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Photoacoustic Evaluation of Supercritically Synthesized Polyacrylic Acid Graft Polybisphenol-A-Carbonate

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Abstract: Graft copolymerization of acrylic acid (AA) onto polybisphenol–A-carbonate (PC) in presence of benzoyl peroxide (BP) as a catalyst in supercritical carbon dioxide afforded a series of polyacrylic acid graft polybisphenol-A-carbonate (PAA-g-PC) within the grafting range of 1.33-17.50%. The process of graft copolymerization was monitored with reference to the variations in concentrations of BP and AA along with supercritical temperature and pressure. These grafts copolymers were optically characterized by UV-VIS spectroscopy and Photoacoustic Spectroscopic (PAS) technique. PA spectra of PAA-g-PC with three grafting percentage clearly indicate that the intensity of PA signals increases with increasing grafting percentage of PAA onto PC. Such type of result was not found with UV-VIS spectroscopy due to the different solubility of grafts in to the chloroform using as a solvent. Thus it revealed that the PAS technique is more convenient than other conventional spectroscopic techniques to monitor the grafting of monomers in polymeric backbone.

1. Introduction

Synthesis and processing of polymers and composite materials in batch reactors at industrial levels require appropriate strategies for the selection and solvent disposal. Most of the developed countries therefore currently replacing such batch reactors to maintain clean environments through applications of supercritical solvents[1]. In this connection, supercritical carbon dioxide as a reaction media offers excellent technological potentials towards replacements of conventional hazardous organic solvents with simultaneous optimization and control in the conditions for processing of polymer based material[1-2]. In the present research work we have studied the graft copolymerization of poly acrylic acid (PAA) onto polybisphenol A Carbonate (PBAC) using supercritical carbon dioxide as a reaction medium[3]. To optimize the reaction conditions a series of graft- copolymers (PAA-

g-PBAC) were synthesized at varying supercritical pressure, temperature and also with concentrations of monomer and peroxide. Graft copolymerization process was carried out in a commercially available high-pressure reactor (PPI, USA) of 100 ml capacity using benzoyl peroxide as a catalyst. Grafting of PAA onto PBAC of the grafted products was characterized by UV-VIS spectroscopy along with Photoacoustic Spectroscopic technique.

2. Experimental

PBAC, acrylic acid (AA) and benzoyl peroxide (BP) were purchased from M/s Sigma Aldrich USA and were used without further purifications. Reactor vessel was charged with calculated quantities of monomer, polymer and benzoyl peroxide catalyst with carbon dioxide. Vessel temperature was then controlled with. The system was heated to temperatures above critical temperature of carbon dioxide to achieve the super critical conditions therein. Graft co polymers with grafting (%)1.33-17.50%. Synthetic process was studied at 1200-2200 psi for 3.0 hours at 70±1°C. The crude graft was then isolated through depressurizing the reactor system and extracted with methanol to remove the catalyst and homopolymer content using soxlet extractor. The grafting (%) has been evaluated as Grafting (%) = $[(W_2—W_1) / W_1] X 10^2$ Where W_1= Weight of backbone polymer and W_2=Weight of graft copolymer[4].

3. Measurements

Selected grafts were characterized by UV-VIS spectroscopy using Gensis10 thermospectronic USA and through Photoacoustic spectral (PAS) technique. In the later technique, which consists of PA, spectra were recorded in the wavelength range of 200-800nm by the homemade PA cell (1.5cm diameter and 2mm depth). The Photoacoustic spectrometer (Fig. 1) consists of a 1000 W tungesten halogen lamp (Phoenix Lamps, India) passing through a monochromator (Cornerstone 130,1/8 m, Thermo Oriel, USA), which was controlled by a personal computer, using appropriate software (TRACQ 32™, model 77788 and Monoutility Program). The emergent beam of monochromatic light was reflected by a concave mirror and then focused by quartz lens of focal length 5.4cm on the window of the home made PA cell. The light beam was modulated at 23Hz by a mechanical chopper (SR540, Stanford, USA). The pre amplified acoustic signal was sent to a phase lock-in amplifier (SR530, Stanford, USA), which was receiving a reference signal from a mechanical chopper. Finally, the acoustic signal was recorded from the lock-in amplifier[5].

4. Results and Discussion

Graft copolymarization of PAA onto PBAC under various concentration variables and super critical parameters were studied. Variations in concentration of BP [0.52-2.28X10^{-5}] M at 1400psi, 70±1°C,Time: 90 min., and [AA]: 3.28X10^{-3} M with [PBAC]: 100 mg afforded PAA-g-PBAC with grafting (%) in the range of 1.33-17.50% . With variations in AA (3.28-

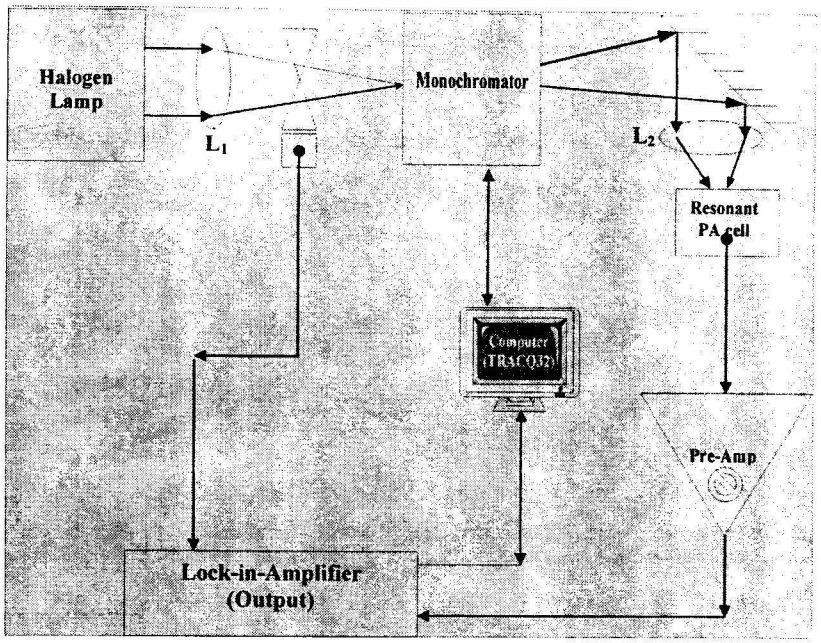

Fig. 1 Schematic diagram of Photoacoustic spectrometer

9.85X10^{-3}M) at 1400psi, 70±1^{0}C [BP] 0.52 X10^{-5}M PAA-g-PBAC with grafting in the range of 1.33-17.50% was obtained with in 90 min. Temperature variations in the range of 60-80: ±1^{0}C at 1400 psi, 90 min, [AA]: 3.28X10^{-3},[BP]: 0.52-2.28X10^{-5}M PAA indicated grafting onto PBAC in the range of 1.33-17.50%. Pressure variations in the range of 1400-1800 psi at90 min, 70±1^{0}C, [AA]: 3.28X10^{-3},[BP]:0.52-2.28X10^{-5}M afforded Grafting (%)1.33-17.50% It was found that maximum grafting occurs at a pressure of 1800 psi as 18.00%.At 1400 psi,, 70±1^{0}C.,[AA]: 3.28X10^{-3},[BP]: 0.52X10^{-5}M and varying range of reaction time of about 45-135:min grafting (%)1.33-17.50% was observed. It was found that maximum grafting occurs at the reaction time of 135 min as 17.91%

5. US-VS Spectroscopy

The UV spectra of Pure PC,AA and their Graft PAA-g-PC were taken out and their characteristic absorption bands were found (Fig.2) as :-

PC: 265nm,1.894,241nm,1.509

AA:241nm,.095

PAA-g-PC : 241nm,1.468,265,.927,271,.901.

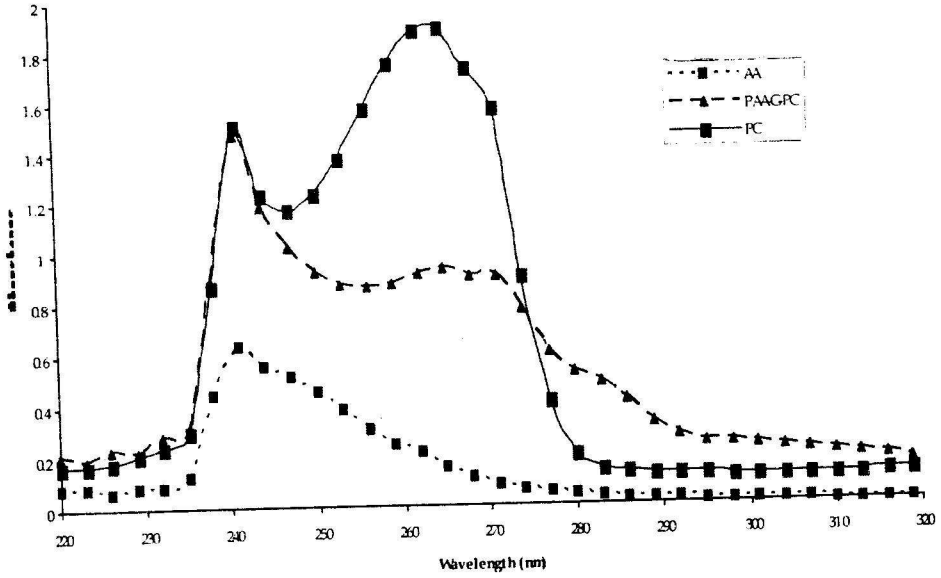

Fig.2 : UV Spectra of AA, PC and PAA-g-PC (14.53%)

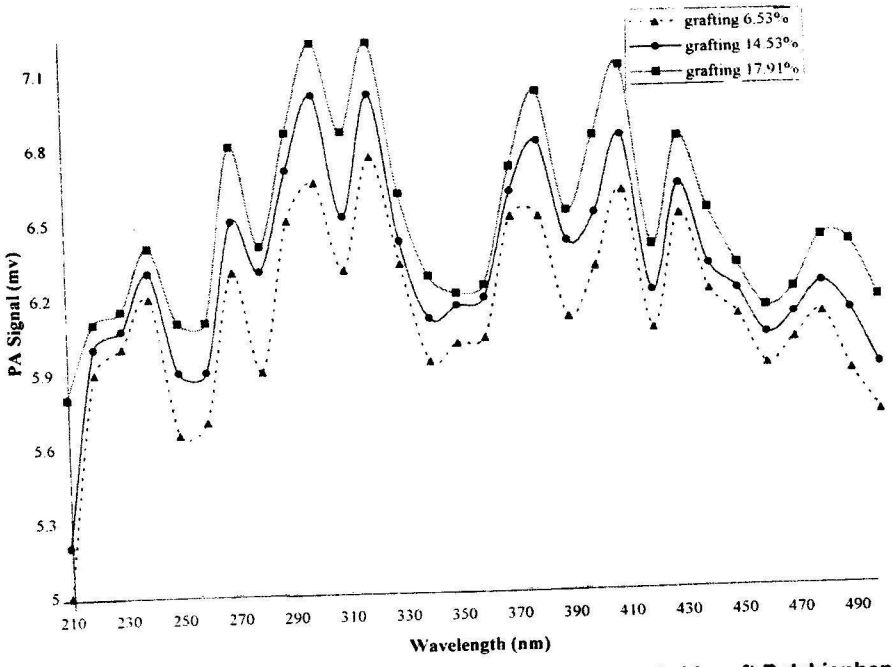

Fig. 3 : PAS of Supercritically Synthesized Polyacrylic Acid graft Polybisphenol-A-Carbonate

6. Photoacoustic Spectroscopy

The three sample of grafting (5%,10 % and 15%) respectively were characterized at wavelength range of about 200 to 500 nm. The seven sharp absorption bands at 240, 275, 300, 320, 385, 410, 430 & 490(nm) with increasing intensity clearly differentiate the three samples with each other. Since all the samples contain the same functional groups so we can say that there is no wavelength difference in the absorption region of the three grafts. However the signal intensity increase with increasing grafting %.(Fig. 3). In this technique there is no need of sample preparation. The solid grafts were directly placed in sample cell and the spectrum was monitored. It is therefore this technique provide valuable aspects for polymer characterizations.

7. References

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