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Notes

Novel acrylate polymer nanocomposites with nano CdS

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Homopolymer of 4-chloro-3,5-dimethylphenylacrylate (CDMPA) and *p*-chlorophenylmethacrylate (PCPMA) and their copolymers with different compositions are synthesized by free radical polymerization technique using 2,2-azo-bis-isobutyronitrile as initiator in N,N-dimethylformamide as solvent at 70 °C. Their polymeric nanocomposites with nano CdS have then been synthesized by in-situ technique. Characterisation of the monomers, polymers and their polymeric nanocomposites with nano CdS have been done by spectroscopic methods. X-ray diffraction studies show cubic structured nanocrystalline CdS with 2.41-3.16 nm diameter. Compositions of the copolymers are determined by ^{1}H-NMR. Linear methods, namely, Finemann-Ross, inverted Finemann-Ross, Kelen-Tudos and extended Kelen-Tudos have been used for the determination of reactivity ratio of the monomers. Thermal analyses of the virgin polymers and their polymeric nanocomposites with nano CdS have been carried out by thermogravimetric studies. The kinetic parameters of virgin polymers and polymeric nanocomposites with nano CdS are determined by Broido method and Coats-Redfern method. Antimicrobial screening of homo and copolymers and one of the polymer nanocomposite with nano CdS has been studied against different microorganisms.

Keywords: Polymer nanocomposites, Acrylate polymer nanocomposites, Nanocomposites, Cadmium sulphide, Thermal analysis

Acrylate and methacrylate polymers are made from the acrylate monomers which are usually esters containing vinyl groups. Acrylates and methacrylates have been polymerized or copolymerized with an variety of different monomers[1-3]. Acrylate and methacrylate polymers have a wide range of applications such as biomedical, adhesive, coating, textile, paper industries and solar cells[4-10]. Nanocomposite is a multiphase compound in which at least one of the phases shows dimensions in the range below 100 nm. Polymers have lower mechanical, thermal and electrical properties than inorganic materials, hence, dispersion of nanoparticles in a polymer matrix would provide excellent possibilities of functional materials with exceptional properties for catalytic, electrical, photodetector, light emitting diodes, laser communication and sensing applications[11-17]. Nanocomposites have improved UV stability, and thermal, mechanical, and other physical properties and offer the combine advantages of organic polymers and inorganic nanomaterials[18, 19].

Presently much attention has been given to studying polymer nanocomposites with nano cadmium sulphide (CdS) due to their applications in areas such as photocatalysis, optoelectronics, photoluminescence, light emitting diodes, thin film transistors, solar cells etc.[20-26] Thermal stability of CdS polymer nanocomposite plays an important role from the application point of view. Thermal stability of polymers and polymer nanocomposites is investigated from thermogravimetric analysis and these data have been employed to investigate the kinetic parameters and thermodynamics of polymer degradation like enthalpy change, entropy change and free energy change. Kinetic study may successfully assist in probing degradation mechanisms as well as predicting the thermal stability of polymers. The effects of metal nanoparticle on polymer molecules at higher temperature has been studied in detail and it was concluded that the concentration of nanoparticles in polymer nanocomposite and its strong/ weak interactions affect the degradation of polymer molecule at higher temperatures[27, 28].

Herein we present the synthesis of monomers 4-chloro-3,5-dimethylphenylacrylate (CDMPA) and *p*-chlorophenylmethacrylate (PCPMA) and their homo and copolymers via free radical polymerization process. The preparation of polymeric composites with nano CdS by an in-situ technique is also discussed. The monomers, homopolymers, copolymers and polymeric nanocomposites with nano CdS are characterized with spectroscopic data. The main focus of this investigation is the thermal stability and kinetic and thermodynamic parameters of the synthesized homo and copolymers and their polymeric nanocomposite with nano CdS. The effect of CdS nanoparticles on polymer degradation at higher temperature has been discussed. The antimicrobial screening of these polymers and polymer nanocomposite containing nano CdS against different microorganism is also reported.

Experimental

Analytical grade N,N-dimethylformamide (DMF), acrylic acid, methacrylic acid, benzoyl chloride, hydroquinone, 4-chloro-3,5-dimethyl phenol, *p*-chlorophenol, trimethylamine (TEA), 2,2-azobisisobutyronitrile (AIBN), cadmium nitrate, sodium sulphide and methanol were obtained from Loba Chemie. Pvt. Ltd. (India). All chemicals were used as such without purification.

^{1}H-NMR spectra were recorded on a Bruker 400 MHZ FT-NMR spectrometer. Nicolet 6700 FT-IR spectrophotometer was employed for recording the IR spectra of the solid sample in KBr pellets. Reactivity ratio and copolymer composition were determined by ^{1}H-NMR data. The phase and size of the nano CdS were determined by X-ray diffraction (XRD, Bruker D2 phaser 3600 diffractometer having Cu-Kα radiation source, λ=0.154 nm). Thermal property was investigated with a Mettler Toledo thermogravimetric analyser for TGA/DSC at a heating rate of 10 °C /min.

Acryloyl chloride and methacryloyl chloride were prepared using the procedure of Stampel *et al*.[29] 4-Chloro-3, 5-dimethylphenyl methacrylate (CDMPA) was prepared using the reported method[30]. *p*-Chloro phenyl methacrylate (PCPMA) was prepared using reported procedure[31].

Homopolymers of CDMPA with PCPMA and their copolymers with different feed ratio (Table 1) were synthesized by free radical polymerization process using DMF as a solvent and AIBN as a free radical initiator. Required quantity of monomer(s), DMF and AIBN (0.5% *w/w* based on total monomers 1 and 2) were added to a flask with reflux condenser. The reaction was carried out at 70±2 °C for 5 h with constant stirring followed by cooling to room temperature. The resulting polymer solution was slowly poured into a large volume of methanol with stirring when the polymer precipitated out. It was filtered, washed with methanol and then dried. The formation of homo and copolymer of CDMPA with PCPMA is shown in Scheme S1 (Supplementary data).

Table 1 — Feed ratio and copolymer composition of CDMPA with PCPMA

Sample code	Monomer feed comp.		Integrated peak area of proton[a]		Yield (%)
	CDMPA (wt. %)	PCPMA (wt. %)	I_{aro}	I_{ali}	
NA 1	100	-	-	-	81
NA 2	80	20	4.37	13.54	78
NA 3	60	40	4.83	8.18	79
NA 4	50	50	6.87	14.81	76
NA 5	40	60	6.3	12.03	79
NA 6	20	80	4.05	6.64	77
NA 7	-	100	-	-	83

[a] I_{aro} and I_{ali} represent respectively the intensity of aromatic and aliphatic protons.

To prepare the polymeric nanocomposite with nano CdS, the polymer (0.5 gm) was dissolved in 50 mL DMF by stirring in a 250 mL conical flask. Cadmium nitrate solution (0.1 *M*) in DMF was slowly added to the polymeric solution under continuous sonication. After complete addition of $Cd(NO_3)_2$, sodium sulphide (0.11 *M*) solution in methanol was added drop wise under sonication. The solution became yellowish and the flask was kept for 4 h at room temperature to allow the CdS to get entrapped in the polymer. The polymer nanocomposites were separated by ultracentrifugation, washed several times with methanol and dried in vacuum desiccators.

Antimicrobial screening of polymers and the polymer (PNA 4) nanocomposite with nano CdS was carried out against different microorganisms like bacteria (*Escherichia coli, Bacillus subtilis and Pseudomonas aeriginosa*), fungi (*Sporotichum pulverulentum, Aspergillusniger and Trichodermalignorum*) and yeast (*Candida utilis, Pichia stipites and Saccharomyces cerevisiae*). Quantitative methods reported in the literature were used for the antimicrobial screening[32].

Results and discussion

^{1}H-NMR spectra of CDMPA and PCPMA are shown in Fig. 1(a & b). CDMPA (DMSO) (δ ppm): 7.1 (2H, d, Ar-CH); 6.5 (1H, d, vinylic H); 6.3 (1H, d, vinylic-H); 2.3 (3H, s, CH_3). PCPMA (DMSO) (δ ppm): 7.6 (2H, d, Ar-CH); 7.2 (2H, d, Ar-CH); 6.3 (1H, d, vinylic-H); 5.9 (1H, d, vinylic-H); 2 (3H, s, CH_3).

FT-IR spectra of monomers along with their starting materials are shown in Fig. 2 (a & b). The broad absorption in the region 3500-3200 cm^{-1} due to the –OH stretching of phenol disappeared on acetylating to obtain the said monomers by converting phenol to ester. The peak near 1750cm^{-1} is the stretching vibration of C=O in the ester group and another peak at 1650 cm^{-1} is due to alkene –C=C- stretching. The FT-IR spectra of homo and copolymers of CDMPA with PCPMA are shown in Fig. 3. Absence of absorption of C=C stretching around 1650 cm^{-1} in IR spectra of homo and copolymers indicates polymer formation. PCPMA contains two neighbouring protons, and hence the peaks at 805 and 833 cm^{-1} are assigned to C-H out-of-plane bending. The absorption at 1196 cm^{-1} is attributed to C-O-C stretching in PCPMA. On increasing the PCPMA content in the

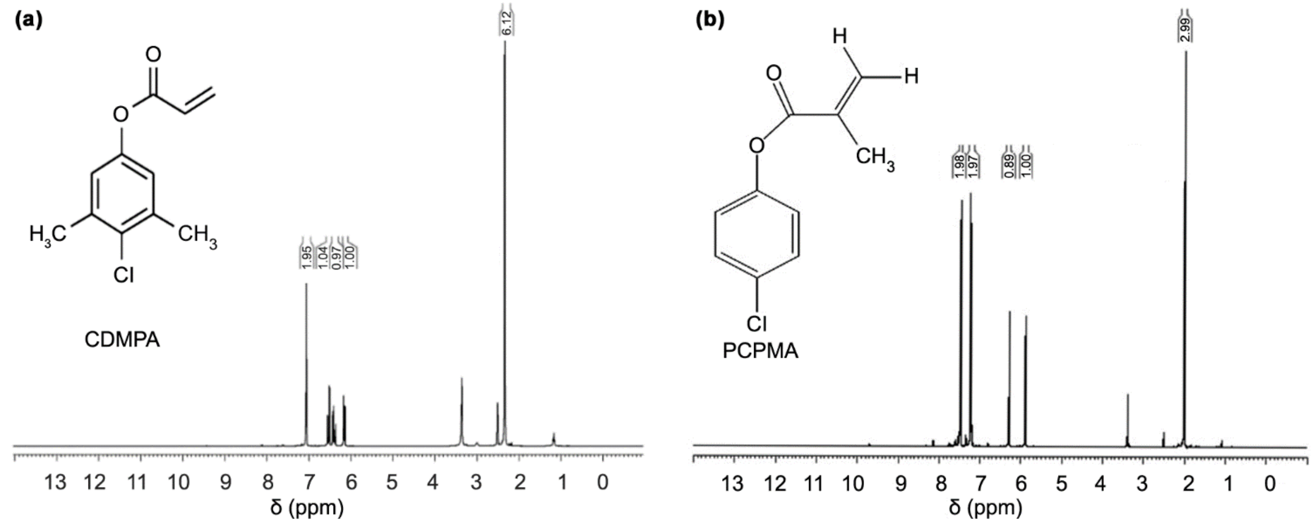

Fig. 1 — ^{1}H-NMR spectra of CDMPA and PCPMA.

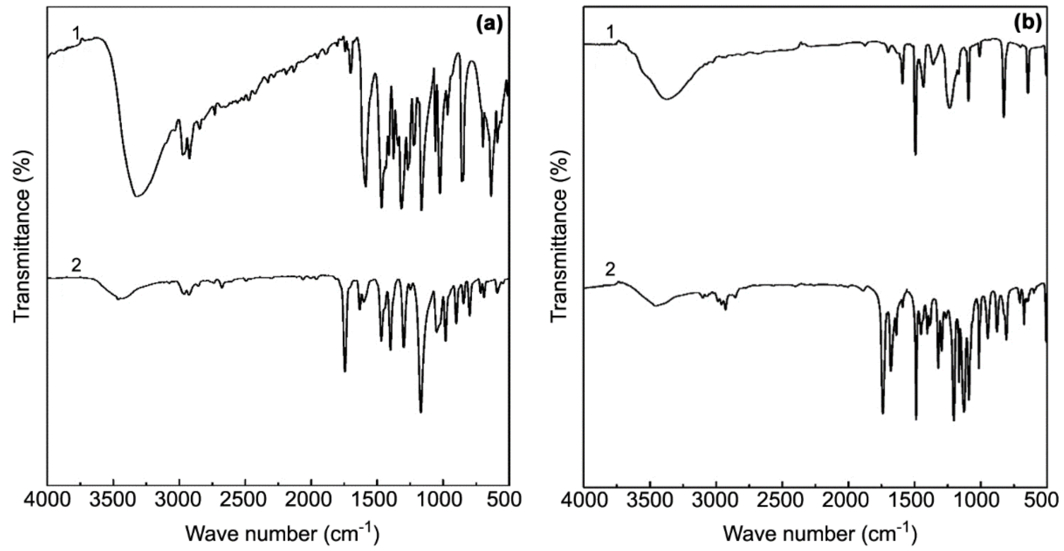

Fig. 2 — IR spectra of (a) CDMP (1) and CDMPA (2), (b) PCP (1) and PCPMA (2).

copolymer, the intensity of CH out-of-plane bending and C-O-C stretching increases.

FT-IR spectra of polymer nanocomposites with nano CdS are shown in Fig. 4. The intensity of the absorptions due to C=O stretching in ester, C-H and C-O-C stretching changes in the nanocomposites compared to the virgin polymers. The absorption in the region 1210-1163 cm^{-1} assigned to C-O-C stretching became broader and the intensity decreased in the nanocomposites. A weak Van der waals interaction between polymer matrix and nano CdS may be envisaged.

XRD spectra of polymeric nanocomposite with nano CdS are shown in Fig. 5. There are three reflection from (111), (220) and (311) planes in all the composites, indicating the cubic phase of CdS nanoparticles. The size of nanoparticles was obtained from Debye-Scherrer's equation[33], $D = 0.94\ \lambda/\ \beta\cos\theta$, where λ is the wavelength of the Cu-Kα radiation, β is the FWHM (full width at half maximum), D is the particle size value and θ is the Bragg angle.

The size of nanoparticles so obtained varied in the range of 2.41-3.16 nm. The nano size of the doped CdS was further confirmed by TEM image of the polymer composites containing nano CdS (Fig. S1, Supplementary data).

The reactivity ratio of the monomers CDMPA and PCPMA, r_1 and r_2 respectively, for the copolymerization of CDMPA with PCPMA were determined using the

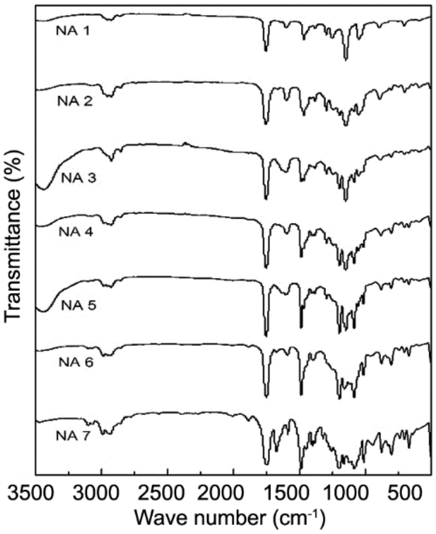

Fig. 3 — IR spectra of poly (CDMPA) (NA 1), poly (PCPMA) (NA 7) and copolymer of CDMPA with PCPMA (NA 2-NA 6).

standard linear methods such as Fineman-Rose (F-R), Inverted Finemen-Rose (Inv. F-R), Kelan-Tudos (K-T) and Extended Kelen-Tudos (Ext. K-T) methods[34-36]. The composition of the monomers in the copolymer was obtained from NMR data (Supplementary data, Fig S2 and Table S1). The mathematical equations for F-R, Inv. F-R, K-T and Ext. K-T methods are shown in Table S2 (Supplementary data). The detailed calculations and plots to obtain the values of r_1 and r_2, are shown in Figs S3-S6 and Tables S2 & S3 (Supplementary data).

The monomer reactivity ratio, (which govern the microstructure of polymer), of CDMPA and PCPMA, are given in Table 2. The values of r_1 are smaller than those of r_2, which indicates lower reactivity of CDMPA as compared to PCPMA, suggesting that as compared to PCPMA units the number of monomeric units of CDMPA will be less in the copolymer chain. The value of $1/r_1$ is greater than $1/r_2$ meaning thereby that CDMPA favours cross propagation while PCPMA favours homo propagation.

The mean sequence lengths, μ_{CDMPA} and μ_{PCPMA}, were calculated using the following equations[37],

$$\mu_1 = 1 + r1\left(\frac{[M1]}{[M2]}\right) \text{ and } \mu_2 = 1 + r2\left(\frac{[M2]}{[M1]}\right)$$

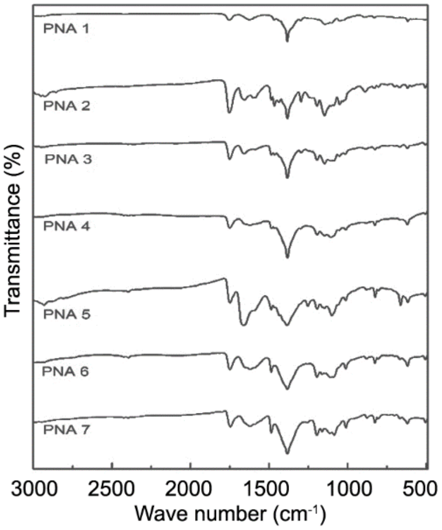

Fig. 4 — IR spectra of polymer nanocomposites with nano CdS. [PNA 1: polymer nanocomposite of CDMPA; PNA 7: polymer nanocomposites of PNA 7; PNA 2–PNA 6: polymer nanocomposites of copolymer of CDMPA with PCPMA].

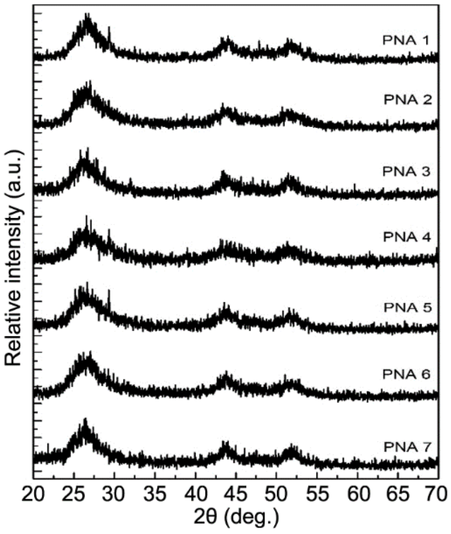

Fig. 5 — XRD patterns of polymeric nanocomposite with nano CdS.

where μ_1 represent sequence length of CDMPA monomer and μ_2 represent sequence length of PCPMA monomer in the copolymer, $[M_1]$ and $[M_2]$ are concentrations of monomers CDMPA and PCPMA feed ratio respectively. As indicated in the preceding section, r_1 and r_2 are the reactivity ratio of the monomers CDMPA and PCPMA respectively.

Theoretically[38], the ratio of the mean sequence lengths distribution depends on the ratio of $[M_1]$ and $[M_2]$. The distributions are shown in Table 3. As an example, in the copolymer of CDMPA with PCPMA, at $[M_1]$ =20.0% and $[M_2]$ =80.0%, mean sequence lengths (theoretically) of CDMPA and PCPMA will be approximately 1:4. The significance of this calculation is that in the said copolymer the segment with M_2 will be approximately four times longer than its adjoining segment with M_1 units (Table 3).

The sequence is expressed as CPPPPCPPPP when C stands for CDMPA and P for PCPMA. The number of CDMPA units in copolymer increases with increasing concentration of CDMPA in the feed. The results of mean sequence length and values of $1/r_1$ and $1/r_2$ compare very well; CDMPA favours cross propagation as evident from its value of $1/r_1$ and the value of $1/r_2$ favours homo propagation for PCPMA.

TGA traces of homopolymers of CDMPA and PCPMA, their copolymers and polymer nanocomposites with nano CdS are shown in Figs 6 and 7 respectively. Decomposition temperature range, integral procedural decomposition temperature (IPDT), Tmax, T50 of virgin polymers are tabulated in Table 4. Decomposition of the polymers may be due to bond scission of the main polymeric chain (-C-C-). It was concluded from the data that homopolymer of CDMPA is less stable than their copolymers with PCPMA and homopolymer of PCPMA. Stability of the copolymers of CDMPA with PCPMA did not follow a regular trend. The integral procedural decomposition temperature (IPDT) calculated by Doyle's method[39] showed the overall thermal stability of the polymers and values of IPDT varied between 374 °C and 410 °C for these polymers. Polymer nanocomposites of nano CdS with the homo and copolymers showed a wide decomposition temperature range. This is due to weak intermolecular attraction between polymer matrix and inorganic nanoparticles. The decomposition temperature range of homo and copolymers of CDMPA with PCPMA and their nanocomposite with nano CdS are shown in Table 5.

The kinetic parameters of thermal degradation were determined by the Broido method[40] and Coats-Redfern method[41]. The activation energies of copolymers of CDMPA with PCPMA varied randomly. Values of R_2, the correlation coefficient obtained from Briodo and Coats-Redfern were nearly 1, which indicated good correlation for the decomposition. The values of Ea, R_2, ΔH, ΔS and ΔG obtained from both methods are comparable and are shown in Tables S4-S7 (Supplementary data).

Table 2 — Monomer reactivity ratio of CDMPA with PCPMA copolymers

Method	Reactivity ratio				
	r_1	r_2	r_1*r_2	$1/r_1$	$1/r_2$
F-R	0.57	0.83	0.47	1.75	1.20
K-T	0.56	0.83	0.46	1.78	1.20
Inve. F-R	0.47	0.75	0.35	2.12	1.33
Ext. K-T	0.55	0.83	0.45	1.81	1.20

Table 3 — Mean sequence length of copolymers

Sample	Monomer feed		μ_C	μ_P	μ_C:μ_P	Distribution
	M_1	M_2				
NA 2	0.8	0.2	3	1	3:1	CCCPCCCP
NA 3	0.6	0.4	2	2	2:2	CCPPCCPP
NA 4	0.5	0.5	2	2	2:2	CCPPCCPP
NA 5	0.4	0.6	1	2	1:2	CPPCPP
NA 6	0.2	0.8	1	4	1:4	CPPPPCPPPP

μ_C = CDMPA (C); μ_P = PCPMA (P)

Table 4 — TGA data of homo and copolymers of CDMPA with PCPMA

Sample	Decomp. temp. range (°C)	T_{max} (°C)	T_{50} (°C)	IPDT
NA 1	215–425	390	383	374
NA 2	211–418	390	384	389
NA 3	218–437	405	384	384
NA 4	216–431	406	393	410
NA 5	218–432	405	387	394
NA 6	224–435	398	382	400
NA 7	232–445	409	388	382

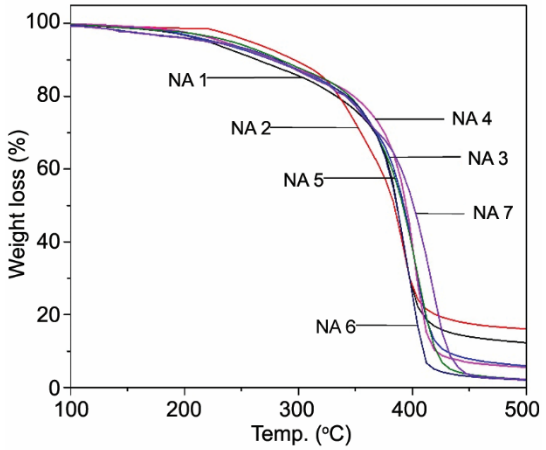

Fig. 6 — TGA of poly(CDMPA) (NA 1), poly(PCPMA) (NA 7) and copolymer of CDMPA with PCPMA (NA 2- NA 6).

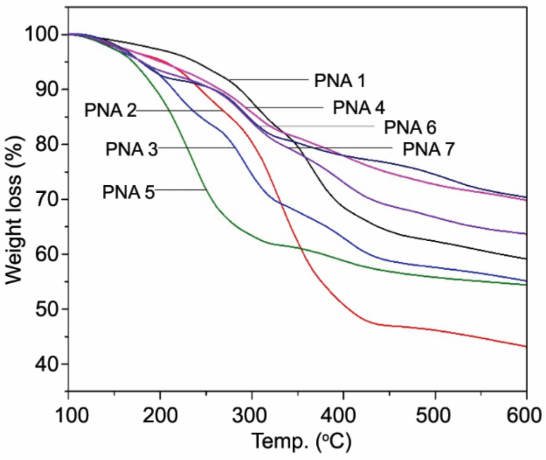

Fig. 7 — TGA of polymer nanocomposites with nano CdS.

Table 5 — TGA data of polymeric nanocomposites with nano CdS

Sample	Decomp. temp. range (°C)	Wt loss due to polymer (%)	Residue due to CdS NPs
PNA 1	198–487	43	57
PNA 2	157–458	59	41
PNA 3	172–479	47	53
PNA 4	164–472	33	67
PNA 5	159–473	47	53
PNA 6	169–430	33	67
PNA 7	165–465	93	61

Enthalpy (ΔH) change was positive indicating endothermic nature of thermal degradation of polymers. The low value of ΔH indicated that the difference between potential energy barrier of reagents and activated complex is low, thus favouring the formation of activated complex and hence degradation process was faster[42, 43]. Lower activation entropy (ΔS) suggests that formation of activated complex is slow and consequently degradation process is slow[42, 43]. If for decomposition process, ΔS is negative and ΔG is positive, then it may be inferred that steps are non-spontaneous. The value of thermodynamics parameters of homo polymers of CDMPA and PCPMA, their copolymers and polymer nanocomposites with nano CdS are tabulated in Tables S4-S7.

The results shows that homopolymer of CDMPA is thermally less stable than homopolymer of PCPMA and the values of activation energy show that virgin polymers are more thermally more stable as compared to polymer nanocomposite. Compared to virgin polymers, the values of ΔS increased and those of ΔH and ΔG decreased for polymer nanocomposites; this indicated that the polymer composites are thermally less stable than virgin polymers. The less thermal stability of the polymer nanocomposites may be attributed to the catalytic effect of CdS nanoparticles on decomposition of polymer molecules at higher temperature.

Antimicrobial screening of the polymers and the nanocomposite of copolymer PNA 4 (0.5:0.5 monomer feed of CDMPA: PCPMA) containing nano CdS was studied. (Supplementary data, Figs S7-S9). Both the monomers CDMPA and PCPMA contain chlorine and can directly attack the DNA of microorganisms, thereby disturbing the DNA system. Consequently, polymers containing these monomers will be most effective for the inhibition of microorganism. Results shows that homopolymer of CDMPA is more effective to inhibit the growth of microorganisms as compared to homopolymer of PCPMA. It was observed that as concentration of CDMPA monomer in the copolymer feed increased, the resulting copolymers with PCPMA was more active against the growth of the microorganisms, i.e., bacteria, fungi and yeast. The polymer (PNA 4) nanocomposite with nano CdS gave total inhibition for the growth of bacteria, fungi and yeast due to the cytotoxic effects CdS nano particles.

In summary, free radical polymerization technique was used for the synthesis of homopolymers of CDMPA and PCPMA and their copolymers with different monomer feed ratio. The polymer nanocomposites with nano CdS with crystalline size in the range of 2.41–3.16 nm were obtained by in-situ technique. Reactivity ratio showed that CDMPA is less reactive compare to PCPMA and product of their reactivity ratios was less than 1, which indicated that the monomers were randomly distributed in the copolymer chain. The kinetic parameters showed that the homopolymer of CDMPA was thermally less stable than homopolymer of PCPMA. The activation energy for thermal decomposition of polymer nanocomposites was less than that of virgin polymers, due to weak interaction between inorganic particle and polymer chain. The thermodynamic parameters demonstrated that polymer nanocomposites were thermally less stable than the virgin polymers because the inorganic nanoparticle acted as a catalyst during the degradation of polymer nanocomposites. CDMPA was more effective in inhibiting the growth of bacteria, fungi and yeast as compared to PCPMA. Polymer nanocomposite with nano CdS totally inhibited the growth of microorganisms possibly because of cytotoxic effects of CdS

Supplementary data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_56A(12)1310-316_SupplData.pdf.

References

1 Patel J N, Dolia M B, Patel K H & Patel R M, *J Polym Res,*13 (2006) 219.

2 Erol I & Ozturk A I, *Polym Res,* 12 (2005) 403.

3 Patel H J, Patel M G, Patel K H, Ray A k & Patel R M, *Chin J Polym Sci,* 27 (2009) 121.

4 Shantha K L & Harding D R K, *Eur Polym J,* 39 (2003) 63.

5 Shekh M I, Patel D M, Patel K P & Patel R M, *Fiber Polym,* 17 (2016) 358.

6 Jovanović R, Ouzineb K, McKenna T F & Dubé M A, *Macromol Symp,* 206 (2004) 43.

7 Chattopadhyay D K, Panda S S & Raju K V S N, *Prog Org Coat,* 54 (2005) 10.

8 Alay S, Gode F & Alkan C, *J Appl Polym Sci,* 120 (2010) 2821.

9 Vitta S B, Stahel E P & Stannett V T, *J Macromol Sci: Chem,* 22 (1985) 579.

10 Bella F, Ozzello E D, Bianco S & Bongiovanni R, *Chem Eng J,* 225 (2013) 873.

11 Paul D R & Robeson L M, *Polym,* 49 (2008) 3187.

12 Henrique P, Camargo C, Satyanarayana K G & Wypych F, *Mater Res,* 12 (2009) 1.

13 Bisio C, Caldeira C, Dal Santo V, Martra G, Massiani P, Psaro R, Ribeiro M F, Silva J M & Stievano L, *Inorg Chim Acta,* 349 (2003) 227.

14 Sanjinés R, Abad M D, Vâju C, Smajda R, Mionić M & Magrez A, *Surf Coat Technol,* 206 (2011) 727.

15 Shen L, Fang Y, Wei H, Yuan Y & Huang J, *Adv Mater,* 28 (2016) 2043.

16 Park J H, Lim Y T, Park O O, Kim J K, Yu J W & Kim Y C, *Chem Mater,* 16 (2004) 688.

17 Sen T, Mishra S & Shimpi N G, *RSC Adv,* 6 (2016) 42196.

18 Devi R R & Maji T K, *Ind Eng Chem Res,* 51 (2012) 3870.

19 Mathur V, Rathore K S & Sharma K, *World J Nanosci Eng,* 3 (2013) 93.

20 Xiong S, Xi B & Qian Y, *J Phys Chem C,* 114 (2010) 14029.

21 Nguyen T P, *Surf Coat Technol,* 206 (2011) 742.

22 Jin Y J, Luo Y J, Li G P, Li J, Wang Y F, Yang R Q & Lu W T, *Forensic Sci Int,* 179 (2008) 34.

23 Zhao J, Bardecker A J A, Munro A M, Liu M S, Niu Y, Ding I-Kang, Luo J, Chen B, Alex K-Y & Ginger D S, *Nano Lett,*6 (2006) 463.

24 Kovtyukhova N I, Kelley B K & Mallouk T E, *J Am Chem Soc,* 126 (2004) 12738.

25 Dowland S A, Reynolds L X, MacLachlan A, Cappel U B & Haque S A, *J Mater Chem A,* 1 (2013) 13896.

26 Akbarzadeh R, Khalili S S & Dehghani H, *New J Chem,* 40 (2016) 3528.

27 Pramoda K P, Liu T, Liu Z, He C & Sue H J, *Polym Degrad Stab,* 81 (2003) 47.

28 Gorghiu L M, Jipa S, Zaharescu T, Setnescu R & Mihalcea I, *Polym Degrad Stab,* 84 (2004) 7.

29 Stempel G H, Cross R P & Mareiolla R P, *J Am Chem Soc,* 72 (1950) 2299.

30 Patel D M, Shekh M I, Patel K P & Patel R M, IN patent 49/MUM/2014 Jan 16, 2015.

31 Patel J N, Patel J R, Patel K H, Patel P M & Patel R M, *J Macromol Sci Part A,* 44 (2007) 395.

32 Patel B T & Patel R M, *Int J Polym*, 41 (1998) 199.

33 Venkatachalam S, Mangalaraj D & Narayandass S K, *J Phys D Appl Phys,* 39 (2006) 4777.

34 Fineman M & Ross S D, *J Polym Sci,* 5 (1950) 259.

35 Kelen T & Tüdõs K, *J Macromol Sci: Part A – Chem,* 9 (1975) 1.

36 Tüdös F, Kelen T, Földes-berezsnich T & Turcsányi B, *J Macromol Sci Part A – Chem,* 10 (1976) 1513.

37 Arshady R, Kenner G W & Laboratories R R, *J Polym Sci,* 12 (1974) 2017.

38 Ueda M, Suzuki T, Takahashi M, Li Z B & Koyama K, *Macromolecules,* 19 (1986) 558.

39 Doyle C D, *Anal Chemi,* 33 (1961) 77.

40 Broido A, *J Polym Sci Part A-2 Polym Phys,* 7 (1969) 1761.

41 Coats A W & Redfern J P, *Nature*, 201 (1964) 68.

42 Georgieva V, Zvezdova D & Vlaev L, *Chem Cent J,* 6 (2012) 81.

43 Georgieva V, Zvezdova, D & Vlaev L, *J Therm Anal Calorim*, 111 (2013) 763.