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Research Article

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Nano CdS Doped Poly (4-Formyl-2-Methoxyphenyl Methacrylate): Synthesis, Characterization and Thermal Properties

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ABSTRACT

Free radical polymerisation was employed for the preparation of homopolymer, poly (4-formyl-2-methoxyphenyl methacrylate) (FMPMA) and 2,2-azo-bisisobutyronitrile (AIBN) used as initiator in N,N-dimethylformamide (DMF) as solvent. Different concentrations of cadmium sulphide nanoparticles were embedded in a poly (FMPMA) matrix by in situ technique. Poly (FMPMA) and CdS/FMPMA nanocomposites were characterized by Fourier transform infrared spectroscopy (FT-IR) and structural characterization of CdS in nanocomposite was done by X-Ray diffraction (XRD). The XRD data showed CdS to have 2.49-3.56 nm diameter with cubic structure. Thermal characteristics of poly (FMPMA) and polymer nano composites were obtained from thermogravimetric analysis (TGA) and kinetic parameters of poly (FMPMA) and polymer nanocomposites were calculated using Broido method.

Keywords: Polymer nanocomposite; CdS nanoparticles; Free radical polymerization; Thermal characteristics; Broido method

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INTRODUCTION

Acrylate and methacrylate polymers have many important avenues of applications, like adhesive, textile, biomedical, coating and paint. The improvement of the mechanical properties of these polymers had been the centre of interest for many years, but presently electrical and optical properties are receiving more attention. Functional group provides the polymer structure special character, substantially different from the inherent properties of the basic polymer chain [1]. Nanocomposite is a multiphase solid material in which at least one of the phases shows dimension in the nanometre range below 100 nm. Inorganic nanoparticles embedded polymer composites have drawn the attention of researchers, because of variety of applications in the field of optics, electronics, magnetic and biology with exclusive mechanical, photoelectric and thermal properties and these have advantages as the polymeric systems are modified [2-5]. The inorganic nanomaterials (rigidity, good thermal stability) and organic polymers (ductility, flexibility, dielectric) provide the combined advantages [6, 7]. Cadmium sulphide (CdS) is a very interesting compound and many studies have focused on CdS because of variety of applications in areas like photocatalysis, optoelectronics, photoluminescence, light emitting diodes, thin film transistors, solar cells and many others [8-17]. Thermogravimetric analysis has been widely used as a method to investigate the thermal stability of polymer/ polymer nanocomposites [18] and to study the kinetic and thermodynamic parameters of polymer degradation such as activation energy, enthalpy change, pre-exponential factor, entropy change and free energy change. Cds/polymer nanocomposite has good thermal stability that is important from application point of view. Here we report the preparations of homopolymer of FMPMA using free radical polymerization and polymer nanocomposite with different concentrations of cadmium sulfide. Poly (FMPMA) and polymer nanocomposites with nanoparticles of CdS were characterized by FT-IR. XRD data was used to identify the CdS nanoparticles. The thermal properties of the polymer and its composites were studied with thermal gravimetric analysis. The energy of activation for themal decomposition was calculated from Broido [19]. The main focus of this investigation has been on the effect of different concentrations of CdS nanoparticles on the thermal stability and consequent kinetic and thermodynamic parameters of thermal decomposition of polymer composites.

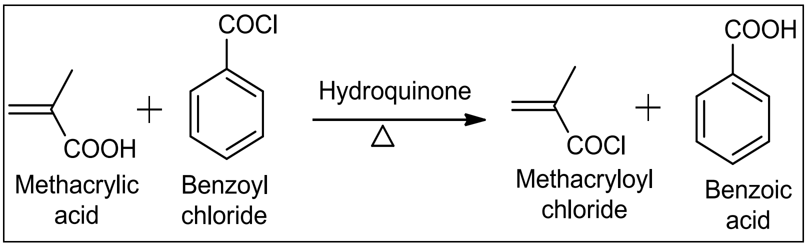
EXPERIMENTAL SECTION

Materials

Analytical grade N,N-dimethylformamide (DMF), methacrylic acid, benzoyl chloride, hydroquinone, 4-formyl-2-methoxy phenol, methacryloyl chloride, trimethylamine (TEA), tetrhydrofuran (THF), 2,2-azobisisobutyronitrile (AIBN), cadmium nitrate, sodium sulphide and methanol were obtained from lobachemie. Pvt. Ltd. (India). The chemicals were used without purification.

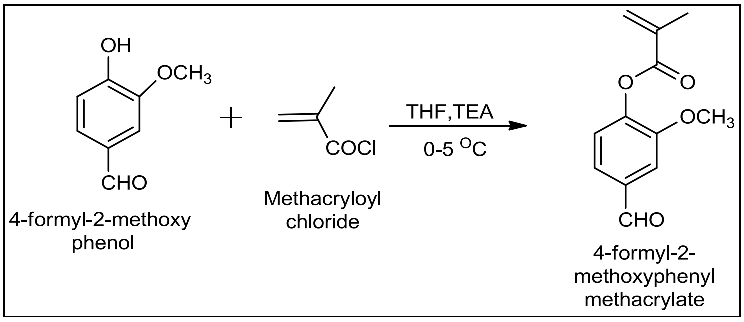
Synthesis

Synthesis of methacryloyl chloride (MAC):



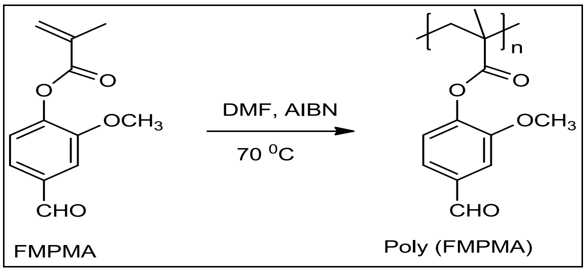
Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride using the procedure of Stampel et al. [20]. A mixture of methacrylic acid (1 mole), benzoyl chloride (2 mole) and hydroquinone (0.0025 mole) was distilled at a fairly high rate through an efficient column. The distillate was collected in a receiver containing hydroquinone (0.0025 mole). The product was obtained at a temperature between 85-100ºC. The crude product was redistilled through the same column. The pure methacryloyl chloride was distilled out at 95-96ºC. The product yield was 70%.

Synthesis of 4-formyl-2-methoxyphenyl Methacrylate (FMPMA):



Tetrahydrofuran (THF) (200 ml) and tri-ethyl amine (TEA) (0.20 mole) were added to a one litter three necked flask equipped with stirrer, thermometer and guard tube. The contents were stirred for 30 minutes. To this, 4-Formyl-2-methoxy phenol (0.20 mole) was added. The reaction mixture was heated to 60ºC for 30 minutes with stirring, cooled to room temperature and then to 0-5ºC. Freshly prepared Methacryloyl chloride (0.21 mole) was added drop wise within 60 minutes to the cooled reaction mixture. The temperature was maintained around 0-5ºC during the addition. After completion of addition, reaction mixture was stirred for 90 minutes and it was poured into crushed ice water mixture when a white colored product separated out. The product was filtered and washed thoroughly with cold water. It was dried at 40ºC in vacuum and recrystallized from methanol.

Synthesis of homopolymer of FMPMA:



Homopolymer of FMPMA was synthesised by free radical polymerization process. Required quantities of FMPMA, DMF as solvent and AIBN (0.5% w/w based on total monomer) as initiator were added to a flask equipped with reflux condenser. The reaction was carried out at 70±2° C for 5 hour with constant stirring followed by cooling to room temperature. The resulting polymer solution was slowly poured in a large volume of methanol with stirring when the polymer precipitated out. It was filtered, washed with methanol and then dried.

Preparation of polymer nanocomposite with Cds:

Polymer (0.5 gm) was dissolved in 50 ml DMF by stirring in a 250 ml conical flask. Cadmium nitrate solution (0.05M, 0.075M, and 0.1M) in DMF was slowly added to the polymeric solution under continuous sonicating. After complete addition of $Cd(NO_3)_2$,sodium sulphide (0.11M) solution in methanol was drop wise added to solution under sonicating. The solution became yellowish and the flask was kept for 4 hours at room temperature to allow the CdS to settle in the polymer. The polymer nanocomposites were separated by ultracentrifugation. The nanocomposites were washed several times with methanol and dried in vacuum desiccators.

Characterization

X-ray diffraction (XRD, Bruckner D2 Phaser 3600 X-ray Diffractometer havingCukα radiation source, λ=0.154 nm) was used to identify the phase and crystallographic structure of CdS in polymer nano composites. The IR spectra of solid samples in KBr pallets were obtained from Nicolet 6700 FT-IRspectrophotometer. Thermal analyses of homopolymer and polymer nanocomposite were carried out by TGA /DSC studies in nitrogen atmosphere at 10 °C /min heating rate with Mettlertoledothermo gravimetric analyser.

RESULTS AND DISCUSSION

IR spectroscopy

IR spectra of homopolymer of FMPMA and polymer nanocomposite are shown in Figure 1.The intensities of the absorptions due to stretching vibrations of C=O (1770-1740 cm^{-1}), C-O-C (1210-1163 cm^{-1}) in ester and bending of CH (1450,1375 cm^{-1}) decreased in the polymer nanocomposites compared to the same in homopolymer of FMPMA; in some cases the bands became broader. A weak Vander Waals interaction between polymer matrix and nano CdS may be envisaged.

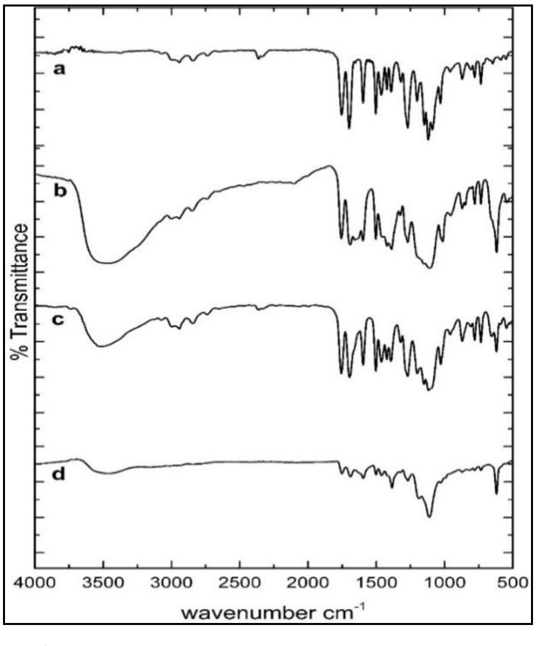


Figure 1: FTIR spectra of (a) homopolymer of FMPMA (b) 0.05M CdS/FMPMA (c) 0.075M CdS/FMPMA (d) 0.1M CdS/FMPMA

Morphology and structure

XRD spectra of polymeric nanocomposite with difference concentration of nano CdS are shown in Figure 2**.** Three XRD peaks at 2θ values of 26.6°, 43.3°, 52.7° correspond to (111), (220), (311) planes and indicated cubic phase of CdS nanoparticles. The size of nanoparticles obtained from Scherer-Debye [21] varied between 2.49-3.56 nm diameters.

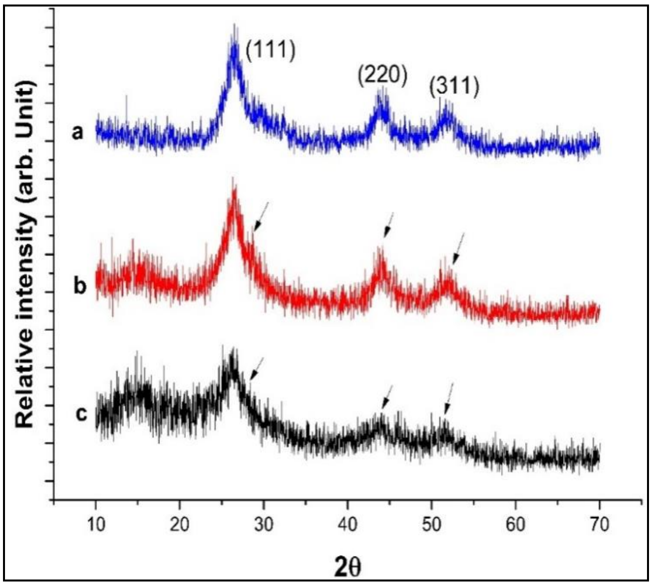


Figure 2: XRD spectrum of (a) 0.1M CdS/FMPMA (b) 0.075M CdS/FMPMA (c) 0.05M CdS/FMPMA

Thermogravimetric analysis

TGA traces of polymer nanocomposites with different concentrations of nano CdS are shown in Figure 3. The decomposition range, % weight loss and % residue are tabulated in Table 1. It is seen from the Table1 that the poly (FMPMA) was more stable thermally compared to polymer composites. As concentration of CdS in polymer composites increased the thermal stability decreased.

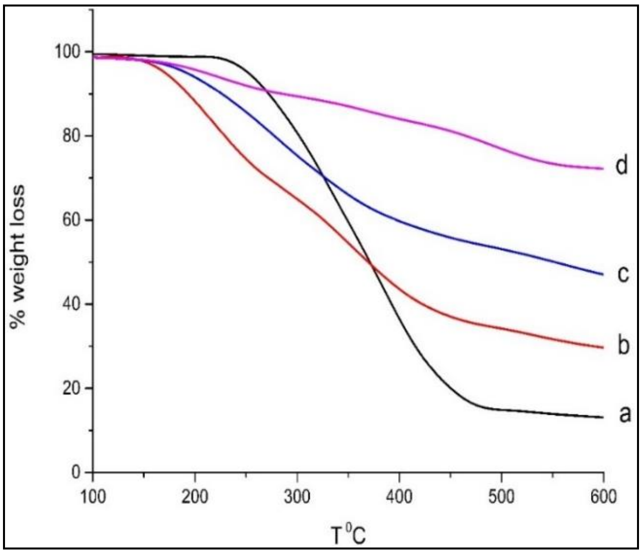


Figure 3: TGA graph of (a) homopolymer of FMPMA (b) 0.05M CdS/FMPMA (c) 0.075M CdS/FMPMA (d) 0.1M CdS/FMPMA

Table 1: TGA data comparison of homo polymer of FMPMA and Polymer nanocomposites of CdS

Sample code.	Decomposition temperature range (°C)	% weight loss due to polymeric part	% residue due to the inorganic CdS nanoparticles
Poly (FMPMA)	209-490	88	12
0.05M CdS/FMPMA	184-479	73	27
0.075M CdS/FMPMA	196-483	57	43
0.1M CdS/FMPMA	204-492	29	71

Kinetics of thermal decomposition

The kinetic parameters of the thermal degradation were determined by the Broido method [19]. In this, plot of ln [ln (1/y)] vs 1/T gave a straight line, activation energy (Ea) was obtained from the slope and the intercept. Activation energy (Table 2) of polymer composites decreased with increasing concentrations of CdS.

Table 2: Kinetic parameter of thermal degradation of homo polymer of FMPMA and polymer nanocomposite of CdS by Broido method

Sample code.	Ea	R^2	ΔS	ΔH	ΔG
Poly (FMPMA)	52	0.972	-239.93	51.96	207.68
0.05M CdS/FMPMA	16.68	0.975	-187.55	11.4	130.68
0.075M CdS/FMPMA	11.61	0.979	-182.76	6.19	125.35
0.1M CdS/FMPMA	8.07	0.973	-179.89	2.85	115.83

The positive value of enthalpy (ΔH) (Table 2) indicated the endothermic nature of thermal degradation of polymer and its composites. The lower the value of ΔH signified that the formation of activated complex was easily favoured in the polymer composites and hence degradation process was faster [22, 23]. The negative value of ΔS and positive value of ΔG (Table 2) for decomposition process indicated that steps are non-spontaneous. The entropy of activation (ΔS) gives information about the degree of order of the system and how close the system is to its own thermodynamic equilibrium. Lower activation entropy suggests that formation of activated complex is slow and consequently degradation process is slow and vice versa [22, 23]. As the values of ΔG increases the process of formation of activated complex is slow which means thermal degradation process is slower and vice versa. The values of thermodynamics parameters of polymer and its composites are presented in Table 2. The attraction of the nanoparticles may be with chain with lower molecular weight. Lower energy is required for scission of chain having lower molecular weight. The value of ΔS increased for polymer composites compared to polymers. Also the lower value of ΔH and ΔG (Table 2) of the composites suggested that these were thermodynamically less stable than that of polymers. Comparison of all the kinetic and thermodynamic parameters of polymer and their composites advocated that in presence of CdS nanoparticle the degradation of polymer was faster. CdS nanoparticals provided catalytic effect on thermal degradation of polymer molecule in polymer nanocomposites.

CONCLUSION

The homopolymer of FMPMA was synthesized by free radical polymerization process. Nanocomposites of homopolymer of FMPMA having different concentrations of CdS were prepared by in situ technique. The homopolymer of FMPMA and polymer nanocomposite were characterized by IR spectroscopy. The X-Ray diffraction showed that CdS nanoparticles had cubic structure with crystalline size between 2.49-3.56 nm. The activation energy for thermal was calculated using Broido method. The activation energy of polymer composites was lower than the same in poly (FMPMA). This may be traced to weak interaction between inorganic CdS particles and polymer chain. The thermodynamic parameters revealed that polymer composites were thermally less stable than the polymers because the inorganic nanoparticle acted as a catalyst during the degradation of polymer nanocomposites.

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