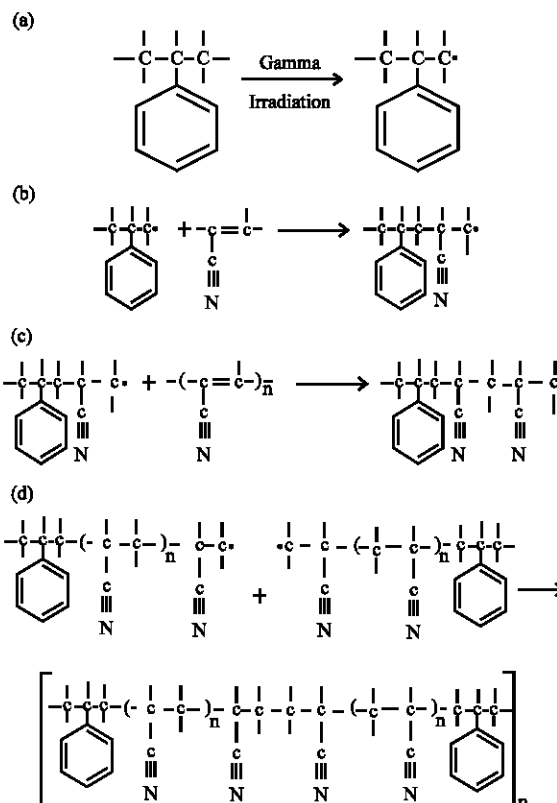
Viscosity study: The effect of grafted lateral chains was studied by determination of intrinsic viscosity $[\eta]$ at different grafted polymer, up to 54.1% grafting, the $[\eta]$ increased linearly as in (Fig. 6) with increasing grafting percent which prove the simple effect of lateral chains on the original macromolecule of polystyrene and the absent of network formation. The values of intrinsic viscosity of grafted polymer are high of the high grafted percentage as shown in Fig. 6.

Thermal degradation properties (TGA and DTG): The TGA curve and DTG curve obtained for Polystyrene is shown in Fig. 7a and 8a, respectively. Degradation commences near 395.96°C and continues rapidly until about 440.89°C.

The TGA curve and DTG curve for grafted polymer (polystyrene grafted with acrylonitrile) are presented in Fig. 7b and 8b, respectively. Degradation proceeds in double steps commencing the first step at 169.45°C and ending at 267.39°C indicating to traces of poly(acrylonitrile) ungrafted in polymer, while the second step begin at 432.64°C and ended at 480.09°C for the Grafted Polymer (polystyrene-acrylonitrile) (Ahmad *et al.*, 2007).

Polymerization methods: Free radicals used to initiate polymerization can be generated in two ways: by temperature-sensitive catalysts or radiation curing. Chemical curing is a cheaper method with small-scale productions, whereas, gamma radiation is more economical on a larger scale, the suggest mechanism of polystyrene by free radical as the following steps Manas (2006). The mechanism of grafted polystyrene with acrylonitrile was proposed at Scheme 1 in the following four steps.

- A free radical catalyst or gamma-irradiated polymer generates the free radicals ($R\cdot + R\cdot$). Polystyrene \cdot + Polystyrene \cdot
- **Initiation step:** $R\cdot + M$ (monomer) $\rightarrow R-M\cdot$
Polystyrene \cdot +Acrylonitrile \rightarrow Polystyrene+Acrylonitrile \cdot



Scheme 1: The proposal mechanism of polystyrene with acrylonitrile

- **Propagation step:** $R-(M)_n-M\cdot + M \rightarrow R-(M)_{n+1}-M\cdot$
Polystyrene-(Acrylonitrile) $_n$ -Acrylonitrile \cdot + Acrylonitrile \rightarrow Polystyrene-(Acrylonitrile) $_{n+1}$ -Acrylonitrile \cdot
- **Termination step (coupling mechanism):** $R-(M)_n-M\cdot + R-(M)_n-M\cdot \rightarrow R-(M)_n-M-M-(M)_n-R$
Polystyrene-(Acrylonitrile) $_n$ -Acrylonitrile \cdot + Polystyrene-(Acrylonitrile) $_n$ -Acrylonitrile \cdot \rightarrow
- Polystyrene-(Acrylonitrile) $_n$ -Acrylonitrile-(Acrylonitrile) $_n$ -Polystyrene.

Our literature review show that no information regarding grafting of polystyrene by gamma radiation.

CONCLUSIONS

It was possible to graft onto polystyrene by a radical process as, used acrylonitrile (monomer) with gamma irradiation. The extent of grafted polymer formation depends upon:

- The percentage of the monomer was about 90% (w/w%)

- The percentage of the catalyst (FAS) was about 2% (w/w%)
- The total gamma dose was around 1.25 Mrad

The formation of a grafted polymer was successfully carried out using gamma irradiation with FAS as a catalyst. The new grafted polymer was characterized by FTIR spectroscopy and TG analyzer.

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