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SYNTHESIS AND CHARACTERIZATION OF 3-CHLORO CINNAMOYL PHENYL METHACRYLAMIDE POLYMERS

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Abstract:

Poly3-chloro cinnamoyl phenyl methacrylamide 3-(CCPM) containing a photosensitive group was synthesized by reacting 3-chlorocinnamoylaniline with methacryloyl chloride in the presence of triethylamineat 0–5◦C. The functional monomer, 3-CCPM was polymerized in ethylmethyl ketone (EMK) under nitrogen atmosphere at 70 ◦C using benzoyl peroxide (BPO) as the initiator. The synthesized polymer was characterized by UV, IR,^{1}H-NMR and ^{13}C-NMR spectroscopy. The molecular weight data of the polymer as obtained from gel permeation chromatography suggests a higher tendency for chain termination by radical recombination than disproportionation. The thermal studies of the polymer were obtained from thermogravimetric analysis. The glass transition temperature of the polymer was determined by differential scanning calorimetry. The solubility of the polymer was tested in various organic solvents at room temperature. The photosensitivity of the polymer was investigated in various solvents in the presence and absence of triplet photosensitizers. The effect of the different solvents nature and concentration on the rate of photocrosslinking of the polymer were also examined for using the polymer as negative photoresist materials.

Key Words: 3-Chloro Cinnamoyl Phenyl Methacrylamide, Chalcone, Crosslinking, Radical Polymerization & Thermal Property

1. Introduction:

Methacrylic copolymers have achieved prime importance in various avenues of industrial application. Copolymers of these activated monomers have been employed to study the kinetic aspects of macromolecular reactions, preparation of macromolecular drug carriers, immobilized enzymes and polymeric reagents for peptide synthesis and transition metal catalysis. Photosensitive polymers with photocrosslinkable groups have gained a considerable interest in recent years due to wide variety of applications in the field of microlithography, printing materials, liquid crystalline display and non-linear optical materials.

2. Experimental:

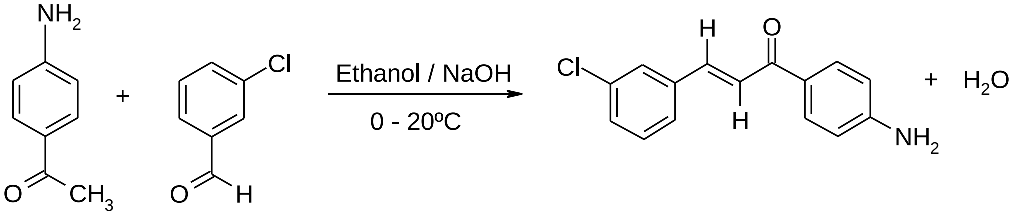
✓ Materials:

4-Aminoacetophenone (Merck) was used as received. 3-chloro benzaldehye (Fluka) were distilled before use. Benzoyl peroxide (BPO) was recrystallised from a chloroform/methanol (1: 1) mixture. Methacryloyl chloride was prepared according to the method of stampel et al. All the other solvents were distilled by standard procedure.

✓ Synthesis of 4-(3′-chlorocinnamoyl)aniline(4,3′-CCA):

4-aminoacetophenone (10.8 g) in 50 ml of ethanol and sodium hydroxide (3.2 g) in 30 ml of distilled water was placed in a three-necked flask equipped with a mechanical stirrer, thermometer and a dropping funnel and were cooled in an ice bath. 3-chlorobenzaldehyde (9.2 ml)dissolved in 20 ml of methanol was added drop wise with constant stirring such that the temperature was not exceeded 25°C. The stirring was continued for 48 h at room temperature and the solid product was filtered, washed with cold water and recrystallized from ethyl acetate to get shining yellow crystals. Yield: 15.72 g (71%); mp. 123-124ºC.

The structure of the compound was confirmed by elemental analysis, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectral techniques.



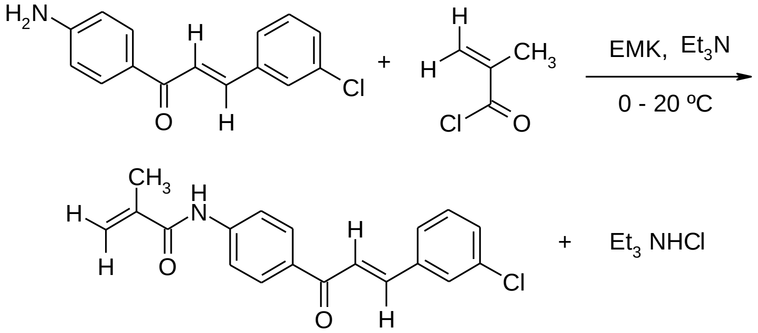
Elemental analysis (%): C: 69.82 (Found): 69.90 (Calcd), H: 4.64 (Found): 4.69 (Calcd), N: 5.38 (Found): 5.43 (Calcd).

FT-IR (KBr, cm^{-1}): 3419 & 3331 (N-H stretching); 3044 (=C-H stretching); 2933 & 2811 (C-H Stretching); 1628 (>C=O); 1608 (olefinic >C=C<); 1580 (N-H bending); 1514 & 1442 (aromatic C=C stretching); 1341 (C-N stretching); 1021 (Ar-Cl); 830 & 791 (=C-H out of plane bending); 663 (N-H wagging); 502 & 437 (C=C out of plane bending);

^{1}H-NMR (DMSO, ppm): 7.92-7.34 (m, 9H, Ar-H & =CH-Ar), 6.55-6.51 (d,1H, -CO-CH=), 6.09 (s, 2H, NH$_2$).

^{13}C-NMR (DMSO, ppm): 186.61 (keto, >C=O), 154.89-113.64 (aromatic carbons & –**C**H=**C**H-), 140.54 (=**C**H-Ar), 125.01 (>CO-**C**H=).

- ✓ **Syntheis of 4-(3′-Chlorocinnamoyl)phenyl methacrylamide:**



4-(3′-Chlorocinnamoyl)phenyl methacrylamide (3-CCPM) was obtained by reacting 4-(3′-chlorocinnamoyl)aniline (16 g, 0.06 mol) and methacryloyl chloride (6 ml, 0.06 mol) in the presence of triethylamine (8.7 ml, 0.06 mol) in EMK by adopting a similar procedure as described in the preparation of 3-bcpm. the crude product was recrystallized from ethyl acetate to get yellow powder. yield: 16.89 g (77 %); mp.138-139 ºc. The structure of the compound was confirmed by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectral techniques.

IR (KBr, cm^{-1}): 3332 (N-H stretching); 3060 (=C-H stretching); 2964 & 2926 (C-H stretching); 1658 (>C=O, amide band I); 1628 (>C=O, keto);1608 (olefinic >C=C<); 1525 (N-H bending, amide band II); 1525,1600, 1501 & 1443 (aromatic >C=C< stretching); 1415 (=CH$_2$ scissoring); 1339 (C-N stretching); 1011 (C-Cl); 979, 895 & 793 (=C-H out of plane bending); 691 (NH wagging); 571 507(>C=C< out of plane bending).

^{1}H-NMR (CDCl$_3$,ppm): 8.08-7.26 **(**1H /8H /2H, NH/Ar-H / =CH-Ar); 6.70 and 5.84 & 5.52 (1H/2H, =CH-CO and CH$_2$= C<); 2.08 (3H, α-CH$_3$).

^{13}C-NMR(DMSO, ppm): 188.53 (keto, >C=O);166.77 (-CO-NH-), 140.76 (=CH-Ar); & 120.53 (=CH-CO), 142.79 & 123.08 (-**C**H=**C**H-), 142.36, 136.88. 135.03, 133.65, 131.22, 130.27, 130.03, 127.96, 126.79, 119.42 (aromatic carbons), α-CH_3 **(**18.71)

✓ Homopolymerization of 3-CCPM:

3-CCPM was polymerized as a 2M solution in EMK, using BPO as the initiator at 70ºC. The predetermined quantities of 3- CCPM, the initiator (0.25 wt % of monomer), and solvent were placed in a polymerization tube and the mixture was flushed with a slow stream of nitrogen for 15 min. Then, the tube was closed and placed in the thermostated oil bath at 70ºC. After 9 h, the reaction mixture was poured into excess methanol to precipitate the polymer, poly 3-(CCPM). The crude polymer was purified by dissolving in EMK and reprecipitated by methanol, filtered, washed with methanol and dried under vacuum at 50◦C. The yield of the polymer was 25%.

✓ Solubility Studies:

Solubility of the polymers was tested in various polar and nonpolar solvents. About 5-10 mg of the polymer was added to about 2 mL of different solvents in a test tube and kept overnight, with the test tube tightly closed. The solubility of the polymers was noted after 24 h.

✓ Measurements:

IR spectra were recorded on a Hitachi model 270-50 spectrophotometer using potassium bromide pellets. ^{1}H-NMR spectra were run on a JOEL 400MHz spectrometer at room temperature using a 15 wt% solution in $CDCl_3$ and tetramethylsilane (TMS) as the internal standard. ^{13}C-NMR were run on a Bruker 270 MHz spectrometer. Elemental analysis was performed with a Perkin-Elmer C-H analyzer. The UV spectrum of poly 3-(CCPM) in chloroform was obtained on a U-2000 Hitachi spectrophotometer. Number and weight-average molecular weights (M_n and M_w) and polydispersity index values were determined using a Waters 501 gel permeation chromatograph (three ultra-styragel columns, refractive index detector, and calibrations with polystyrene standards) with tetrahydrofuran (THF) as the eluent. Thermogravimetric analysis was performed on a Mettler TA 3000 thermal analyser. Thermogravimetric (TG) traces were recorded on 10 mg samples at a heating rate of 20ºC/min ain air. The glass transition temperature was determined with a Perkin-Elmer DSC d^7 differential scanning calorimeter (DSC) at a heating rate of 10ºC /min using air as the purge gas.

✓ Photoreactivity Measurements:

The photoreactivity of the prepared polymers was studied by dissolving the polymers in chloroform solution and irradiated with a medium - pressure mercury lamp (Toshiba SHL-100 UV, 6W, 254 nm) in air atmosphere. The quartz cell containing the polymer solutions was kept at a distance at 10 cm from the UV lamp for different time intervals of irradiation. The UV spectra of the polymer solution were recorded immediately after each exposure to UV light, and the rate of disappearance of the C=C double bond of the chalcone moiety of the polymer was followed by using the following expression.

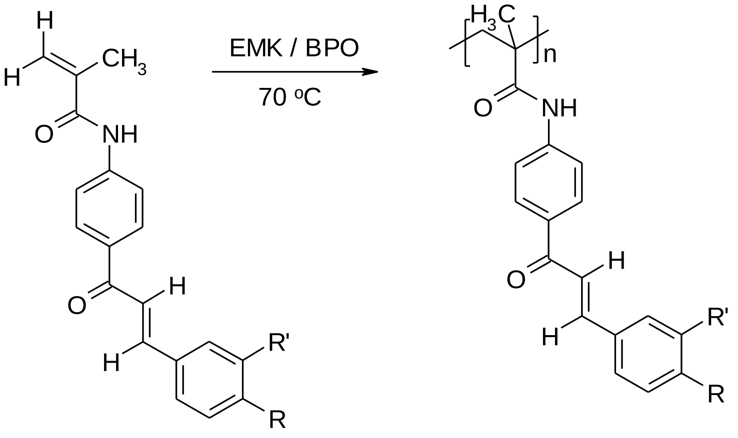
Extent of conversion (%) = $(A_0 - A_T)100/ A_0 - A_\infty$

where A_0, A_T and A_∞ are absorption intensities due to C=C after irradiation times t = 0, t = T and t = ∞, respectively.

3. Results and Discussion:

✓ Synthesis of Polymer:

The photosensitive methacrylamide monomer, 3-CCPM having a free radical polymerisable olefinic group and pendant chalcone as photosensitive group was synthesized according to equatons 1 and 2 in Sch. 1. Poly 3-CCPM was synthesized by free radical polymerization 3-CCPM in EMK using BPO as a free radical-initiator at moderate and high conversions as in Eq. 3 scheme 1. The conversion was restricted to 45%-50 %



R’ = Cl; R = H : Poly[4-(3’-chlorocinnamoyl)phenyl methacrylamide]

- **Solubility:**

The important requirement for a photosensitive polymer is its solubility in different organic solvents. The polymer obtained up to 9 hr of polymerization (29% yield) was found to be soluble in polar aprotic solvents such as DMSO, THF, DMF and chlorinated solvents like chloroform, dichrloromethane. It was insoluble in aliphatic and aromatic nonpolar solvents such as benzene and xylene and hydroxyl group containing solvents like methanol, ethanol, 2-propanol, water etc. The solubility of poly CCPM is generally very low (29%). After 16 hr of homopolymerization is 80% yield, poly CCPM obtained was completely insoluble in common organic solvents even at boiling temperature. This might have been the result of crosslinking. The infrared spectra of both the soluble and insoluble portion of the polymer are identical and hence do not prove any crosslinks due to an obviously very small crosslink density. However, swelling studies performed with dry polymer samples and EMK as the solvent proved the presence of crosslinks in the insoluble polymer.

- **UV Spectroscopy:**

The UV spectrum of poly CCPM shows an absorption maxima on the long wavelength 320 nm due to the π – π* transitions of >C=C< of the pendant chalcone moiety. The bathochromic shift of UV absorption maxima in poly CCPM is due to the presence of electron donating group in the aromatic ring of styryl unit. The electron donating groups are in extended conjugation with carbon-oxygen double bond through the aromatic ring of styryl group and the carbon – carbon double bond.

- **Infrared Spectroscopy:**

The IR spectrum of poly 3-(CCPM) is shown in Fig. 1. It displays strong bands at 3433 and 1514 cm^{-1} due to N-H stretching and N-H bending, respectively. An absorption band at $3094cm^{-1}$ is due to the =C-H stretching vibrations. The symmetrical and asymmetrical C-H stretching due to the methyl and methylene groups are observed at 2984 and $2899cm^{-1}$ respectively. The amide band I due to C=O stretching and the amide band II due to the –CONHAr group are observed at 1657 and 1514 cm^{-1} respectively. Strong absorption at 1600 cm^{-1} is due to C=C stretching of olefin and the aromatic moiety. The absorption due to the C-H out of plane bending vibration is observed at 979, 833 and 784cm^{-1}. The C-Cl absorption bond appears at 1026 cm^{-1} The peak at 572cm^{-1} is due to the C=C out of plane bending vibrations.

- ✓ **^{1}H-NMR Spectroscopy:**

The ^{1}H-NMR spectrum of the poly 3-CCPM shows resonance signals between 8.04 and 6.70 ppm due to the aromatic protons, NH proton, and olefinic (-CH=CH-)protons of the pendant chalcone group. The backbone methylene (-CH_2) protons are observed as broad signals at 2.16-1.68 ppm, indicating the presence of conformational tacticity. The α-methyl protons give a resonance signal at 1.25 ppm.

- ✓ **^{13}C-NMR spectroscopy:**

The proton-decoupled ^{13}C-NMR spectrum of poly 3-CCPM has shown the resonance signals at 188.55 and 175.05 ppm are due to the ketone and amide carbonyl groups, respectively. The signals at 142.84 and 123.08ppm are due to the olifinic carbons attached to the aromatic ring and keto groups, respectively. The resonance signals of aromatic carbon atoms in the benzene ring are observed at 142.28, 136.88, 135.04, 133.70, 130.24, 130.06, 127.97, 126.80, 120.594& 119.38 ppm. The signals at 52.46 and 46.07 ppm are due to backbone methylene and tertiary carbon atoms respectively. The α- methyl group shows signal at 18.71 ppm.

- ✓ **Molecular Weight:**

The Weight average (M_w) molecular weights, number average (M_n) molecular weights and polydispersity index of poly 3-(CCPM) were determined by gel permeation chromatography. $M_w = 5.37 \times 10^4$ and $M_n = 2.74 \times 10^4$. The polydispersity index (M_w/M_n) =for the polymer is 1.96. The theoretical value of M_w/M_n for polymers produced by radical combination and disproportionation are 1.5 and 2.0 respectively. The polydispersity index value of poly3- (CCPM) suggests that in homopolymerization of 3-CCPM there is a strong tendency for chain termination by disproportionation.

- ✓ **Thermal Properties:**

The thermal stability of poly 3-(CCPM) was studied in air by estimating the percentage weight loss of the polymer on heating. The thermogram of poly3-(CCPM) clearly shows that the decomposition of the polymer occurs in three stages. The initial decomposition temperature is 273°C, which indicates that the polymer has good thermal stability required for a negative photoresist. The first stage decomposition (273°- 377°C) may be attributed to the cleaving of the pendant group and the second stage (377 - 458) and the third stage (458-587°C) decomposition may be due to the cleavage of the main chain bonds. A weight loss of 10, 30, 50, 70 and 90 % occurred at 307, 330, 432, 488 and 537°C, respectively. The total weight loss was at 90%. Glass transition temperature (T_g) of poly3-CCPM was determined by differential scanning calorimetry and was found to be 156°C. The high value of T_g may be attributed to the inflexible and bulky pendant chalcone units and the short methyl chains, which facilitate chain entanglement.

4. Conclusion:

A new 3- chlorocinnamoyl phenylmethacrylamide based photocrosslinkable polymer was synthesized by free radical polymerization in solution using benzoyl peroxide as initiator. IR, 1H-NMR and 13C-NMRcharacterized the structure of the chalcone, monomer and the polymer. The polymer was easily soluble in polar aprotic solvents and chlorinated solvents. The molecular weight data of the polymer suggests that in homopolymerization chain termination takes place mainly by disproportionation than radical recombination. Thermal studies indicate that polyme has good thermal stability required for a negative photoresist.

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