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Synthesis, Characterization and Photocrosslinking Properties of Poly(1-(4-Methacrylamidophenyl)-1-(4-nitrophenyl)prop-1-en-3-one)

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The phenylmethacrylamide monomer, 1-(4-methacrylamidophenyl)-1-(4-nitrophenyl)-prop-1-en-3-one (MPNP) containing a photosensitive group was synthesized by reacting 4-nitrocinnamoylaniline with methacryloyl chloride in the presence of triethylamine at 0–5°C. The functional monomer, MPNP was polymerized in ethyl methyl 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.

Keywords 1-(4-methacrylamidophenyl)-1-(4-nitrophenyl)prop-1-en-3-one, chalcone, crosslinking, radical polymerization, thermal property

Introduction

Photosensitive polymers with photo-crosslinkable groups have gained considerable interest in recent years owing to a wide variety of applications in microlithography (1, 2), printing materials (3), photocrosslinkable paints (4), liquid crystalline display (5, 6), nonlinear optical materials (7, 8), tissue engineering (9, 10), biosensors (11), smart polymers responding to pH, temperature, and ionic strength (12), photo-orientation of mesoporous silica thin films (13), formation of polarization gratings and surface relief gratings (14), permseparation of water and ethanol by pervaporation (15).

Among various photocrosslinkable groups, α,β-unsaturated carbonyl unit has attracted particular attention due to its excellent photoreactivity at UV absorption wavelength (16–20). They possess properties of good solubility, ability to form films, high

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photosensitivity, and resistance towards solvents after crosslinking, etching agents and thermal stability. These properties in combination in a polymer are needed for practical use as negative photoresist material.

Polymers with cinnamoyl group either in the backbone or side chain undergo crosslinking through [2π + 2π] cycloaddition of the carbon-carbon double bond upon irradiation with UV light (21–24). Several polymers having photofunctional groups such as poly(vinyl cinnamate) (25), poly(vinylcyanocinnamoxy acetate) (26), poly (vinylcinnamoyl acetate) (27), phosphazenes based cinnamate photopolymers (28, 29), polysaccharides based on chondroitin sulfate (30), poly{11-[4-(3-ethoxycarbonyl-coumarin-7-oxy)-carbonylphenyloxy]-undecyl methacrylate} containing a coumarin moiety (31), spiroxazine polymer (32), poly(nonbornene derivatives) (33), polymers bearing pendant conjugated heterocyclic chromophores (34), polymers based on 4-[5-(4-hydroxyphenyl)-3-oxopenta-1,4-dienyl]phenyl-2-methacrylate (35), copolymers of 4-methacryloyloxy phenyl-3′,4′-dimethoxystyryl ketone (36) copolymers based on 4-acryloyloxyphenyl-3′-chlorostyryl ketone (37) polymers with bis(benzylidene) cyclohexanone unit (38) methacrylate polymer comprising 2-cinnamoyloxyethoxy biphenyl side group (39) poly(2-trimethylsilyl-2-propyl methacrylate) (40) have been reported. In continuation of our earlier reports on photocrosslinkable acrylamide polymers containing bromo (41), N, N dimethylamino and benzo substituted chalcone moiety (42) we report the synthesis, characterization, thermal stability and photocrosslinking properties of a methacrylamide based photocrosslinkable polymer, poly(4-methacrylamidophenyl)-1-(4-nitrophenyl) prop-1-en-3-one). The methacrylamide polymers were found to be more photosensitive than the acrylate or methacrylate polymers. The introduction of electron withdrawing nitro group would increase the thermal stability of the polymers. The work was also carried out to see the effect of nitro group on the photocrosslinking properties of the polymer. The effect of concentration of the polymer, solvent and triplet sensitizers on the photocrosslinking property of the polymer is also studied.

Experimental

Materials and Methods

4-Aminoacetophenone (SRL) and 4-nitrobenzaldehyde (SRL) were used as received. Benzoyl peroxide (BPO) was recrystallized from a 1:1 mixture of methanol and chloroform. Methacryloyl chloride was synthesized according to the method of Stampel et al. (43). All the other chemicals were distilled before use.

Synthesis of Chalcone

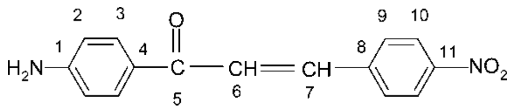
4-Nitrocinnamoylaniline (NCA) (1) was prepared by Claisen-Schmidt condensation of 4-nitrobenzaldehyde and 4-aminoacetophenone. 4-Amino acetophenone (7 g) in 50 ml of ethanol and a solution of sodium hydroxide (2 g) in distilled water (20 mL) was taken in a three-necked flask and the contents were cooled in an ice bath. 4-Nitrobenzaldehyde (7.8 g) dissolved in 40 ml of ethanol was added dropwise to the reaction mixture with constant stirring and cooling such that the temperature was not allowed to exceed 20°C. After the mixture was stirred for 24 h at room temperature, the precipitate was filtered and successfully washed with ice-cold water and cold alcohol. The crude product was recrystallized from ethyl acetate to obtain pure NCA. The yield of the product was 13.9 g (53%) m.p. 223–224°C.

The structure of NCA was confirmed by elemental analysis, FT-IR, ^{1}H-NMR, and ^{13}NMR spectroscopy.

Elemental analysis (%): C: 67.13 (Found), 67.16 (Calcd); H: 4.45(Found), 4.51 (Calcd); N: 10.38 (Found), 10.44 (Calcd).

FT-IR (KBr, cm^{-1}): 3485 and 3388 (N-H stretching); 3065 (=C-H stretching); 2925 and 2778 (C-H stretching); 1637 (>C=O); 1595 (olefinic >C=C <); 1508 (N-H bending); 1595 and 1441 (aromatic C=C stretching); 1341 (C-N stretching); 1230 (NO$_2$); 828 and 758 (=C-H out of plane bending); 669 (N-H wagging); 502 (C=C out of plane bending).

^{1}H-NMR (DMSO, ppm): ^{1}H-NMR (DMSO, ppm): 8.18–7.62 (m, 9H, Ar-H and =CH-Ar), 6.62–6.60 (d, 1H, -CO-CH=), 6.22 (s, 2H, NH$_2$).



^{13}C-NMR (DMSO, ppm): 186.26 (C$_5$), 155.11 (C$_1$), 148.52 (C$_{11}$), 142.66 (C$_7$), 139.47 (C$_8$), 132.27 (C$_3$), 130.28 (C$_9$), 127.51 (C$_4$), 125.87 (C$_6$), 124.72 (C$_{10}$), 113.65 (C$_2$).

Synthesis of Monomer

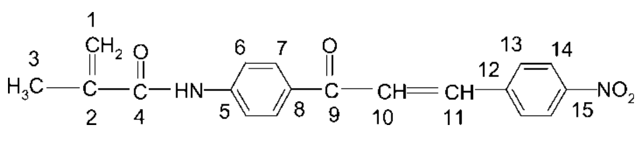
For the synthesis of 1-(4-methacrylamidophenyl)-1-(4-nitrophenyl)prop-1-en-3-one (MPNP) (2), methacryloyl chloride (2 g, 0.02 mol) in 40 ml of MEK was added dropwise with stirring to a mixture containing NCA (6 g, 0.02 mol), triethylamine (2.3 g) and methyl ethyl ketone (MEK) (250 ml) in a three necked flask and cooled between 0 and −5°C. Then, the reaction mixture was stirred for 2 h at room temperature and the precipitated quaternary ammonium salt was filtered off. Then, the solvent was removed using a rotary evaporator. The residue obtained was washed thoroughly with distilled water and then with cold ethanol. The crude product was recrystallized from ethyl acetate to obtain pure 1-(4-methacrylamidophenyl)-1-(4-nitrophenyl)prop-1-en-3-one; yield: 4.6 g (62%), m.p. 141°C.

The structure of MPNP was confirmed by elemental analysis, FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy.

Elemental analysis: ($C_{18}H_{14}N_2O_4$): C = 67.13 (Found), 67.16 (Calcd); H = 4.45 (Found), 4.51 (Calcd); N = 10.38 (Found), 10.44 (Calcd).

IR (KBr, cm^{-1}): FT-IR (KBr, cm^{-1}): 3485 and 3388 (N-H stretching); 3107 (=C-H stretching); 2925 and 2778 (C-H Stretching); 1637 (>C=O); 1595 (olefinic and aromatic >C=C <); 1508 (N-H bending); 1595 and 1441 (aromatic C=C stretching); 1341 (C-N stretching); 1230 (NO$_2$); 828 and 758 (=C-H out of plane bending); 669 (N-H wagging); 502 (C=C out of plane bending).

^{1}H-NMR (CDCl$_3$, ppm): ^{1}H-NMR (DMSO, ppm): 8.18–7.62 (m, 9H, Ar-H and =CH-Ar), 6.62–6.60 (d, 1H, -CO-CH=), 6.22 (s, 2H, NH$_2$).



^{13}C-NMR (DMSO, ppm): 188.11 (C_9), 166.64 (C_4), 151.65, (C_{15}), 141.69 (C_{11}), 141. 25 (C_5), 139.91 (C_{12}), 139.31(C_2), 131.33 (C_8), 130.15 (C_7), 128.75(C_{13}), 126.05 (C_{14}), 124.19 (C_{10}), 120.61 (C_1), 119.13 (C_6), 18.70 (C_3).

Synthesis of Polymer

The polymer, poly(1-(4-methacrylamidophenyl)-1-(4-nitrophenyl)prop-1-en-3-one), [poly(MPNP)] (3) was synthesized by free-radical polymerization of MPNP at 70°C as a 2M solution in MEK using BPO as the initiator. The reaction tube was purged with oxygen-free nitrogen gas for 25 min. The tube was tightly sealed and kept in a thermostat at 70°C. After 12 h, the polymer was precipitated by adding into the excess methanol, redissolved in MEK, reprecipitated by methanol, filtered, washed with methanol and dried *in vacuo* at 40°C. Yield was 46%.

Solubility Studies

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

Spectral Measurements

IR spectra were recorded on a Hitachi model 270–50 spectrophotometer using potassium bromide pellets. ^{1}H-NMR spectra were run on a JEOL 400 MHz spectrometer at room temperature using 15 wt% solutions in $CDCl_3$ and tetramethylsilane (TMS) as the internal standard. ^{13}C-NMR spectra were run on a Bruker 270 MHz spectrometer. Elemental analysis was performed with a Perkin-Elmer C-H analyzer. The UV spectrum of poly(MPNP) in chloroform was obtained on a U-2000 Hitachi spectrophotometer. Number and weight-average molecular weights ($\bar{M}_w$ and $\bar{M}_n$) and polydispersity index values were determined using a Waters 501 gel permeation chromatograph (three ultrastyragel 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 analyzer. TG traces were recorded on 10 mg samples at a heating rate of 10°C/min in air. The glass transition temperature was determined with a Perkin-Elmer DSC d7 differential scanning calorimeter (DSC) at a heating rate of 10°C/min using air as the purge gas. The thickness of the polymer film was measured using Sloan Dektak-3030 surface profile measuring equipment. An average of three readings were noted.

Photoreactivity Measurement

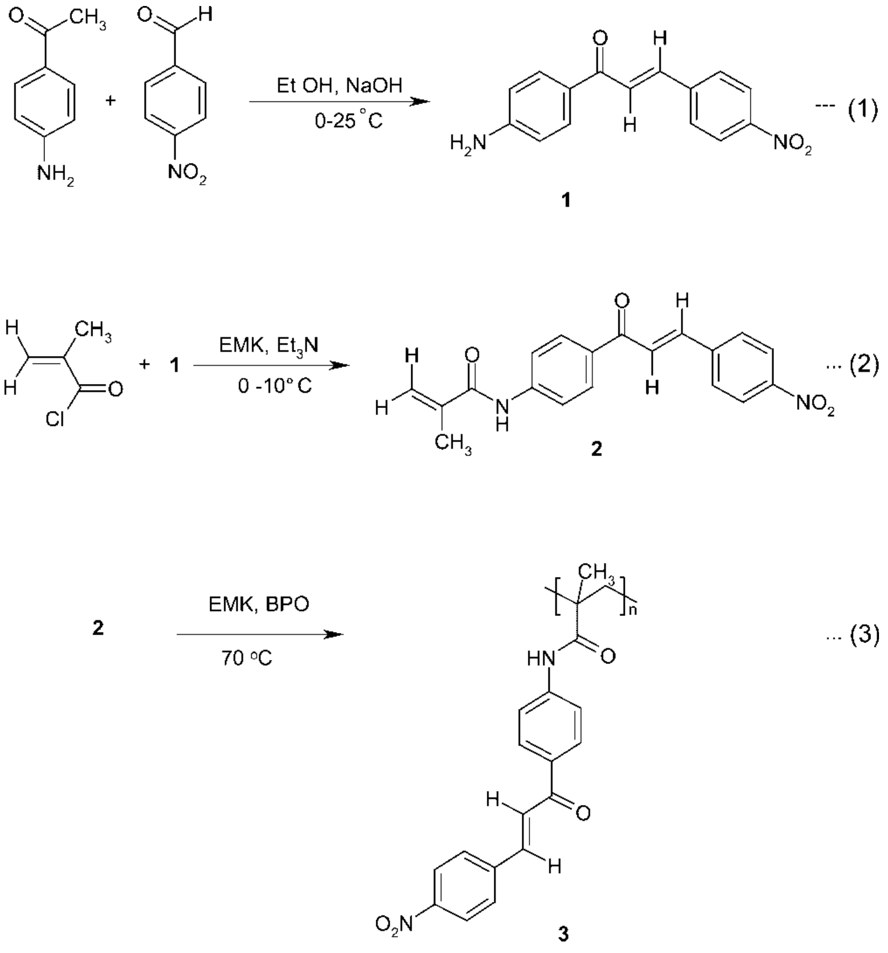
A thin film of the polymer, prepared from a 2% solution in chloroform and polymer in solution (45 mg/L) were irradiated in air with a medium pressure mercury lamp (Toshiba SHL-100 UV, 75 W frequency). The quartz plate coated with thin film of the polymer or the quartz cell containing the polymer solution (the path length of the cell was 1 cm) was kept at a distance of 10 cm from the UV lamp for different time intervals of irradiation. After each exposure, the UV spectra of the polymer film/solution were recorded on an UV-visible spectrophotometer. The extend of disappearance of the double bond in the reactive chalcone group was monitored according to equation (1):

$$\text{Extent of conversion}(\%) = \frac{(A_0 - A_T)}{(A_0 - A_\infty)} \times 100 \qquad (1)$$

Where A_0, A_T and A_∞ are the absorbance after irradiation time $t = 0$, $t = T$ and $t = \infty$, respectively.

Results and Discussion

4-Nitrocinnamoylaniline (1) and the photosensitive acrylamide monomer, 1-(4-methacrylamidophenyl)-1-(4-nitrophenyl) prop-1-en-3-one (**2**) were synthesized according to Scheme 1. Polymer **3**, poly(MPNP) was synthesized by free radical polymerization of **2** in MEK using BPO as a free radical initiator (Scheme 1).



Scheme 1. Synthesis of chalcone, monomer and homopolymer.

Characterization

Solubility. One of the important requirements for a photosensitive polymer is its solubility in different organic solvents. Polymer **3** (obtained after 14 h, 46% yield) is completely soluble in chlorinated solvents like chloroform, dichloromethane and chlorobenzene and polar aprotic solvents such as dimethyl formamide, dimethyl sulphoxide, 1,4-dioxane and tetrahydrofuran. The complete solubility indicates that the cinnamoyl double bond is not involved in crosslinking during polymerization. The polymer was insoluble in non-polar solvents such as benzene, toluene and xylene and hydroxy group containing solvents like methanol, ethanol, 2-propanol, water etc. The solubility of **3** is generally very low when the conversion is above 60%, which might be due to crosslinking. The infrared spectra of both the soluble and insoluble polymers 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 MEK as the solvent prove the presence of crosslinks in the insoluble polymer.

UV Spectrum

The UV spectrum of poly(MPNP) shows an absorption band at 340 nm due to the л-л* transition of the $>C{=}C<$ moiety of the pendant chalcone moiety.

IR Spectrum

The IR spectrum of poly(MPNP) is shown in Figure 1. It displays strong bands at 3426 cm^{-1} due to N-H stretching vibrations. An absorption band at 3097 cm^{-1} is due to the aromatic and olefinic $=$C-H stretching vibrations. The asymmetrical and symmetrical C-H stretching is observed at 2929, 2906 and 2881 cm^{-1}. The $>C{=}O$ stretching due to the keto and the amide group (amide band I) is observed at 1656 cm^{-1}. The amide band II due to the N-H bending is observed at 1519 cm^{-1}. Strong absorption at

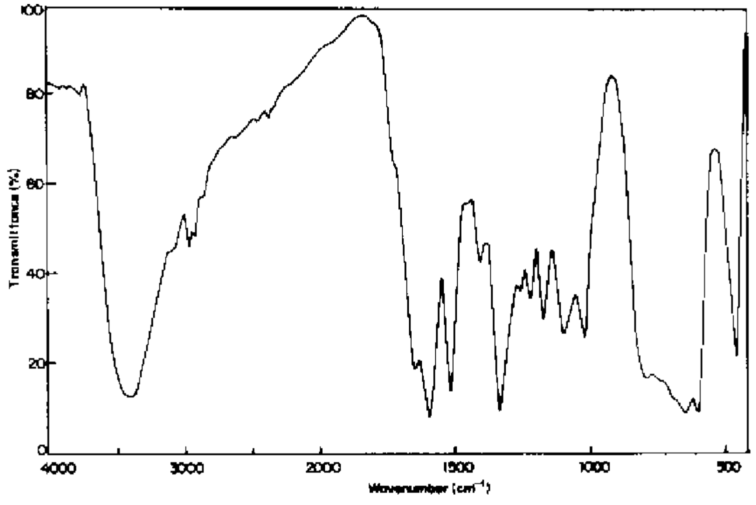


Figure 1. FT-IR Spectrum of poly(MPNP).

1599 cm^{-1} and 1410 cm^{-1} are due to C=C stretching of the olefinic and aromatic moiety, respectively. The peak at 1339 cm^{-1} is attributed to the C-N stretching. The peak at 1223 cm^{-1} is due to the nitro group. The absorption due to the aromatic C-H out of plane bending vibrations is observed at 836 and 788 cm^{-1}. The peak at 652 cm^{-1} is due to the out of plane NH wagging.

^{1}H-NMR Spectrum

The ^{1}H-NMR spectrum of the poly(MPNP) is shown in Figure 2. It shows multiple resonance signals at 8.73–7.26 ppm. The signals due to NH and olefinic protons of the pendant group are overlapped with that of aromatic protons. The backbone methylene proton signal is observed at 2.09 ppm. The peak due to the α-methyl group is observed at 1.20 ppm.

^{13}C-NMR Spectroscopy

The ^{13}C-NMR chemical shift assignments are made from off-resonance decoupled spectra of the polymer (Figure 3). The resonance signals at 188.86 and 175.58 ppm are due to the ketone and amide carbonyl groups, respectively. The signals at 141.71 and 124.17 ppm are due the olefinic carbons attached to the aromatic ring and keto group, respectively. The resonances of aromatic carbon atoms are observed between 151.61 and 119.18 ppm. The signals at 54.23 and 46.04 ppm are due to backbone methylene and tertiary carbons, respectively. A series of peaks due to the α-methyl carbon at 18.69–18.74 suggests the existence of tacticity.

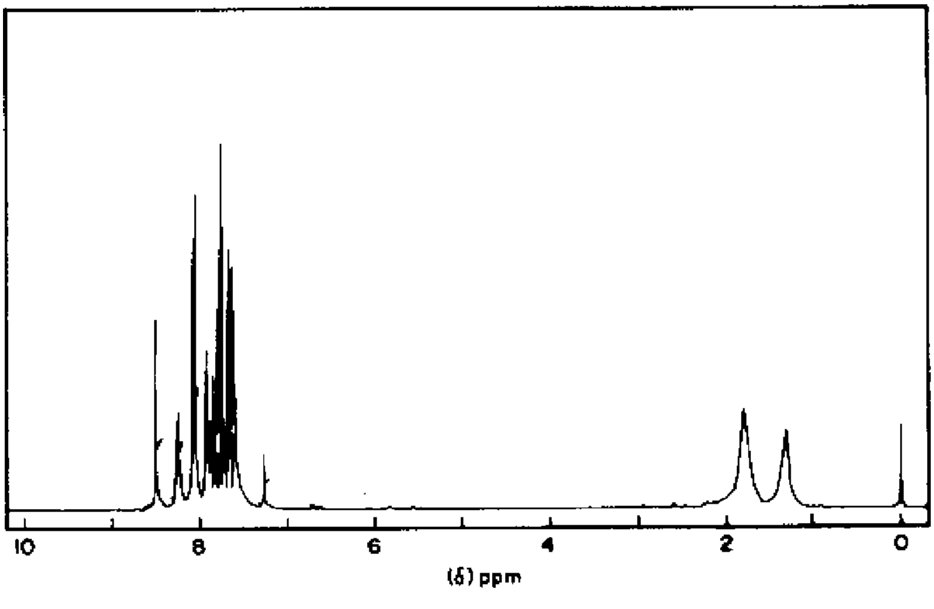


Figure 2. ^{1}H-NMR Spectrum of poly(MPNP).

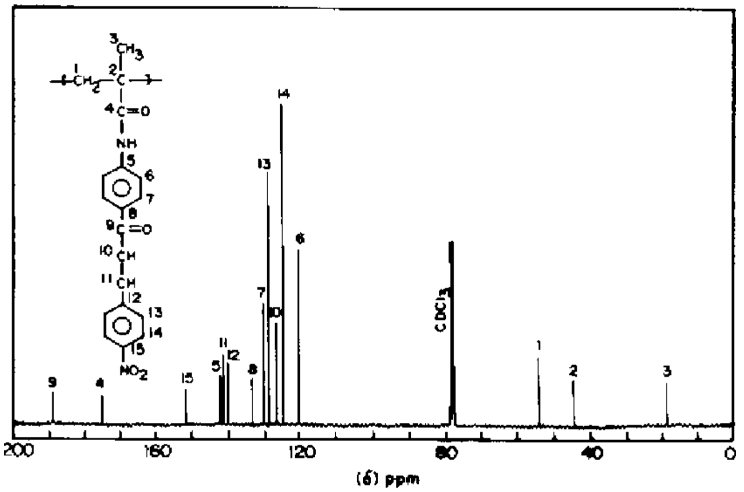


Figure 3. ^{13}C-NMR Spectrum of poly(MPNP).

Molecular Weights

Weight average ($\bar{M}_w$) and number average ($\bar{M}_n$) molecular weights of poly(MPNP) determined from gel permeation chromatography and are $\bar{M}_w = 6.31 \times 10^4$ and $\bar{M}_n = 3.25 \times 10^4$, respectively. The polydispersity index ($\bar{M}_w/\bar{M}_n$) for the polymer is 1.94. The theoretical values of $\bar{M}_w/\bar{M}_n$ for polymer produced via radical recombination and disproportionation are 1.5 and 2.0, respectively (44). The polydispersity index value of poly(MPNP) suggests that in homopolymerization of MPNP chain termination takes place mainly by disproportionation.

Thermal Properties

The TGA trace (Figure 4) of poly(MPNP) clearly shows that the decomposition of the polymer occurs in three stages. The initial decomposition temperature is 288°C, which indicates that polymer 3 has good thermal stability required for a negative photoresist. The first stage decomposition (288°C–348°C) may be attributed to the cleaving of the pendant group and the second stage (348°C–476°C) and the third stage (476°C–619°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 304, 326, 459, 541, and 592°C, respectively.

Glass transition temperature (T_g) of poly(MPNP) was determined by differential scanning calorimetry and was found to be 171°C. The higher T_g value for the polymer may be attributed to the α-methyl groups and the inflexible and bulky pendant chalcone units. The introduction of methyl groups into the backbone of the polymer would lead to more chain entanglement that would result in a high T_g value.

Photocrosslinking Properties

The thickness of the polymer film was measured as an average of three readings using a Sloan Dektak-3030 surface profile measuring equipment. The thickness of the film was roughly 1 μm. The photocrosslinking property of polymer **3** was studied in film, as well

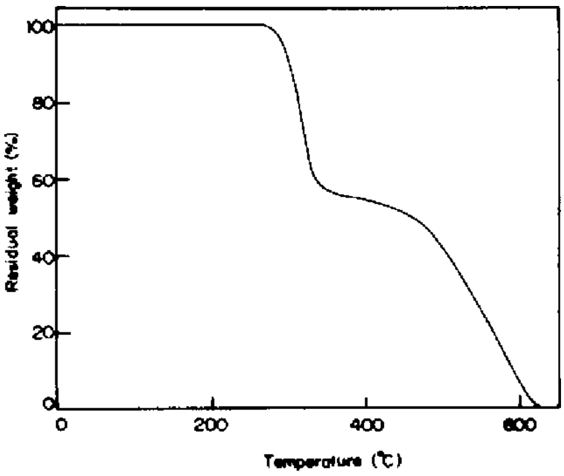


Figure 4. Thermogravimetric (TG) analysis of poly(MPNP).

as in a solution using chloroform ($CHCl_3$), 1,4-dioxane, tetrahydrofuran (THF), dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) as solvents with a concentration of 45 mg/L in the presence and absence of photosensitizers. The polymer film showed an UV absorption maximum at 340 nm due to the л-л* transitions of >C=C< of the pendant chalcone moiety. Figure 5 shows the UV spectrum of the polymer film before and after irradiation at different time intervals. For the polymer in thin film, photoconversions of about 33%, 50%, and 63% were observed after 240, 1000, and 2400s of irradiation time, respectively. It was found that even after a photoconversion of about 8%, which takes place within 30 sec of irradiation, the polymer film was rendered completely insoluble in chloroform with the help of which the original film was casted.

In the $CHCl_3$ solution, the polymer shows an UV absorption at 340 nm due to the л-л* transitions of >C=C< of the pendant chalcone moiety. Figure 6 shows the UV spectra of the

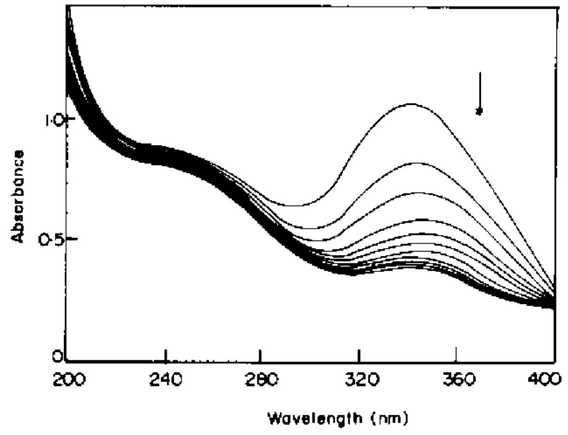


Figure 5. Changes in the UV spectral pattern of poly(MPNP) in chloroform solution upon irradiation. Top to bottom: irradiation times t = 0, 240, 1000, 2400, 2800, 3600, 4000, 5000, 5400, 6000, and 6000 s.

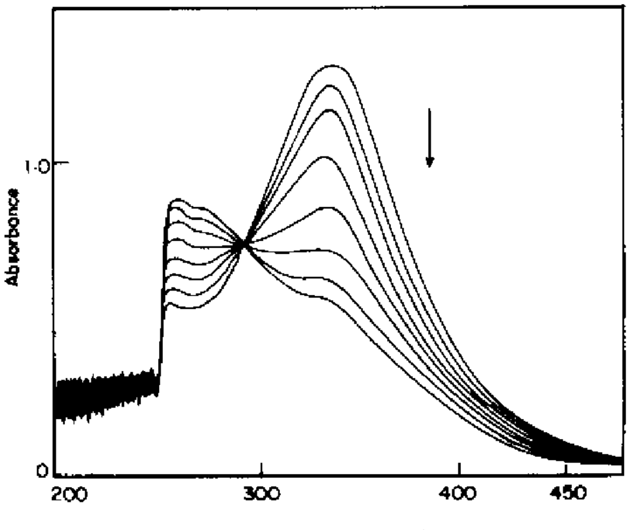
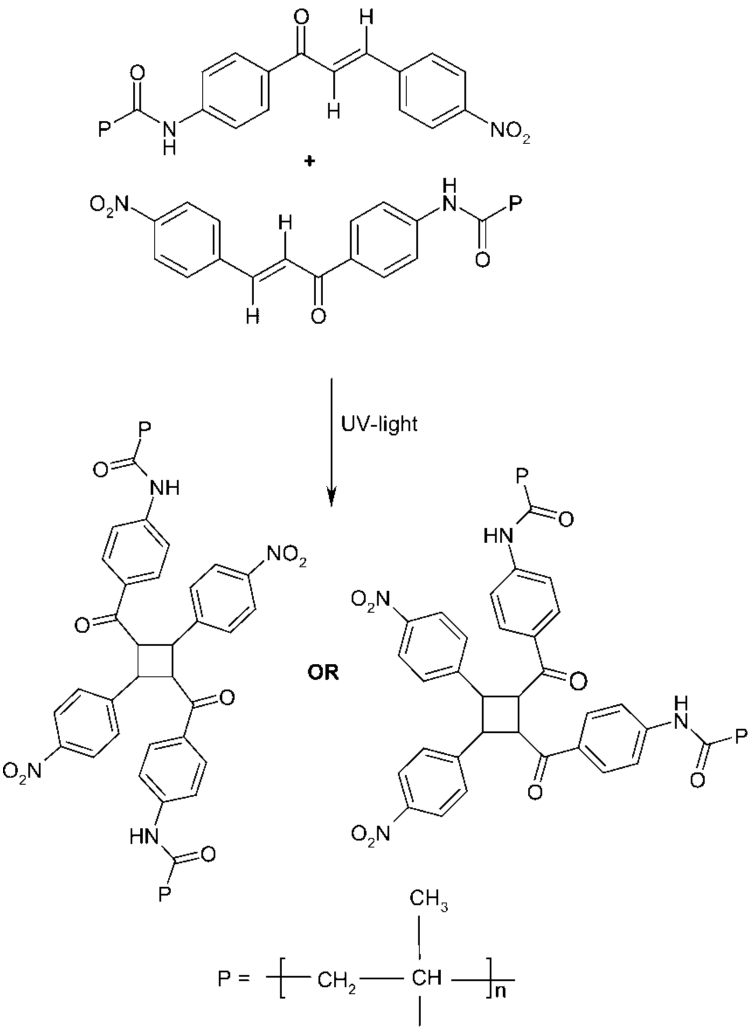


Figure 6. Changes in the UV spectral pattern of poly(MPNP) in chloroform solution upon irradiation. Top to bottom: irradiation times t = 0, 20, 300, 1200, 2000, 2700, 36000, and 4400 s.

polymer before and after irradiation at different time intervals. The >C=C< bond absorption decreases drastically upon irradiation. An isobestic point appears which can be attributed to the cis–trans isomerization of the pendant chalcone moiety. The decrease in the absorbance of the polymer film/solution at 340 nm on irradiation with UV light may be due to the disappearance of the chalcone double bond with the formation of a cyclobutane ring via [2 + 2] addition of the >C=C< bond (45) of the pendant chalcone units as shown in Scheme 2. This ring formation destroys the conjugated л-electron system and, hence results in a decrease in the UV absorption intensity. Thus polymer **3** responded to irradiation similarly as found for cinnamic acid and its derivative (46, 47).

The rate of photocrosslinking of polymer **3** was studied in terms of the rate of disappearance of the >C=C< group with irradiation time. The extent of crosslinking was evaluated by calculating the conversion of the photoreactive olefinic chromophore (-CH=CH-) using the equation (1). In $CHCl_3$ solution polymer 3 showed photoconversion of 8%, 14%, and 31% after 40, 76 and 300s of irradiation respectively and about 69% conversion occurred within 45 min of irradiation (Figure 6). However, when compared with the corresponding polymers containing para-methoxy, para-N,N dimethylamino and 2,3-benzosubstituted chalcone moiety (41, 42) the rate of disappearance of >C=C< of poly(MPNP) is very slow in the solution for the same time of irradiation. The electron withdrawing tendency of the -NO_2 group weakens the electron density of -CH=CH- double bond of the chalcone moiety through an extended conjugation and this is responsible for the lower crosslinking efficiency of poly(APNK). It was found that the initial rate of photocrosslinking of the polymer film was faster than that in the solution. This may be due to the close proximity of the polymer molecules in polymer film than in solution. However, the maximum percentage of crosslinking in the solution was greater than that in the film because in solution there can be proper alignment of the polymer molecules for crosslinking due to its ability to move. Such a movement is not possible in the polymer film. For the same reason, the polymer film does not exhibit any isobestic point on irradiation.



Scheme 2. Photocrosslinking reaction of the polymer.

When chloroform solutions of the polymers at higher concentration (520 mg/L) were irradiated for 1 h and the solvent was evaporated, the residue obtained was found to be insoluble in the organic solvent, in which the original polymers were easily soluble before irradiation. The FT-IR spectrum of the irradiated polymer shows the shifting of the carbonyl peak to a higher wavelength, 1695 cm^{-1} that is attributed to the loss of the extended conjugation (with olefinic and the para-nitrophenyl groups) after the photocrosslinking reactions. The decrease in the intensity of absorption peak at 1599 cm^{-1} after the photocrosslinking reactions is attributed to the disappearance of olefinic bonds of the chalcone moiety. These observations are an indirect proof for the formation of a cyclobutane ring after irradiation.

The effect of solvents on the rate of crosslinking of poly(MPNP) was studied. There is clear difference on the rate of disappearance of >C=C< of chalcone units in poly(MPNP) in various solvents such as chloroform, 1,4-dioxane, tetrahydrofuran, dimethylfarmamide and dimethylsulphoxide. The rates of crosslinking of poly(MPNP) in different solvents (Figure 7) are associated in the following order: $CHCl_3 > 1,4$-dioxane > THF > DMF > DMSO indicating that the type of solvents used also have a significant effect in the rate of photocrosslinking (48).

The effect of polymer concentration on the rate of photocrosslinking was studied in the chloroform solution with a concentration rage 21–166 mg/l. Figure 8 shows the results concerning the rate of disappearance of >C=C< of the chalcone units in the polymer **3**. It shows that the rate of crosslinking increases with an increase in concentration because of greater proximity of photoactive chalcone moieties in concentrated solutions (49).

The photocrosslinking reactions were are also carried out in the presence of various triplet sensitizers such as benzoin, benzophenone, etc., but they are not effective in increasing the sensitivity further. This behavior of the polymer **3** strongly indicates that the photocrosslinking might not be taking place through the triplet (T) state, but alternatively through singlet state electrons leading to a one-step, concerted [2 + 2] cycloaddition (50). Thus, the polymer **3** with a pendant chalcone moiety has a higher rate of photocrosslinking, even in the absence of sensitizers, leading to insolubility of the polymer upon irradiation. It is expected that this type of polymer might be useful as a negative photoresist for various applications.

Conclusions

A new methacrylamide based photocrosslinkable polymer was synthesized by free radical polymerization in solution using benzoyl peroxide as initiator. IR, ^{1}H-NMR and ^{13}C-NMR characterized 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 polymer **3** has good thermal stability required for a negative photoresist. The

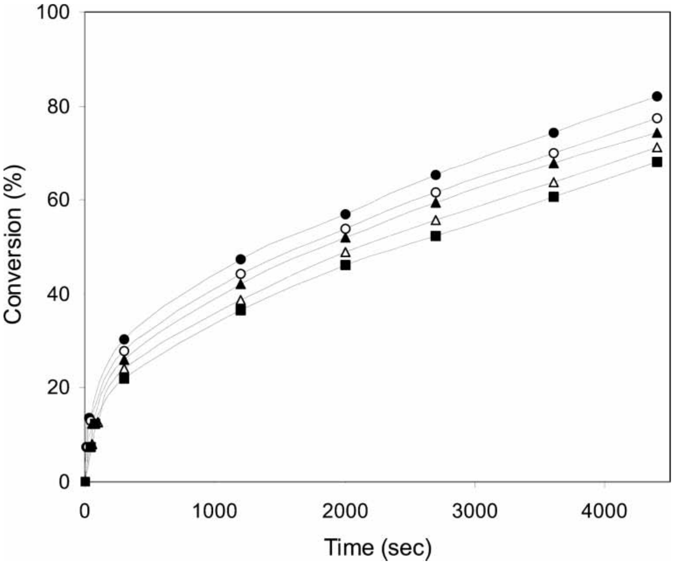


Figure 7. Rate of disappearance of >C=C< of the chalcone unit of poly(MPNP) with irradiation time in different solvents: (●) $CHCl_3$, (○) 1,4-dioxane, (▲) THF, (△) DMF and (■) DMSO.

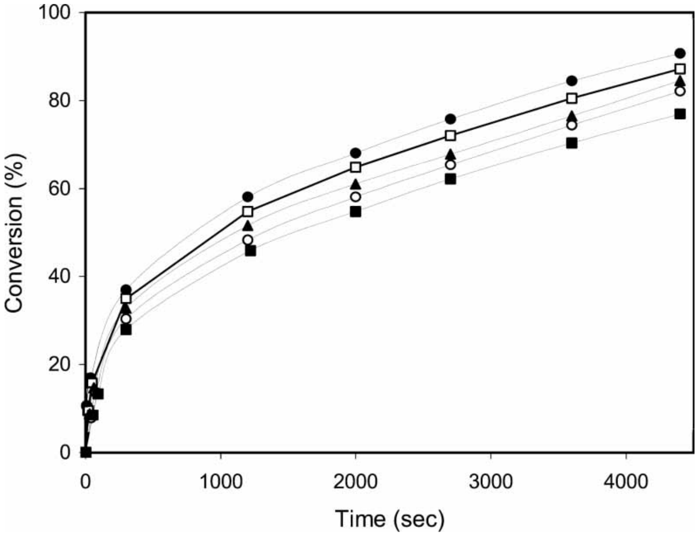


Figure 8. Rate of disappearance of >C=C< of the chalcone unit of poly(MPNP) in chloroform solution at different concentrations: (●) 166 mg l^{-1}; (□) 124.4 mg l^{-1}; (▲) 92 mg l^{-1}; (○) 45 mg l^{-1}; (■) 21 mg l^{-1}.

photocrosslinking behavior of the polymer tested in various solvents strongly suggests easy photoconversion of the photoactive groups during UV irradiation as required for a photopolymer. The initial rate of photocrosslinking of the polymer film was faster than that in solution. It was found that even after a photoconversion of about 8%, which takes place within 30 sec of irradiation, the polymer film was rendered completely insoluble in chloroform with the help of which the original film was casted. It was found that there was no enhanced rate of photocrosslinking of the polymer when irradiated in the presence of triplet sanitizers suggesting that the photocrosslinking might not be taking place through the triplet state, but alternatively through singlet state electrons leading to a one-step, concerted [2 + 2] cycloaddition. The overall property of the polymer suggests that it would be useful as a good negative photoresist for various applications. The copolymerization of monomer **2** with photosensitive monomers and vinyl monomers is under investigation.

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References

1. Reiser, A. (1989) *Photoreactive Polymers-The Science and Technology of Resists*, 2nd ed.; Wiley: New York.
2. Thompson, L.F., Wilson, C.G., and Bowden, M.J. (1994) Introduction to microlithography. *Am. Chem. Soc*. Washington, DC.
3. Tazuke, S. (1982) *Developments in Polymer Photochemistry*; Applied Science Publishers: London; Vol. 3.

4. Eiselé, G., Fouassier, J.P., and Reeb, R. (1999) *Die Angewandte Makromolekulare Chemie*, 264 (1): 10–20.
5. Kawatsuki, N., Fukumoto, H., Takeuchi, O., Furuso, N., and Yamamoto, T. (2004) *Polymer*, 45 (8): 2615–2621.
6. Kawatsuki, N., Tachibana, T., and Kamada, K. (2005) *Advanced Materials*, 17 (15): 1886–1890.
7. Zhang, L., Cai, Z., Yu, Z., and Liang, Z. (1999) *J. App. Polym. Sci.*, 71: 1081–1087.
8. Bagheri, M. and Entezami, A. (2002) *Eur. Polym. J.*, 38: 317–326.
9. Schmedlen, R.H., Masters, K.S., and West, J.L. (2002) *Biomaterials*, 23 (22): 4325–4332.
10. Mapili, G., Lu, Y., Chen, S., and Roy, K. (2005) *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, 75B (2): 414–424.
11. Tsafack, V.C., Marquette, C.A., Pizzolato, F., and Blum, L.J. (2000) *Biosens. Bioelectronics*, 15 (3–4): 125–133.
12. Szczubialka, K., Moczek, L., Blaszkiewicz, S., and Nowakowska, M. (2004) *J. Polym. Sci. Part A: Polym. Chem.*, 42 (15): 3879–3886.
13. Fukumoto, H., Nagano, S., Kawatsuki, N., and Seki, T. (2005) *Advanced Materials*, 17 (8): 1035–1039.
14. Kawatsuki, N., Hasegawa, T., Ono, H., and Tamoto, T. (2003) *Advanced Materials*, 15 (12): 991–994.
15. Hirotsu, T., Ichimura, K., Mizoguchi, K., and Nakamura, E. (1988) *J. App. Polym. Sci.*, 36 (8): 1717–1729.
16. Rehab, A. and Salahuddin, N. (1999) *Polymer*, 40 (9): 2197–2207.
17. Watanabe, S., Harashima, S., and Tsukada, N. (1986) *J. Polym. Sci. Part A: Polym. Chem.*, 24: 1227–1237.
18. Sierocka, M., Zakrzewski Lyk, B., Paczkowski, J., and Wrzyszczyski, A. (1984) *Polym. Photochem.*, 4: 207–210.
19. Achari, E.I. and Coqueret, X. (1997) *J. Polym. Sci. Part A: Polym Chem.*, 35: 2513–2520.
20. Lee, J., Kim, H., and Kim, H. (2001) *Bull. Korean Chem. Soc.*, 22 (2): 1006–10121.
21. Choi, D.H. and Cha, Y.K. (2002) *Bull. Korean Chem. Soc.*, 23 (3): 469–476.
22. Watanabe, S. and Kato, M. (1984) *J. Polym. Sci. Polym. Chem. Edn.*, 22: 2801–2808.
23. Feng, K., Tsushima, M., Matsumoto, T., and Kurosaki, T. (1998) *J. Polym. Sci. Part A: Polym. Chem.*, 36: 685–693.
24. Balaji, R. and Nanjundan, S. (2001) *Macromol. Rapid Communi.*, 22 (2): 1186–1190.
25. Minsk, L.M., Smith, J.G., Vandeusen, W.P., and Wright, J.F. (1959) *J. Appl. Polym. Sci.*, 2: 302–307.
26. Nishikubo, T., Ichijyo, T., and Takaoka, T. (1974) *J. Appl. Polym. Sci.*, 18: 2009–2013.
27. Uchida, T. and Sawada, S. (1988) *J. Photoplym. Sci. Technol.*, 1: 163–170.
28. Allcock, H.R. and Cameron, C.G. (1994) *Macromol.*, 27: 3125–3130.
29. Allcock, H.R. and Cameron, C.G. (1994) *Macromol.*, 27: 3131–3135.
30. Li, Q., Williams, C.G., Danny Sun, D.N., Wang, J., Leong, K., and Elisseeff, J.H. (2004) *Journal of Biomedical Materials Research Part A*, 68A (1): 28–33.
31. Tian, Y., Kong, N., Yu, N., and Iyoda, T. (2003) *J. Polym. Sci. Part A: Polym. Chem.*, 41 (14): 2197–2206.
32. Kim, S.-H., Ahn, C.-H., Keun, S.-R., and Koh, K. (2005) *Dyes and Pigments*, 65 (2): 179–182.
33. Rehab, A. (2003) *J. Mac. Sci., Part A, Pure and Appl. Chem.*, A (40): 687–703.
34. Fang, S.W., Timpe, H.J., and Gandini, A. (2002) *Polymer*, 43 (12): 3505–3510.
35. Arun, A. and Reddy, B.S.R. (2004) *Eur. Polym. J.*, 40 (3): 589–597.
36. Selvam, P., Victor Babu, K., Penlidis, A., and Nanjundan, S. (2005) *Eur. Polym. J.*, 41 (4): 831–841.
37. Balaji, R., Grande, D., and Nanjundan, S. (2004) *Polym. Int.*, 53 (11): 1735–1743.
38. Kishore, K. and Gangadhara. (1995) *Macromol.*, 28 (4): 806–815.
39. Kawatsuki, N., Matsuyoshi, K., Takatsuka, H., and Yamamoto, T. (2000) *Chem. Mater.*, 12 (6): 1549–1555.
40. Kim, J.B., Kim, H., and Choi, J.H. (1999) *Polymer*, 40 (6): 1617–1621.

41. Selvam, P. and Nanjundan, S. (2005) *React. Funct. Polym.*, 62 (2): 179–192.
42. Selvam, P., Victor Babu, K., and Nanjundan, S. (2005) *Eur. Polym. J.*, 41 (1): 35–45.
43. Stampel, G.H., Cross, R.P., and Mariella, R.P. (1950) *J. Am. Chem. Soc.*, 72: 2299–2301.
44. Teramachi, S., Hasegawa, A., Akatsuka, M., Yamashita, A., and Takemoto, N. (1978) *Macromol.*, 11 (6): 1206–1210.
45. Nishikudo, T., Iizawa, T., Yamada, M., and Tsuchiya, K. (1983) *J. Polym. Sci. Part A: Polym. Chem.*, 21: 2025–2028.
46. Watanabe, S. and Ichimura, K. (1982) *J. Polym. Sci. Polym. Chem. Edn.*, 20: 3261–3263.
47. Subramanian, K., Krishnasamy, V., Nanjundan, S., and Rami Reddy, A.V. (2000) *Polym. Int.*, 49: 579–584.
48. Balaji, R., Grande, D., and Nanjundan, S. (2004) *Polymer*, 45 (4): 1089–1099.
49. Egertpm, P.L., Pilts, E., and Reiser, A. (1981) *Macromol.*, 14: 95–100.
50. Anderson, T.F., Mecsick, V.B., and Pritchard, G. (eds.) *Developments in Reinforced Plastics 1: Resin Matrix Aspects*; Applied Science Publishers: London, 1980.