

Synthesis and Characterization of Copolymer of Styrene and Acrylonitrile by Emulsion and Microemulsion Polymerization Using Different Emulsifiers

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Stable poly(styrene/acrylonitrile) (SAN) latexes were produced by polymerization of styrene and acrylonitrile in emulsion and microemulsion using sodium dodecyl sulfate and potassium oleate anionic emulsifiers. Their chemical structure, morphology and thermal behaviour were inspected by fourier transform infrared spectroscopy, scanning electron microscopy, thermo-gravimetric analysis and differential scanning calorimeter analysis respectively. Fourier transform infrared spectroscopy analysis verified the successful formation of copolymers of poly(styrene/acrylonitrile). The addition of different emulsifiers and acrylonitrile to the polystyrene improves its structure and thermal stability. Copolymer produced by microemulsion polymerization of styrene and acrylonitrile was found to be more thermally stable with higher molecular weight and molar mass and long range ordered microporous morphology with the reduction of particle size from 2-12 nm to 1-10 μm as compared to other copolymers synthesized by emulsion polymerization.

Key Words: Microemulsion, Poly(styrene/acrylonitrile), Latexes.

INTRODUCTION

Microemulsion is a heterogeneous system of oil, water and amphiphilic compounds which is optically isotropic, transparent and thermodynamically stable liquid firstly introduced by Hoar and Schulman^{1,2}. Emulsions and microemulsions are proficient to yield well defined latex particles with controllable high molecular weights. However the main difference between emulsions and microemulsions lies in the size and shape of the particles disseminated in the continuous phase. Particle nucleation in microemulsion polymerization of size smaller than 1-20 μm than those of conventional emulsion of size 2-100 nm is considered to be a continuous process and the locus of nucleation is shown to be the microemulsion droplet^{3,4} but exact mechanism of microemulsion copolymerization remained focused in the last decade by several authors^{5,6}. Because of its smaller sized particles, thermodynamically optimized structure and unique solubilization properties, microemulsions have attracted increasing attention as potential drug delivery systems, either as vehicles for topical applications or as bioavailability enhancers for poorly water soluble active pharmaceutical ingredients and in dermal or transdermal drug delivery^{7,8}.

Poly(styrene/acrylonitrile) (SAN) is copolymer of styrene and acrylonitrile with superior mechanical properties, chemical and heat resistance as compared to polystyrene of general

purposes. Copolymers of styrene and acrylonitrile (SAN) are well known to have broad spectrum of applications such as automotive parts, battery cases, kitchenware, appliances, furniture and medical supplies due to their chemical, mechanical and optical nature. Furthermore they possess easy processibility and thermal stability. The copolymerization of these two monomers in bulk, solution or emulsion system has been widely reported^{9,10}. Accessible approach through literature reveals that little work has been done to synthesize copolymer of styrene and acrylonitrile using emulsifier in microemulsion process^{11,12}. It has been observed that this type of polymerization in the presence of co-emulsifiers was complex, because they impart partition among different domains of microemulsions, monomers and aqueous phase and can change the location of monomers. It can modify the partitioning of monomer and may act as chain transfer agents^{13,14}.

Keeping in attention in this complex copolymerization, we have synthesized the copolymer of styrene and acrylonitrile by emulsion and microemulsion polymerization by using two different emulsifiers. The variations in their properties have been investigated by using different analytical techniques.

EXPERIMENTAL

Styrene by Sigma-Aldrich chemie, acrylonitrile by Acros organics was distilled prior to use and kept under nitrogen.

Sodium dodecylsulfate (SDS) and potassium oleate (PO) was purchased from Merck-Schuchardt. Potassium persulphate ($K_2S_2O_8$) and sodium thiosulphate by M and B chemicals were used in this research work.

Synthesis of polystyrene and polyacrylonitrile: Monomers of styrene and acrylonitrile were washed firstly with 5 % solution of NaOH to remove inhibitors and then distilled under reduce pressure and nitrogen flow. 0.5 M solutions of sodium thiosulphate and ammonium persulphate were prepared in distilled water and then 40 mL of both solutions were added in 0.4 g of sodium dodecylsulfate. After mixing 20 mL of styrene or acrylonitrile was added in the above solution under constant magnetic stirring at 70 °C for 4 h. The reaction mixture was coagulated in 5 % NaCl solution and filtered under vacuum. The latex was washed by distilled water to remove surfactant and was dried by keeping in vacuum oven at 50 °C for 24 h to get polystyrene or polyacrylonitrile respectively¹⁵.

Synthesis of copolymers of styrene and acrylonitrile: Copolymers of styrene and acrylonitrile were prepared by adding 10 mL of both pure styrene and acrylonitrile monomers in different emulsifiers such as sodium dodecylsulfate, polystyrene and emulsifier free solutions to get SAN-I, SAN-2 and SAN-3 respectively as given in Table-1 and reflux at 70 °C for 4 h. After reflux the reaction mixture was cooled and added to the 400 mL of 5 % NaCl solution until white polymer has formed. Copolymer was pressed and their salt solutions were decanted and collected samples were dried at 50 °C for 24 h.

TABLE-1
CHEMICAL COMPOSITION OF ALL SAMPLES

Sample name	Emulsifier	Styrene: acrylonitrile	Reaction temp. (°C)	Copolymerization
PS	SDS	100:0	70	Emulsion
PAN	SDS	0:100	70	Emulsion
SAN-1	SDS	50:50	70	Emulsion
SAN-2	PO	50:50	70	Emulsion
SAN-3	×	50:50	70	Emulsion
SAN-4	SDS	50:50	70	Microemulsion

Microemulsion polymerization: In microemulsion polymerization, the amount of emulsifier (sodium dodecyl sulfate) was increased from 0.4 to 1.5 g. 10 mL of both styrene and acrylonitrile were added in the above reaction mixture. The microemulsion polymerization reaction was proceed at 70 °C for 4 h and latex was purified as described above and dried at 50 °C under *vacuum*¹⁶.

Characterization: IR-Prestige-21-fourier transfer infrared spectroscopic instrument operated at room temperature in the normal IR region 4000-650 cm^{-1} and 4 cm^{-1} band resolution was used for structural analysis. Polymers were dispersed in potassium bromide and compressed into pellets. S-3400 Hitachi scanning electron microscope was used for morphological analysis. Scanning electron microscope was operated in back scattered electron image mode. All images were obtained at an accelerating voltage of 25 KV. Thermal analysis of polystyrene, polyacrylonitrile and all SAN samples was studied by SDT Q-600 TGA/DSC instrument in the temperature range of 25 °C to 1500 °C and at heating rate of 10 °C/min under inert atmosphere. Differential scanning calorimetry measurements were performed in Q-200 DSC, TA instrument from 25

to 400 °C with refrigerated cooling system (RCS) at 10 °C/min under inert atmosphere. Ostwald viscometer was used to determine molecular masses of all samples. Dimethylformamide (DMF) was used as a solvent and molar masses of all samples have been determined by viscosity method at 25 °C by using Mark Hounwink equation:

$$[\eta] = k M^a$$

where $k = 1.2 \times 10^{-4}$ and $a = 0.77$

RESULTS AND DISCUSSION

FT-IR analysis: Fig. 1 shows the FT-IR spectrum of polystyrene that exhibits the characteristic frequency of aromatic C-H stretching at 3107 cm^{-1} , aliphatic C-H stretching at 2771 cm^{-1} , aromatic ring of styrene at 1523 cm^{-1} and the peak of C-H bending of mono-substituted ring at 694 cm^{-1} ¹⁷. Polyacrylonitrile shows the characteristic vibrational bands at 2883 cm^{-1} for aliphatic C-H stretching and 2304 cm^{-1} which are assigned to -C=N stretching vibration, while the peak appeared at 1413 cm^{-1} is due to CH₂ scissoring mode as shown in Fig. 1 (b)¹⁸. FTIR spectra of SAN-1, SAN-2, SAN-3 and SAN-4 also exhibit the characteristic frequency of -C=N stretching at 2334, 2338, 2339 and 2339 cm^{-1} , aliphatic C-H stretching at 2839, 2960, 2920 and 2960 cm^{-1} respectively. Characteristic peak of aromatic ring of styrene appeared almost at 1530 cm^{-1} in all SAN copolymers, C-H bending and CH₂ scissoring modes appeared in the range of 710-650 cm^{-1} and 1400-1350 cm^{-1} , respectively. Band showing C-N stretching and aromatic ring is the characteristic bands of SAN copolymers¹⁹.

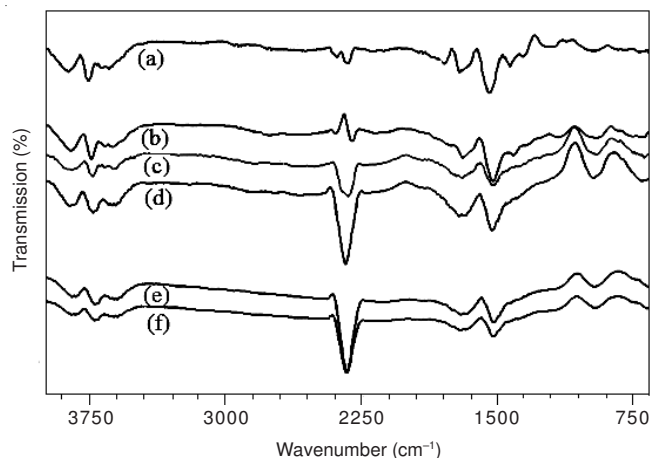


Fig. 1. FTIR spectra of (a) PAN (b) PS (c) SAN-1 (d) SAN-2 (e) SAN-3 (f) SAN-4

Percentage yield and molar mass determination: The percentage yield and molar mass of all SAN samples indicates that molecular weight of all copolymers is dependent on composition and nature of used emulsifiers (Table-2). It is also cleared from results that copolymer of SAN synthesized under microemulsion polymerization offered highest yield and molar mass among all prepared samples.

Scanning electron microscopy analysis: Fig. 2a shows the SEM micrograph of SAN-1 in which rectangular shaped particles of size 2-12 nm are seen to be bounded firmly with each other in a highly blended material. In SAN-2 particles of irregular shape and the size in the range of 10-35 μm are

scattered to some extent in the form of long range small branches on the surface. Grains of SAN-3 have much irregular shape and particles are not oriented in a well-defined way. It may be due to the fact that no emulsifier has been used during fabrication that could bind the particles together. Fig. 2d shows the copolymer of SAN synthesized in microemulsion polymerization having microporous pronged morphology with clear and denser branched shape assembly with small branches attached to long ones. They are elongated up to more than 500 μm length to form a continuous phase with particles of size 1-10 μm bounded with each other in an interesting way.

TABLE-2
MOLAR MASS AND PERCENTAGE YIELD
OF COPOLYMERS OF SAN

Sample	Yield (%)	Mol. mass (10^5 g/mol)
SAN-1	82.06	0.11
SAN-2	47	1.02
SAN-3	35.3	0.91
SAN-4	92	2.09

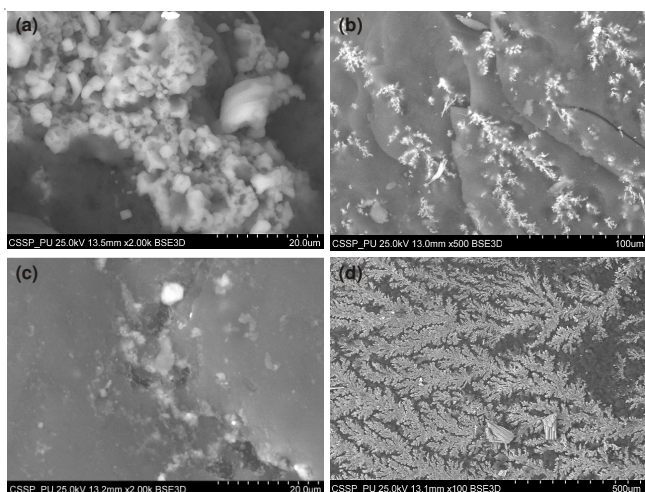


Fig. 2 SEM images of (a) SAN-1 (b) SAN-2 (c) SAN-3 (d) SAN-4

Thermal gravimetric analysis: Thermal degradation of polystyrene, polyacrylonitrile and their copolymers have been studied in an inert atmosphere and the percentage weight loss as the function of temperature for all samples are given in Table-3 (Fig. 3). The TGA thermograms of polystyrene and polyacrylonitrile (PAN) exhibited two-step weight loss in the range of 25-475 $^{\circ}\text{C}$. Weight loss in first step is assigned to the loss of moisture and in second step due to the degradation of copolymer^{20,21}. Polyacrylonitrile was found to be more thermally stable than polystyrene with 57.24 % weight loss from 290-470 $^{\circ}\text{C}$, which degrades 86 % in that given temperature range. Above 500 $^{\circ}\text{C}$ the weight loss is very slow this is due to the char-oxidation of polyacrylonitrile residues²². While copolymer of styrene and acrylonitrile revealed one step thermal degradation initiated from 340 $^{\circ}\text{C}$ and decomposed completely at 435 $^{\circ}\text{C}$ with 94.86 % weight loss. SAN-2 and SAN-3 also followed the similar trend of two zones of weight loss like polystyrene and polyacrylonitrile. The first weight loss of 7.37 and 16.95 % and second weight loss of 80 and 82 % for SAN-2 and SAN-3 respectively as given in Table-3. Microemulsive copolymer showed maximum thermal stability

among all copolymers with the weight loss of only 75.83 % in one step like SAN-1 in the temperature range of 300 to 460 $^{\circ}\text{C}$ that can be attributed to the long range continuous phase of micro latex particles nucleation^{23,24}.

TABLE-3
DSC AND TGA DATA OF PS, PAN, SAN-1,
SAN-2, SAN-3 AND SAN-4

Sample	Onset Temp. ($^{\circ}\text{C}$)	Ending Temp. ($^{\circ}\text{C}$)	Weight loss (%)	Tg ($^{\circ}\text{C}$)
PS	350	490	34.17	100
PAN	240	450	87.38	98
SAN-1	240	460	86.31	112
SAN-2	270	500	85.91	109
SAN-3	290	460	83.79	88
SAN-4	300	500	75.83	114

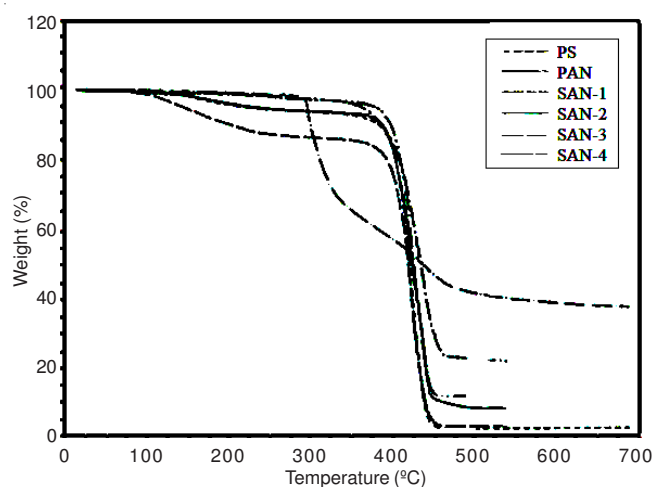


Fig. 3. TGA thermograms of PS, PAN, SAN-1, SAN-2, SAN-3, SAN-4

Differential scanning calorimeter analysis: The DSC thermograms of polystyrene, polyacrylonitrile and all SAN samples are depicted in Fig. 4. Polyacrylonitrile showed an endothermic curve in heat flux at 95 $^{\circ}\text{C}$ due to transformation from amorphous glassy phase to a flexible substance and an exothermic curve at initial stabilization temperature 300.66 $^{\circ}\text{C}$, due to its glassy nature contributed towards the cyclization of nitrile group contributed to the evolution of large amount of heat released from the polyacrylonitrile homopolymer^{21,22,24}. It can be seen that glass transition temperatures of all copolymers except SAN-2 are shifted towards higher temperatures as compared to the pure polystyrene and polyacrylonitrile as shown in Table-3. This decrease in glass transition temperature of SAN-2 may be attributed to the higher symmetry and low chain rigidity offered by potassium oleate emulsifier to lower its thermal stability²⁵.

Continuing to heat copolymers former to its glass transition temperature eventually leads to another endothermic transition peak due to melting of polystyrene in the range of 350-490 $^{\circ}\text{C}$. All samples were found to be more thermally stable than polystyrene but the microemulsive SAN presented highest glass transition and melting temperatures of 114 $^{\circ}\text{C}$ and 440.54 $^{\circ}\text{C}$ due to bulky chains, higher molecular weight, molar mass and crosslinking as indicated by viscometer and SEM studies.

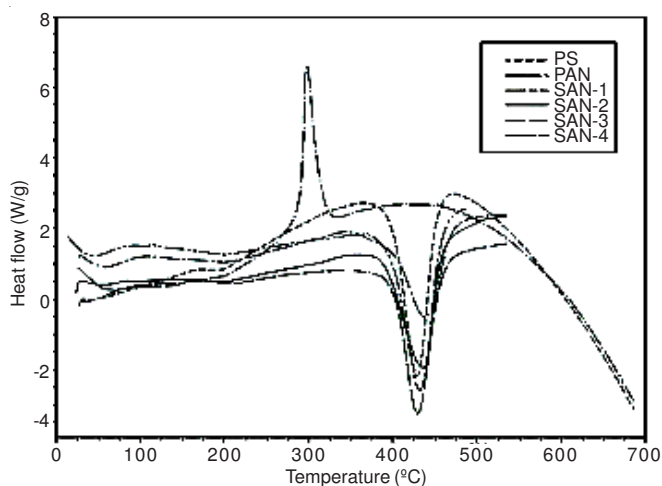


Fig. 4. DSC thermograms of PS, PAN, SAN-1, SAN-2, SAN-3, SAN-4

Conclusion

Copolymers of styrene and acrylonitrile are successfully prepared by emulsion and microemulsion polymerization by using two different emulsifiers. Copolymer produced under microemulsion exhibit dramatically enhanced structural and thermal properties among all other prepared samples due to its higher molecular weight, molar mass, micro-porous particles and bulky nature as inferred from viscometer and SEM studies. Glass transition temperature was also explored to depend on the molecular weight of copolymer.

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