

# Investigation on Nonlinear Optical (NLO) Properties and Surface Morphologies of Organic Chiral Monomer Crystals of (R)-N-(1-phenyl-ethyl) methacrylamide and its Polymer and Copolymers

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## ABSTRACT

*(R)-N-(1-phenyl-ethyl) methacrylamide (R-NPEMAM) was synthesized which is an organic chiral monomer. The crystals of such monomer were obtained by recrystallization of the synthesized product from ethanol-water mixture. It was polymerized with 2-hydroxyethyl methacrylate (HEMA) and a crosslinking monomer, N,N' methylene bisacrylamide in toluene medium. These materials have been characterized by different analytical techniques such as FTIR, elemental and SEM analyses for their structural and morphological investigation. The organic monomer is a chiral molecule and its optical rotation was observed to be:  $[\alpha]_D^{25} = 28^\circ$  (C 1.0 DMF). On the other hand, optical rotations were observed to be:  $35^\circ$  for its polymer (CP) and 8 to  $21^\circ$  for its copolymers having different chiral content. Such organic and polymeric materials were studied for their NLO properties. The relative second harmonic generation (SHG) efficiency of organic chiral monomer crystal (CCM) was 1.22 times that of KDP, whereas the values of polymer and copolymers were slightly less (0.87 to 0.94) than that of the KDP crystal. However, all these values are comparable to the property of other organic crystals and also to the recently reported SHG efficiency of 1.5 times for organic 4-chloroanilinium-L-tartrate monohydrate single crystal. These materials may find their potential nonlinear optical applications.*

**KEYWORDS:** *Chiral organic monomer crystals, Chiral copolymers, Crosslinked polymers, Non-linear optical properties*

## 1. INTRODUCTION

Nonlinear optical (NLO) materials are an important class of materials for photonics applications as they exhibit large second-order nonlinear optical (NLO) susceptibilities, such as frequency doubling by second harmonic generation (SHG), frequency tuning by optical parametric oscillation (OPO), light amplification by optical parametric amplification (OPA), electrooptic modulation (EOM) for optical signal transmission and ultra-short electric pulses generation through the linear rectification effect<sup>[1]</sup>. Second-order non-linear optical organic materials are mainly based on  $\pi$ -conjugated chromophores at the ends of the  $\pi$ -conjugated structures along with strong electron donor and acceptor groups. Such NLO organic and polymeric materials have attracted considerable interest due to their potential optoelectronic applications in ultrahigh-speed electro-optic (EO) switches and modulators<sup>[2-6]</sup>. About last two decades, NLO polymers due to their large optical nonlinearity, relatively high laser damage threshold, ultrafast optical response and high transparency over a wide range of wavelengths have drawn remarkable interest as potential candidates for application in electro-optic and photonic devices<sup>[7-9]</sup>. Moreover, polymeric materials have other advantages like mechanical and thermal stability over the small organic molecules. They also have the advantages of ease of processing and architectural flexibility for optimizing optical nonlinearities as compared to those of existing technology based on inorganic NLO materials<sup>[10-11]</sup>.

The recent developments of electro-optic polymers combine excellent light propagation

properties of the matrix enhanced nonlinear optical response of noncentrosymmetric charge transfer molecules<sup>[1]</sup>. Multiple type of successful approaches for making noncentrosymmetric thin films were employed, such as Langmuir-Blodgett (LB) layers<sup>[12]</sup>, intermolecular charge transfer layers (ICTL)<sup>[13]</sup>. Functionalized soluble polymers were used for electro-optic as primarily developed electro-optic modulation application<sup>[14]</sup>. The noncentrosymmetric materials were used in second order NLO for waveguide configuration, which was most successful approach for obtaining electro-optic polymers<sup>[15-18]</sup>. The advanced optical properties of amorphous polymers were used primarily as matrix for electro-optic chromophores<sup>[19]</sup>.

Organic NLO crystals form noncentrosymmetric structures which exhibit second-order nonlinear optical properties, which have potential applications in laser printing, optical switching, displays, signal transmission, data storage, remote sensing, chemical and biological species detection, high resolution spectroscopy, underwater monitoring and communication<sup>[20]</sup>. L-valine zinc hydrochloride nonlinear optical single crystal was synthesized from L-valine and zinc sulphate heptahydrate and studied its optical and nonlinear optical properties<sup>[21]</sup>. Noncentrosymmetric (NCS) compounds are of great interest in materials science for their physical properties like piezoelectricity, ferroelectricity, pyroelectricity, and especially second-order NLO properties<sup>[22-26]</sup>.

Many of organic crystals have been extensively studied for their NLO properties and applications. Their NLO coefficients have been observed to be larger than those of inorganic

materials [27-29]. The recent progress in the development of photonic applications based on the organic crystal especially based on 4-N, N-dimethylamino-4'-N'-methyl-stilbazolium tosylate (DAST) has been reviewed [27]. Urea is an excellent organic NLO crystal. Optical second harmonic generation in benzophenone was also reported [28]. However, growth of large high-quality crystals for practical use still remains a challenge due to its unfavorable growth properties. Improved crystalline and optical quality was expected in mixed systems. Hence, two component organic NLO systems especially urea doped organic systems were studied widely [29-30]. Urea doped benzophenone single crystals having different concentrations of urea were studied for their Second Harmonic Generation (SHG) efficiencies in comparison with Potassium Dihydrogen Phosphate (KDP) [30]. The synthesis, growth and second-harmonic-generation (SHG) of two-component organic NLO systems like urea–meta nitro benzoic acid (mNBA) and urea–l-malic acid were reported [29]. The material property of urea was modified by the addition of mNBA and l-malic acid. The SHG efficiency measured by Kurtz powder method showed the variation of properties with composition. NLO organic single crystals of pure lauric acid (LA) obtained from ethanol solution was crystallized in the monoclinic system which exhibited the second-harmonic generation efficiency of 0.87 times that of potassium dihydrogen phosphate (measured using the Kurtz–Perry powder technique) [31]. The LA crystal is stable only up to 45°C. Recently, organic second order nonlinear optical 4-chloroanilinium-L-tartrate monohydrate single crystals were successfully grown by slow evaporation

solution technique at room temperature. Kurtz-Perry powder technique showed the second harmonic generation efficiency of 1.5 times greater than KDP crystals [32].

The research on organic nonlinear optical (NLO) materials is strongly motivated by the demand for higher data rates in future optical communication technologies. Organic NLO materials can reach much larger NLO efficiencies and show extremely fast optical nonlinearities compared to their inorganic counterparts. Additionally they offer a large number of design possibilities. Therefore, organic NLO materials promise to meet future requirements for ultrahigh bandwidth photonic devices. However, the limitations of organic crystals are their low mechanical and thermal stability. On the other hand, the present technologies based on inorganic materials (such as LiNbO<sub>3</sub>, GaAs, and InP) are well understood and they have good mechanical and chemical stability, and sufficiently large NLO coefficients for many applications.

In view of the above, in this investigation, we have attempted to synthesize an organic crystal which is chiral (noncentrosymmetric) in nature. Moreover, it is a monomer which could be easily converted into its polymer and copolymers. These may have better materials properties (sufficient strength and thermal stability) in comparison to the organic crystals. Thus we have synthesized (R)-N-(1-phenyl-ethyl) methacrylamide (R-NPEMAM) as the organic chiral monomer (CCM). Polymer, copolymers and crosslinked copolymer (CP and CCPs) of (R)-N-(1-phenyl-ethyl) methacrylamide were synthesized by the free radical polymerization of R-NPEMAM, 2-

hydroxy ethyl methacrylate (HEMA) and crosslinker, N,N'-methylene bisacrylamide (MBA). The nonlinear optical (NLO) properties of the chiral organic monomer crystal and its polymer/copolymer materials were evaluated and compared with the standard KDP crystal.

## 2. EXPERIMENTAL

### 2.1 Materials

The chemicals, (R)-1-phenyl-ethyl amine and methacryloyl chloride (Alfa Aesar), N,N'-methylene bisacrylamide (MBA) (Aldrich) were used as received. Other chemicals like ethanol, methanol, hexane and NaOH from Samir Tech chem. Pvt. Ltd. were also used as received. 2-hydroxy ethyl methacrylate (HEMA) (97%, Lancaster) was purified, vacuum distilled and stored at 5°C in a refrigerator before use. Benzoyl peroxide (BPO) (ACROSS) was recrystallized twice from cold chloroform, dried in a vacuum desiccator at room temperature and stored in dark at 5°C in a refrigerator before use. Toluene (Ranbaxy) was dried over calcium chloride for 24h, refluxed with sodium metal and finally distilled prior to use.

### 2.2. Crystals of Chiral Monomer, (R)-N-(1-phenyl-ethyl) methacrylamide (CCM)

(R)-N-(1-phenyl-ethyl) methacrylamide (R-NPEMAM) was synthesized by the condensation reaction of (R)-1-phenyl-ethyl amine (77.5 mmol) and methacryloyl chloride (102.3 mmol) in ethanol (40 ml) in the presence of alkali following our previously reported method [33]. The alkali solution (10 ml of 36% NaOH) was added dropwise. The reaction mixture was stirred at 4°C for 24 hrs using a magnetic stirrer. The reaction mixture was then poured into water to obtain the product. The white precipitate product of the reaction was recrystallized from 1:1 ethanol-water mixture. The synthesized material was first dissolved in slight warm ethanol and then to it distilled water was added appropriately till the turbidity appears. The beaker containing this turbid solution was properly closed and kept in ice-cooled water. Needle like Crystals were obtained. Yield: 82%, Melting point: 95-96°C. Optical rotation (C 1.0, DMF):  $[\alpha]_D^{25} = 28^\circ$  (C 1.0, DMF).

### 2.3 Chiral Polymer and Copolymers of CCM

Chiral polymer (CP) of (R)-N-(1-phenyl-ethyl) methacrylamide was synthesized by free radical polymerization of the monomer in toluene medium following our previously reported method [33]. Also the chiral copolymers (CCP-1, CCP-2 and CCP-3) of the monomer along with 2-hydroxy ethyl methacrylate having different feed composition were synthesized following our reported method [34]. Crosslinked copolymer (CCP-X) of (R)-N-(1-phenyl-ethyl) methacrylamide in the forms of beads was obtained by the free radical polymerization of R-NPEMAM (0.0106 mole), 2-hydroxy ethyl methacrylate (HEMA) (0.0710 mole) and crosslinker, N, N'-methylene bisacrylamide (MBA) (2mole % of total monomer i.e.,  $1.632 \times 10^{-3}$  mole). R-NPEMAM, HEMA and MBA were taken along with 20 ml of toluene solvent in a three necked flask assembled with a dropping funnel for addition of initiator solution, a nitrogen inlet and a condenser. The reactor was kept in an oil bath placed on a hot plate with magnetic stirring arrangement. Polymerization was carried out using benzoyl peroxide (BPO) initiator (1.0 wt% of total monomer) at 80°C under N<sub>2</sub> atmosphere for 5 hrs. The product was precipitated in hexane and filtered. The collected crosslinked polymer was dried at 70°C under vacuum. Yield of the crosslinked polymer was 89-90%.

### 2.4 Characterization

The organic monomer crystals and synthesized polymeric materials were characterized by FTIR spectroscopy and elemental analysis. FTIR spectra of the samples were measured with KBr pellets in a Nicolet Magna IR-750 spectrophotometer. Elemental analysis was performed on a VARIO-EL ELEMENTAR (CHNSO) ANALYSER. Chiral monomer crystals and polymeric materials were characterized using a Hitachi 3000N scanning electron microscope (SEM) (Hitachi, Japan) and also by using a Carl Zeiss scanning electron microscope (SEM). The optical rotation of the chiral organic monomer crystal and synthesized polymers and copolymers was measured in DMF solvent using a polarimeter (Autopol II, Rudolph). Thermal analyses of the samples were carried out using METTLER TOLEDO (TGA/SDTA 851) and TA Instrument (DSC Q200) under N<sub>2</sub> atmosphere at a heating rate of 10°C/min.

### NLO Study

The relative second harmonic generation efficiency of the samples with respect to potassium dihydrogen phosphate (KDP) was measured using the setup as shown in Fig. 1. A Q-switched Nd: YAG laser (Continuum, USA, Model: Surelite-III) emitting radiation at wavelength of 1064nm and pulse of width 27 ns with a repetition rate of 10 Hz was used. The powdered form of the samples put in a sample holder was exposed to laser radiations. The second harmonic radiation generated by the randomly oriented microcrystals/particles was imaged by a lens on a PMT. The fundamental and trace amount of ambient light was filtered by the use of interference filter in a rectangular experimental scheme. PIN type Si photodiode was used for detection of fundamental radiation. Both, PMT and photodiode were connected to a oscilloscope (Tektronix: TDS 3054B). The set-up was calibrated by using the samples of potassium dihydrogen phosphate (KDP) and urea. KDP was used as a reference material for the measurement with the samples. The generated second harmonic beam

intensity is proportional to the square of the fundamental beam intensity and to the square of the effective coefficients respectively. The following formula is used here:

$$\frac{I_{SH}^{Sample}}{I_{SH}^{KDP}} = \left[ \frac{d^{Sample} \times I_{FW}^{Sample}}{d^{KDP} \times I_{FW}^{KDP}} \right]$$

OR

$$\frac{d^{Sample}}{d^{KDP}} = \frac{I_{FW}^{KDP}}{I_{FW}^{Sample}} \times \sqrt{\frac{I_{SH}^{Sample}}{I_{SH}^{KDP}}}$$

Where,  $I_{SH}$  and  $I_{FW}$  are the second harmonic and fundamental signals and 'd' is the effective nonlinearity of the sample.

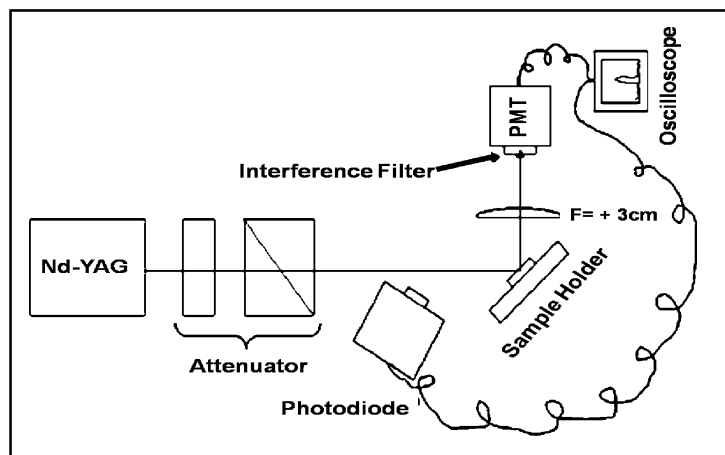


Fig. 1. Schematic of the experimental set up of NLO measurement

### 3. RESULTS AND DISCUSSION

(R)-N-(1-phenyl-ethyl) methacrylamide (R-NPEMAM) was synthesized by the

condensation reaction of (R)-1-phenyl-ethyl amine and methacryloyl chloride in ethanol in the presence of alkali following our previously reported method<sup>[33]</sup>. The creamy white product

was recrystallized from 1:1 ethanol-water mixture. The synthesized (R)-N-(1-phenyl-ethyl) methacrylamide (R-NPEMAM) formed colorless crystal and its melting point was 95-96°C. Fig.2 shows the chemical structure and energy minimized structure of the compound. The photograph of grown crystals of the compound clearly indicates the needle-like crystal formation [Fig. 2(c)]. Since (R)-N-(1-phenyl-ethyl) methacrylamide is a chiral molecule, its optical rotation was observed using a polarimeter and its optical rotation (C 1.0, DMF) value was found to be  $[\alpha]_D^{25} = 28^\circ$  [33-34].

The organic crystal, (R)-N-(1-phenyl-ethyl) methacrylamide (R-NPEMAM) is a chiral monomer which was converted by free radical polymerization to more stable forms i.e., its polymer and copolymers with 2-hydroxy ethyl methacrylate (HEMA) monomer and crosslinked copolymer along with HEMA monomer and crosslinker, N, N'-methylene bisacrylamide (MBA) (Table 1). The copolymers and a crosslinked copolymer were precipitated in the form of beads,

whereas the homopolymer was obtained as powder form having no regular shape of beads (See SEM analysis). This might be because of the nature of the monomers (R-NPEMAM and HEMA) and toluene solvent which are involved in the process of precipitation polymerization. As the chiral crosslinked polymer (CCP-X) does not dissolve in common organic solvent, its molecular weight and optical activity could not be measured. However, molecular weights of the chiral polymer and copolymers were reported to be:  $M_w = 2.78 \times 10^3$  for CP,  $4.75 \times 10^4$  for CCP-1,  $4.63 \times 10^4$  for CCP-2 and  $2.82 \times 10^4$  for CCP-3. The optical rotation (C 1.0, DMF) of the chiral polymer and copolymers were observed to be:  $[\alpha]_D^{25} = 35^\circ$  for CP,  $21^\circ$  for CCP-1,  $11^\circ$  for CCP-2 and  $8^\circ$  for CCP-3 [33-34]. The crystal of chiral monomer, its polymer, copolymers and crosslinked chiral copolymers were characterized by different analytical techniques for their structural and morphological investigations. They were also studied for their functional NLO properties.

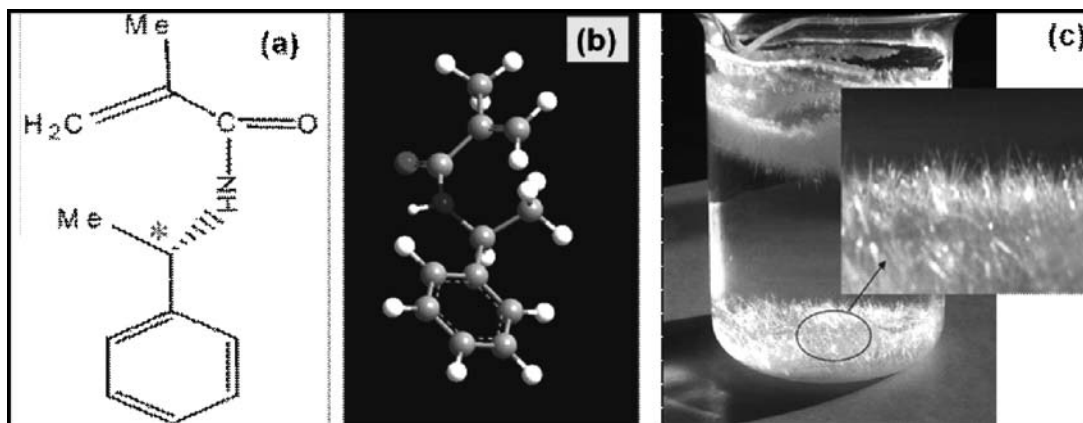


Fig. 2 (a) Chemical structure, (b) minimized energy structure and (c) photograph of the grown crystals of (R)-N-(1-phenyl-ethyl) methacrylamide (CCM)

### 3.1 Elemental Analysis

The organic crystals of (R)-N-(1-phenyl-ethyl) methacrylamide (R-NPEMAM i.e., CCM) and its polymer (CP) and copolymer (CCP) samples were studied by elemental analysis. The elemental compositions of the samples are given in Table 1. The concentration of R-NPEMAM in the copolymers and crosslinked polymer sample is estimated from the results of elemental analysis using the following equation:

Mole % of R-NPEMAM in copolymers

$$= \frac{36N}{7C - 36N} \quad (1)$$

Where,  $F_1$  is the mole fraction of the chiral monomer in the copolymers. C and N are the %C and %N as obtained from the elemental analysis. Since the amount of crosslinker, MBA was very small in polymerization system, it was not considered in the above calculation in case of the crosslinked polymer. In all the cases, the concentration of R-NPEMAM in the copolymers is somewhat lesser than taken in the feed for copolymerization which is quite obvious. The concentration of R-NPEMAM in the crosslinked polymer is 10.2 mole %.

### 3.2 FTIR Analysis

The chiral monomer crystal (CCM i.e., R-NPEMAM) was characterized by FTIR analysis

TABLE 1. Results of Elemental (CHNSO) Analysis<sup>a</sup> and Composition of Copolymers

Sample Code (Ratio of R-NPEMAM and HEMA)	Mole% of R-NPEMAM in the feed of polymerization	Mole% of R-NPEMAM in Polymer/ Copolymer	% C	%N	%H	%O
CCM	-	-	73.68	7.04	8.03	12.28
CP	100	100	72.19	6.40	8.07	13.95
CCP-1(1:0.5)	66.6	41.6	62.04	3.16	8.04	27.03
CCP-2(1:2.5)	28.6	24.9	56.33	1.46	8.21	34.00
CCP-3 (1:6.7)	12.98	9.9	55.25	0.69	7.76	36.30
CCP-X (1:6.7+ CL)	12.98	10.2	54.45	0.98	7.73	36.84

<sup>a</sup> Average of 4 measurements

Chiral monomer (CCM); Chiral Polymer (CP); Chiral copolymer (CCP)

Crosslinked chiral copolymer (CCP-X) (having R-NPEMAM: HEMA=1:6.7mole ratio and CL=2 mole% MBA of the total monomer)

(Fig. 3). The peak assignment is given in Table 2. The absorption band at 1527cm<sup>-1</sup> due to the -CONHR functional group indicates the formation of the monomer as a result of the condensation reaction of R-NPEMAM and

methacryloyl chloride. Moreover, the characteristic signal of the double bond stretching vibration (band of C=C) at 1614 cm<sup>-1</sup> and the absorption band at 924 cm<sup>-1</sup> due to C-H bending of vinyl group (=CH<sub>2</sub>) are present in

the spectrum. On the other hand, in the FTIR spectrum of the chiral polymer, copolymers and crosslinked copolymer of the monomer there is no such observation of double bond stretching as well as C-H bending of vinyl group because of its involvement in polymerization by opening up for forming polymer and copolymers (Figs. 4 to 6). Moreover, a new

peak due to carbonyl group (C=O) stretching of ester of HEMA unit appears at  $1724\text{ cm}^{-1}$  in the copolymers (Figs. 5 and 6). A broad peak at around  $3315\text{ cm}^{-1}$  is due to hydroxyl group (OH) of HEMA; on which the characteristic absorption of NH *trans* stretching ( $3335\text{ cm}^{-1}$ ) of R-NPEMAM is merged [33-34]. The OC-O of ester appears at  $1266\text{ cm}^{-1}$ ; on the other hand

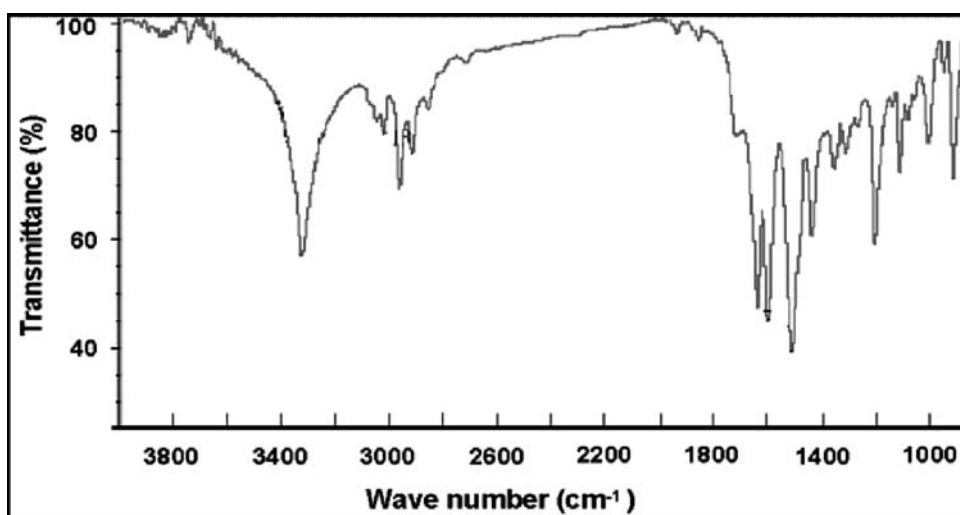


Fig. 3. FTIR spectrum of (R)-N-(1-phenyl-ethyl) methacrylamide (CCM)

TABLE 2. FTIR Peak Assignment of R-NPEMAM Monomer Crystals

Frequency (cm <sup>-1</sup> )	Mode of Assignment
3347	NH <i>trans</i> stretching vib. of the secondary amide
2974	C-H stretching of CH <sub>3</sub> groups
1653	C=O stretching of amide
1615	C=C stretching vib. attached to $\alpha$ , $\beta$ -unsaturated carbonyl compound
1525	N-H bending of -CONHR functional group (secondary amide)
9241	C-H bending of vinyl (=CH <sub>2</sub> ) group
1369	OC-N vib.
1200	In plane C-H bending of aromatic ring
1450	C=C stretching of aromatic skeletal



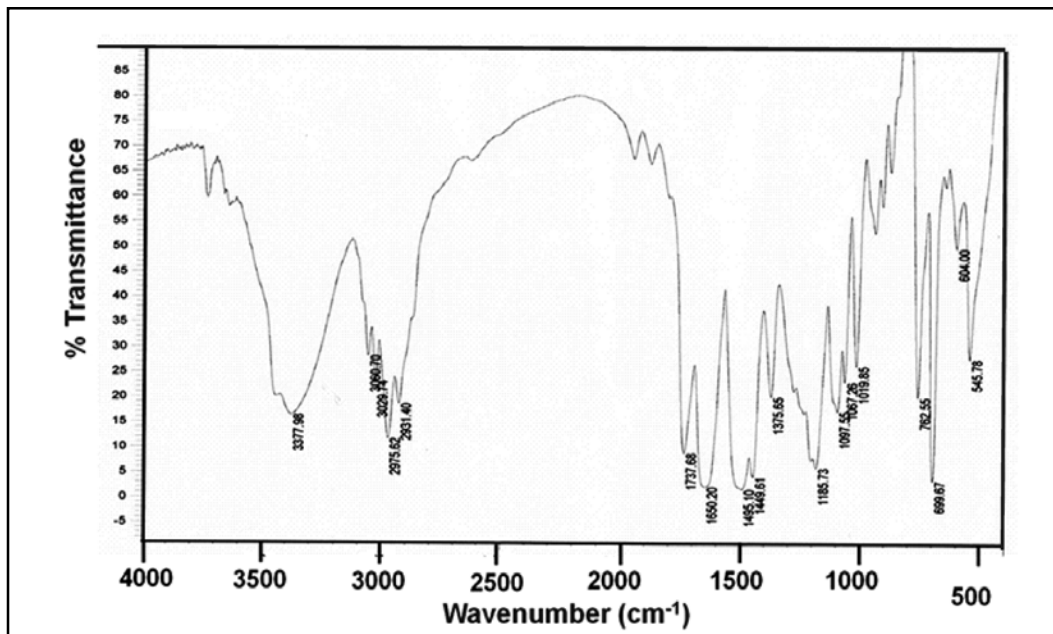


Fig. 4. FTIR spectrum of chiral polymer of R-NPEMAM (CP)

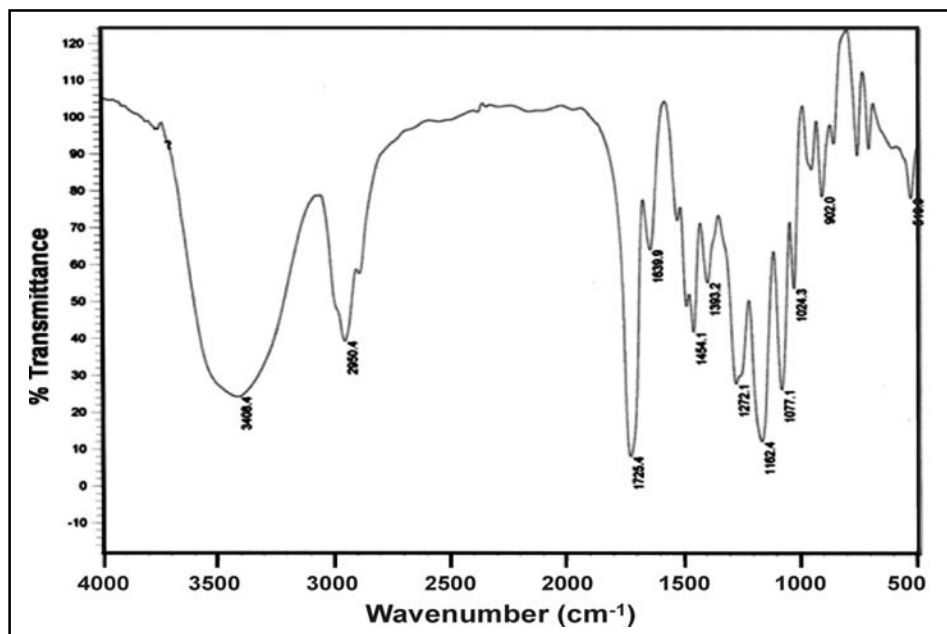


Fig. 5. FTIR spectrum of chiral copolymer of R-NPEMAM (CCP-3)

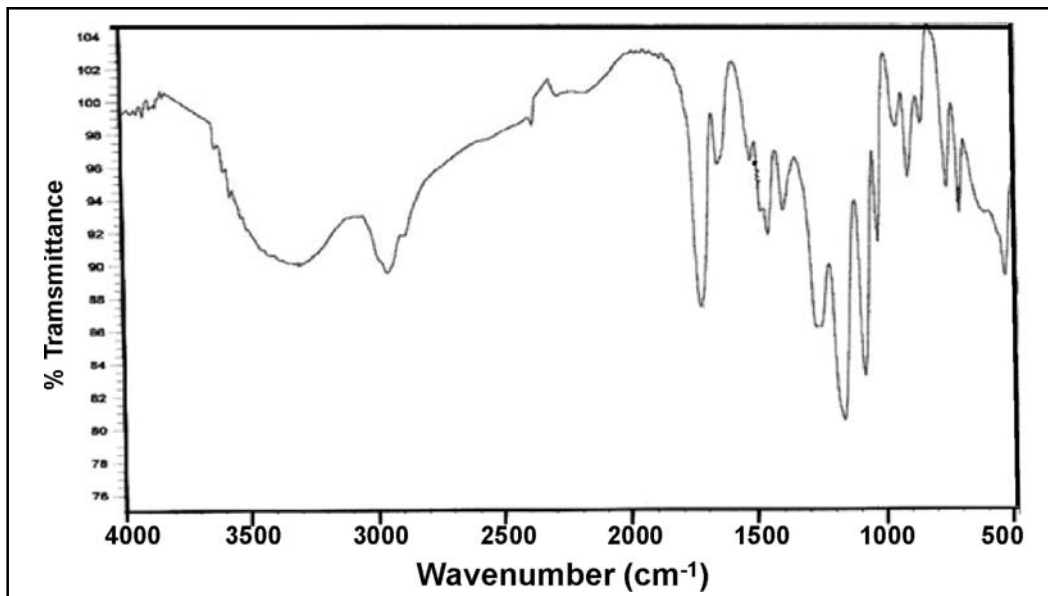


Fig. 6. FTIR spectrum of crosslinked copolymer of R-NPEMAM (CCP-X)

the C-O stretching vibration of  $-\text{CH}_2\text{-OH}$  of HEMA appears at  $1162\text{ cm}^{-1}$ .

### 3.3 SEM Analysis

SEM micrographs of organic monomer crystals are shown in Fig.7. The needle-like (or fibre-like) crystals of R-NPEMAM obtained by recrystallization process have length varying between 1 to 3 cm. The diameter of such crystals ranges between  $80\text{-}100\text{ }\mu\text{m}$ . The surface features of such crystals shown in Fig. 7 (c) indicate the fibrils growth during crystallization. This uniform fibril growth of the crystal may be due to the crystallization of similar molecular structure of the compound which is represented by the energy minimized structure [Fig. 2 (b)].

The surface morphologies of the chiral polymer, copolymers and the crosslinked copolymer

were also analyzed by SEM analysis (Fig. 8 and 9). The polymer and copolymers were obtained by precipitation polymerization process in toluene medium. Although the chiral monomer was dissolved in toluene, its polymer and copolymers with HEMA were not dissolved in the medium and obtained as precipitates. The chiral homopolymer was obtained as irregular shaped powder form. On the other hand, the copolymers and a crosslinked copolymer were obtained as precipitates in the form of regular shaped beads (or pearls). These are clearly observed in the SEM micrographs.

In general, in precipitation polymerization, beads are obtained. However, the actual physical structures of the precipitates depend on the nature of the monomers and solvent used for polymerization. This difference observed here might be because of the nature of the monomers (R-NPEMAM and HEMA) and toluene solvent

which are involved in the process of precipitation polymerization. In case of copolymers and the crosslinked copolymer in which HEMA (which is more hydrophilic in nature than R-NPEMAM) was taken as comonomer, the precipitates

occured at relatively early stage than the case of polymer (using only R-NPEMAM) in toluene medium. The precipitation was more prominent resulting regular beads in the precipitates. The particle size is observed to be 1.0- 1.2  $\mu\text{m}$  (in

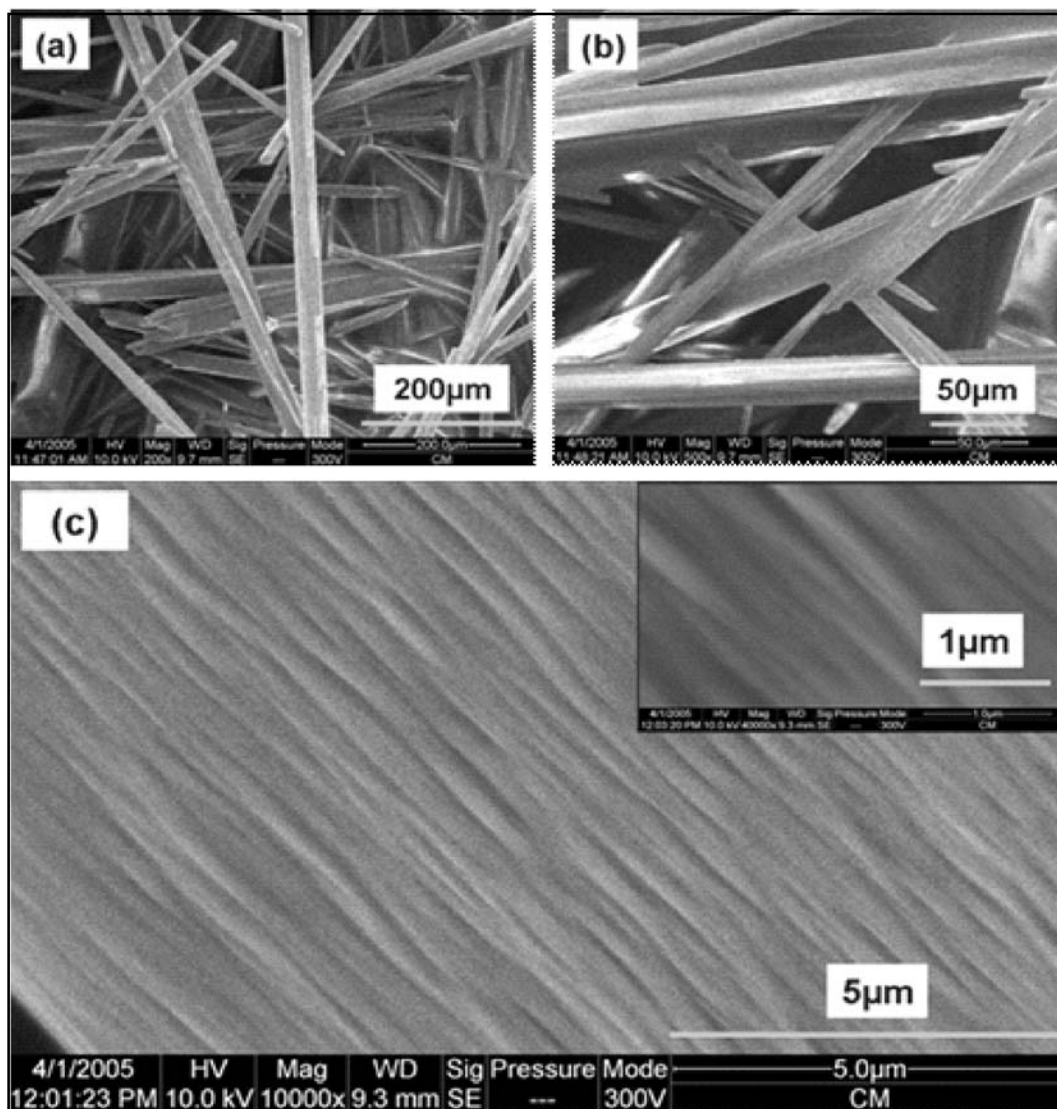


Fig. 7. SEM micrographs of chiral monomer crystals (CCM) at different Magnification

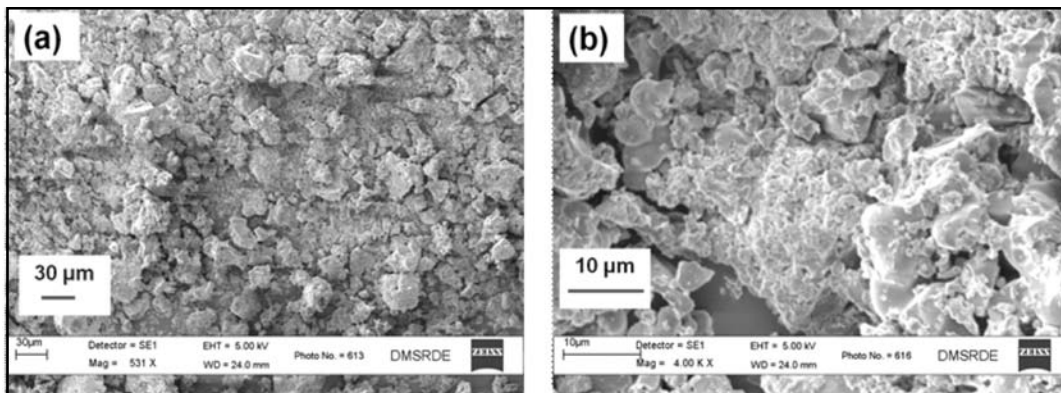


Fig. 8. SEM micrographs of chiral polymer (CP) particles at two different magnification : (a) 0.531 KX and (b) 4.00 KX

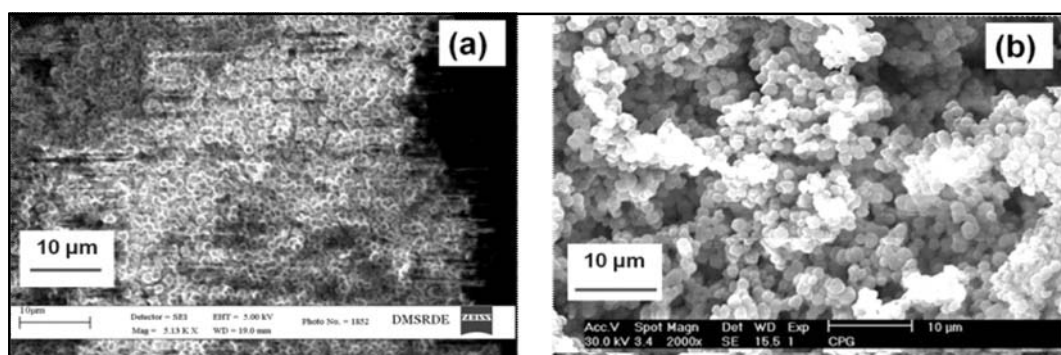


Fig. 9 SEM micrographs of (a) chiral copolymer (CCP-3) (Magnification: 5.13 KX) and chiral crosslinked polymer (CCP-X) beads (Magnification: 2.00 KX)

diameter) for copolymer and 1.2-1.5 μm (in diameter) for crosslinked copolymer (Fig. 8 and 9).

### 3.4 Study of NLO Properties

The relative second harmonic generation (SHG) efficiency of organic chiral monomer crystal of (R)-N-(1-phenyl-ethyl) methacrylamide (CCM) and its polymer (CP), copolymers (CCP-1, CCP-2 and CCP-3) and crosslinked copolymer (CCP-X) samples was measured with respect to potassium dihydrogen phosphate (KDP). Chiral monomer crystals exhibited the second-

harmonic generation efficiency of 1.22 times that of KDP which is much higher than that of organic single crystals of pure lauric acid (LA) (SHG efficiency of 0.87 times that of KDP) [31]. Again this NLO property is comparable to the recently reported property of organic 4-chloroanilinium-L-tartrate monohydrate single crystals (SHG efficiency of 1.5 times greater than KDP) [32].

All the samples, the organic crystals and its polymer, copolymers and crosslinked

copolymer beads exhibit SHG (Fig. 10 and 11). The results are given in Table 3. It is observed to have second harmonic generation (SHG) or second order nonlinearity (pm/V) value of organic monomer crystals is more than the KDP crystal. On the other hand, the values are less for the polymeric materials than that of KDP. The value of organic crystal chiral monomer (CCM) 0.475 pm/V is reduced to 0.366 pm/V for its transformation to its polymer resulting 22.94% reduction. Although the chiral unit responsible for the NLO property may be same, but its molecular arrangement in the polymeric chain may be responsible for such reduction. In the copolymers, the second order nonlinearity again decreases as the concentration of CCM content decreases in the copolymers. The lower value of SHG for the copolymers in comparison to the organic chiral monomer crystal may be due to the low concentration of second harmonic generating CCM component in the polymer materials. Moreover, the organic monomer crystals may no longer remain crystal on

polymerization, it is converted to polymers and crosslinked polymer of semicrystalline in nature. In case of copolymer (CCP-3) and crosslinked copolymer (CCP-X), the chiral (CCM) content in these materials is about the same (9.9 mole% and 10.2 mole% respectively) (in feed composition same amount of CCM was taken along with HEMA comonomer in both the cases). However, it is observed to a decrease of SHG value from 0.343pm/V of copolymer to 0.339pm/V of crosslinked copolymer. Thus there is a reduction of SHG which might be because of the crosslinked structure as it restricted the chiral monomer units.

In the search of new NLO materials, many organic crystals with high SHG efficiency such as urea, urea doped benzophenone and others have been reported [27-32]. The chiral organic monomer reported here is an organic crystal exhibiting NLO property. However, the organic crystals limited for their application as they are not thermostable materials. Here we have converted such organic monomer crystals to

TABLE 3. Measured SHG efficiency of the grown crystals of organic chiral monomer (CCM) and its polymer (CP)/copolymers(CCP)

Sample	Mole% of R-NPEMAM in Polymer/Copolymer <sup>a</sup>	SHG Efficiency Efficiency with respect to KDP	Second order nonlinearity (pm/V)
CCM	-	1.22	0.475
CP	100	0.94	0.366
CCP-1(1:0.5)	41.8	0.93	0.362
CCP-2(1:2.5)	24.9	0.92	0.358
CCP-3 (1:6.7)	9.9	0.88	0.343
CCP-X (1:6.7+ CL)	10.2	0.87	0.339
KDP crystal	-	1.00	0.390

its polymer/copolymers which also exhibit NLO properties. Therefore, the results of these materials reported in this investigation indicate that materials may also be used for nonlinear optical applications.

### 3.5 Thermal Analysis

The DSC and TGA thermograms of the crosslinked chiral copolymer (CCP-X) are shown in Figs.12 and 13. The glass transition temperature of the crosslinked chiral copolymer

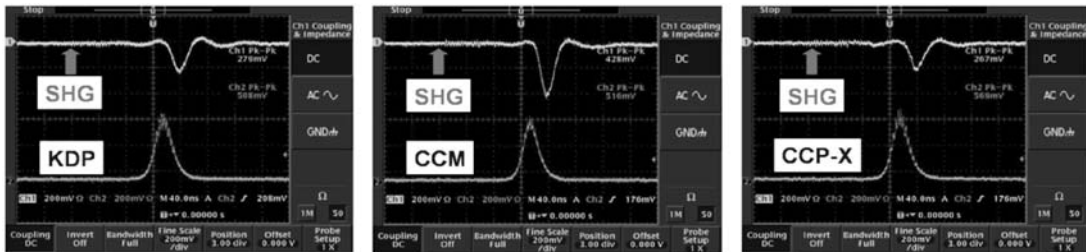


Fig. 10. Oscilloscope traces of input and generated SHG from KDP crystal, chiral monomer crystal (CCM) and its crosslinked copolymer (CCP-X)

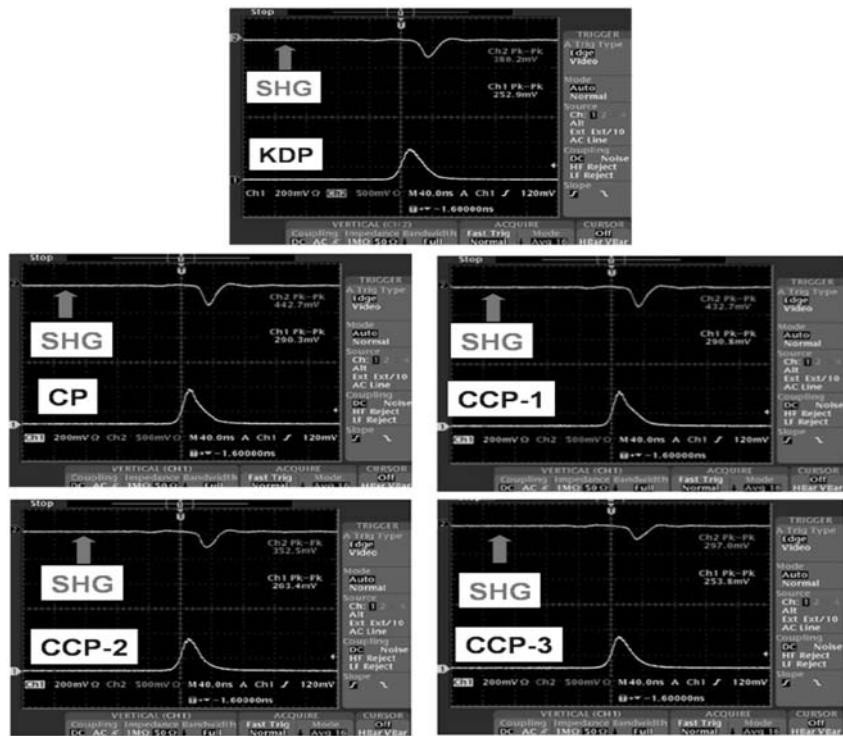


Fig. 11. Oscilloscope traces of input and generated SHG from KDP crystal, chiral polymer (CP), copolymers (CCP-1, CCP-2 and CCP-3)

sample is estimated to be 121.5°C from the DSC analysis. However, the glass transition temperature of corresponding chiral copolymer (CCP-3) which is not crosslinked was reported to be 93.7 °C [35]. The higher glass transition temperature for the CCP-X sample than that of the CCP-3 sample is due to its crosslinked structure as crosslinking increases the glass transition temperature. However, unlike copolymers, single step decomposition of the

crosslinked copolymer is clearly observed from the TGA thermogram. It starts degrading at 270°C and ends at 433 °C having the peak decomposition temperature at 407°C. This single step degradation may be associated with the single crosslinked structure of the polymer which is not the case for the copolymers. The polymer/crosslinked polymer materials are highly thermally stable than that of the organic monomer crystal which is quite obvious.

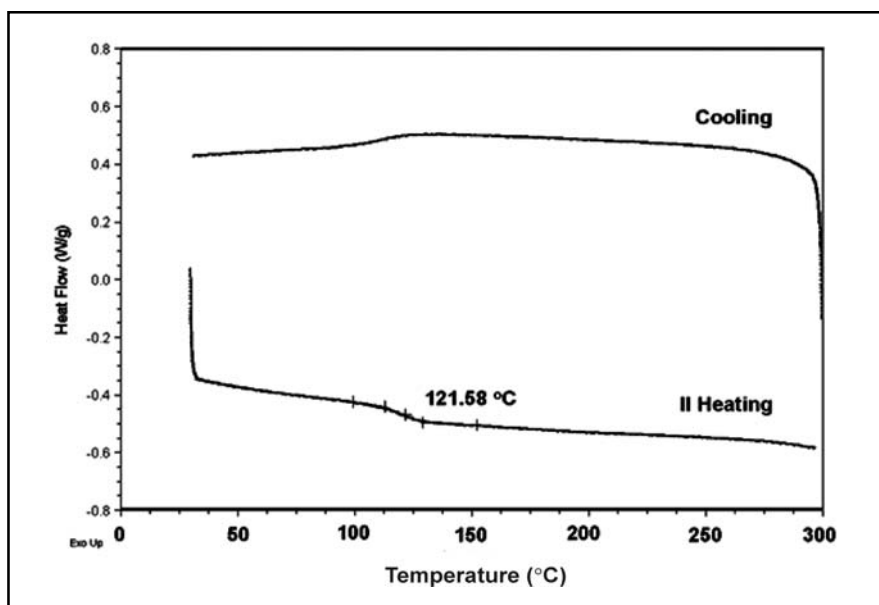


Fig.12 DSC thermograms of crosslinked chiral copolymer (CCP-X)

Therefore, these polymeric materials having SHG properties are very suitable NLO applications.

Thermal analysis of the chiral monomer and its polymer was reported in our previous publication [33]. Its melting point was observed to be 95.5°C by DSC analysis. It was started

decomposing at 130°C and ended at 242°C leading to 98% decomposition and no char residue was observed above 285°C. On the other hand, the glass transition and melting temperatures of the chiral polymer were observed to be 100.6°C and 255°C respectively. Such polymer undergoes two-staged decomposition at 295 °C and 400°C [33].

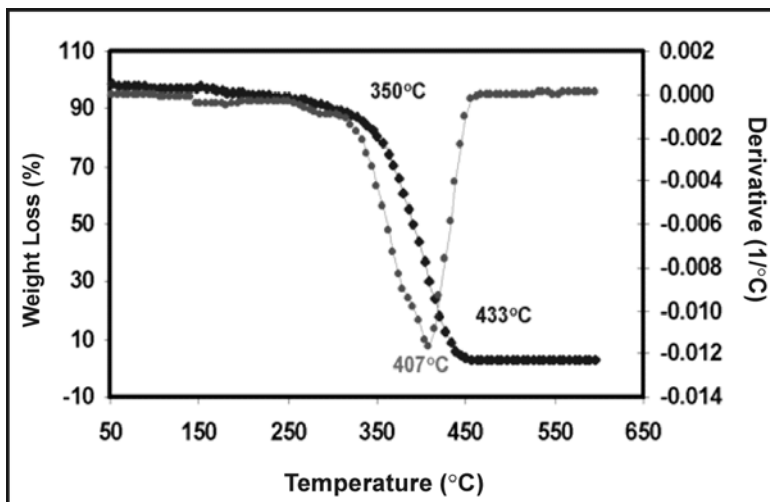


Fig. 13. TGA thermograms of crosslinked chiral copolymer (CCP-X)

The chiral copolymers of the chiral monomer with HEMA are usually degraded in three-staged like at 292°C, 372°C and 419°C (DTG peaks, heating rate of 10°C/min, Ar-atmosphere) [36]. The first and third stages of decompositions are associated with the chiral (R-NPEMAM) unit whereas the second stage decomposition indicates the degradation due to HEMA unit present in the copolymer chain. The results are corroborated with the reported results [36-37]. Two stages of decomposition of similar kind of polymer, polyacrylamide was reported [36]. Also the thermal decomposition of polyHEMA was reported as single peak at 361°C in the DTG curve (heating rate of 10°C/min, N<sub>2</sub>-atmosphere) [37].

### CONCLUSION

Chiral organic monomer crystal of (R)-N-(1-phenyl-ethyl) methacrylamide (R-NPEMAM) was obtained by the condensation reaction of (R)-1-phenyl-ethyl amine and methacryloyl chloride in ethanol in the presence of alkali

followed by recrystallization. The surface features of such crystals indicate the fibrils growth during crystallization and the diameter of such crystals ranges between 80-100 μm. The synthesized crystal of chiral monomer (CCM) was polymerized and copolymerized with 2-hydroxy ethyl methacrylate (HEMA) and a crosslinker, N, N-methylene bisacrylamide (MBA). The optical rotations of chiral monomer, its polymer and copolymers were observed to be  $[\alpha]_D^{25}$  (C 1.0, DMF): 28° for CCM, 35° for CP, 21° for CCP-1, 11° for CCP-2 and 8° for CCP-3. These organic crystals and polymeric materials were studied for their NLO properties with respect to potassium dihydrogen phosphate (KDP). Chiral monomer crystals exhibited the second-harmonic generation efficiency of 1.22 which is comparable to the recently reported SHG efficiency of 1.5 for organic 4-chloroanilinium-L-tartrate monohydrate single crystals. The NLO property exhibited by the polymer and copolymers of the chiral monomer varies between 0.87 and 0.94 which



is comparable to the property of other organic crystals. Moreover, such polymeric materials are thermostable compared to the organic crystals. Hence these NLO materials may have potential NLO application.

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