

A methacrylate monomer bearing nitro, aryl, and hydroxyl side groups: Homopolymerization, characterization, dielectric, and thermal degradation behaviors

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ABSTRACT: 2-Hydroxy-3-(4-nitrophenoxy)propyl methacrylate (HNPPMA) monomer was synthesized. The poly(HNPPMA) was prepared by free radical polymerization (FRP) method. The characterization of poly(HNPPMA) was carried out using FT-IR, NMR, differential scanning calorimetry, and GPC techniques. The thermal stability and degradation behavior of this polymer have been studied by using thermogravimetry (TG), GC-MS, NMR, and FT-IR. The results were in comparison to poly[2-hydroxy-3-(1-naphthoxy)propyl methacrylate] sample with α -naphthoxy side group prepared by the same method in the our previous study. The effect of thermal activation on non-isothermal decomposition kinetics of poly(HNPPMA) was investigated using thermogravimetric analysis according to Flynn-Wall-Ozawa method. The dielectric measurements of poly(HNPPMA) and doped with europium(III)chloride (EuCl_3) were investigated by impedance analyzer technique in range of 10–4000 Hz frequency by depending on the alternating current conductivities. The mode of thermal degradation including formation of the main products of poly(HNPPMA) degraded from ambient temperature to 500 °C was identified. S° , the cold ring fraction (CRF) was collected from room temperature to 500 °C. The structure of the degradation products has also been studied depending on the GC-MS analysis. The thermal degradation mechanism for poly(HNPPMA) with radical degradation processes thought to dominate at high temperature was proposed based on GC/MS, NMR, FT-IR, and taking into account the new products and differences in stability. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43925.

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INTRODUCTION

Thermal degradation of functionalized polymers has been intensely studied in order to control the accessibility of polymers in solid and liquid states, increase the fire retardation properties, to secure the performance of a material over long periods of time under changeable environmental conditions and increase the commercial value and importance of these materials.^{1–3} The chemical structure of polymer having a reactive side group during degradation of polymer may change through intra- and interchain reaction of this side groups resulting in formation of cross-linking, depolymerization, cyclization structure, unsaturated end termination, and so on.^{4,5} The polymers and substances with various organic structures may participate as combustible material in case of fire or in the controlled combustion processes, resulting in toxic and corrosive gaseous products, harmful to the environment and for human health.⁶ Therefore, it is necessary to determine diversity and the composition of gases obtained by combustion. This is possible using

the TG/FT-IR/NMR/GC-MS analysis, which are methods much used lately.⁷ According to TG/FT-IR/NMR/GC-MS analysis, the results obtained are showing that the released compounds by thermal degradation are mainly water, carbon dioxide, carbon monoxide, saturated and unsaturated aliphatic hydrocarbons (linear and cyclic), anhydrides with ring, aldehydes, ketones, esters, and carboxylic acids.^{8,9} The investigation of product analysis and degradation kinetics is one of the most crucial methods for thermal behavior of a material.^{10,11} The mathematical modulations of conversion and decomposition rate and temperature can be related to kinetic study. Generally, kinetic deals with parameterization and measurement of the process rates, and thermal analysis are related with thermally stimulated processes.

In the recent years, and dielectric properties of polymers have been extensively investigated. From the perspective of developing electronic or optoelectronic application technologies, these materials incorporating other various materials also show

potential for electronic applications. Dielectric variability in polymers is because of electronic, molecular, ionic, and interfacial polarization. These properties are associated with the chemical and physical structure of the polymers. On the other hand, the surface morphology chemistry and morphology of the polymeric materials are important for technological applications. Polymer materials can be characterized by their electric parameters such as dielectric constant, which change with frequency.¹²

In this work, we synthesized a novel monomer 2-Hydroxy-3-(4-nitrophenoxy)propyl methacrylate (HNPPMA) and our investigation concentrates on synthesis of poly(HNPPMA), determining the dependency of activation energy on conversion by means of the model-free methods (Flynn–Wall–Ozawa analysis), and product determination during thermal degradation from ambient temperature to 500 °C. The thermal degradation behavior of poly(HNPPMA) has been determined by using FT-IR, GC-MS, and NMR. A mode of degradation, which accounts for the formation of observed degradation products has been formulated based on the results of thermogravimetric analysis (TGA), FT-IR, GC-MS, and NMR analyses. It has been investigated that the dielectric constant of residue polymer at 340 °C during thermal degradation of poly(HNPPMA). The dielectric constants of pure poly(HNPPMA) and those of doped with EuCl_3 were measured by comparison depending on frequency or temperature.

EXPERIMENTAL

Materials and Methods

1,2-Epoxy-3-(4-nitro phenoxy) propane, pyridine, and methacrylic acid were kindly supplied by Sigma-Aldrich and used as received. The AIBN used as initiator (2,2'-azobisisobutyronitrile) was crystallized within methanol–chloroform mixture. All of the other materials used were of analytical purity and used as received commercially.

Synthesis of HNPPMA Monomer

The HNPPMA was prepared from reaction of 1,2-epoxy-3-(4-nitro phenoxy)propane with methacrylic acid in presence of hydroquinone in accordance with the procedure given for the epoxy-carboxy reaction.¹³ For this purpose, the methacrylic acid (1.47 g, 0.017 mol) and pyridine (1 mL) was added to two-edged a flask. A solution of 1,2-epoxy-3-(4-nitro phenoxy)propane (3.32 g, 0.017 mol) in dry dioxane (25 mL) was slowly added over 30 min at room temperature and then, the solution was stirred for 22 h at 85 °C in presence of 1–2 ppm hydroquinone. The monomer was all washed with an aqueous solution of sodium hydroxide (5% by wt) for five times, and then it was washed with water until pH 7. After being dried within anhydrous MgSO_4 overnight and stored in refrigerator prior to use. The structure of HNPPMA synthesized was illustrated in Scheme 1. The some signals for structure of monomer are summarized following as:

FT-IR (ν_{max} , cm^{-1}): 3482 (O–H stretching), 1718 (C=O stretching), 1636 (C=C stretching), 1542 and 1342 (asymmetric and symmetric stretching for NO_2 group).

$^1\text{H-NMR}$ (CDCl_3 , δ ppm): 8.24 (2H, $\text{H}^{8,9}$ -ortho protons on the aromatic ring according to NO_2 group), 6.53 (2H, $\text{H}^{6,7}$ -

meta protons on the aromatic ring according to NO_2 group), 6.2 and 5.6 (2H, H^{2} -cis and trans protons on $\text{CH}_2=\text{C}$, respectively), 1.97 (3H, H^1 - CH_3 protons).

$^{13}\text{C-NMR}$ (CDCl_3 , δ ppm): 18.2 (C^1 - CH_3), 65.4, (C^5 - OCH_2 next to ester group), 163.5 (C^8 -ipso carbon on aromatic ring), 142.0 (C^{11} -ipso carbon next to NO_2 group), and 136.7 (C^3 - $\text{C}=\text{CCH}_3$), 167.7 (C^4 - $\text{C}=\text{O}$).

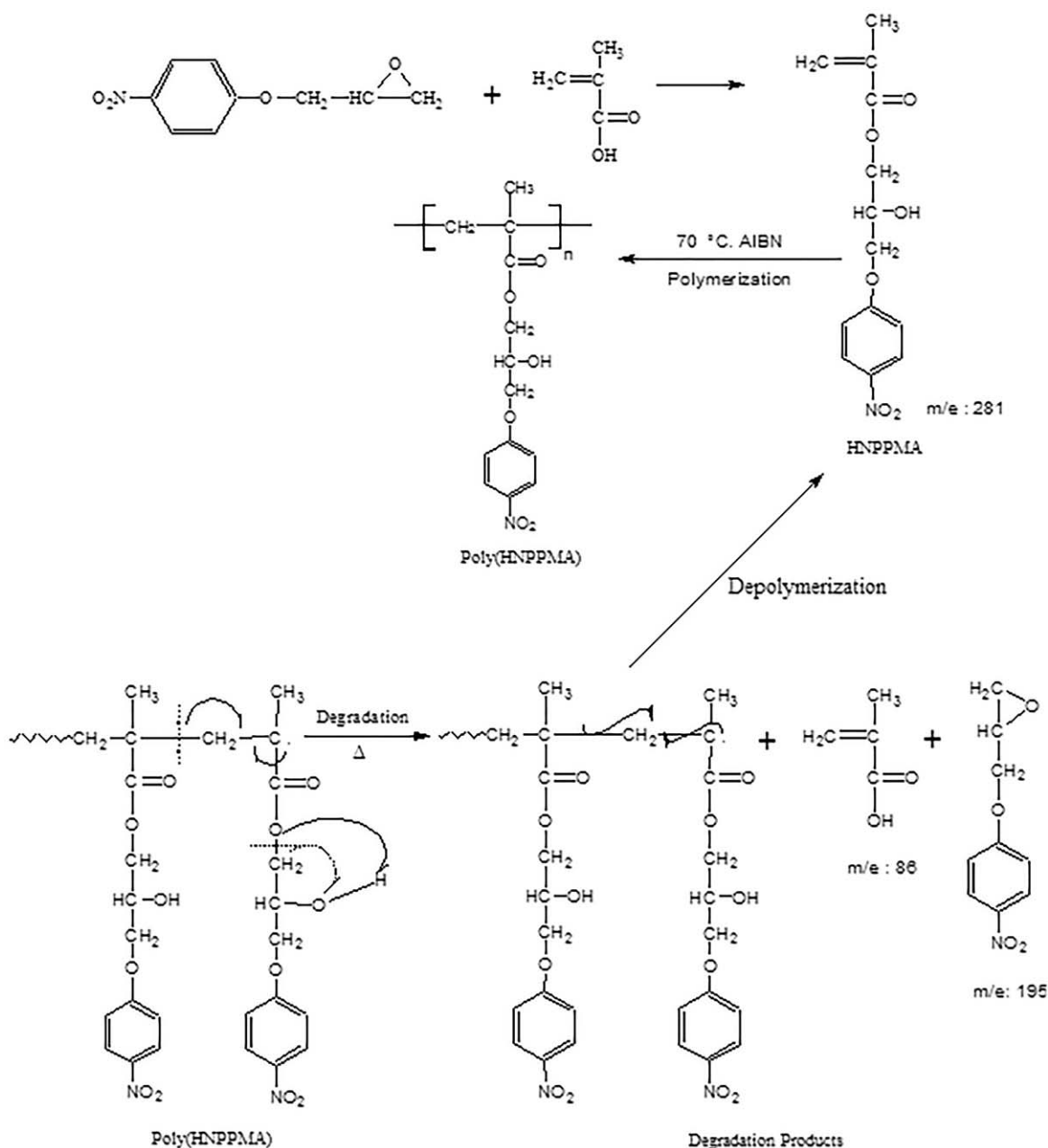
Characterization

The ^1H - ^{13}C -NMR and infrared spectra were carried out on an AVANCE III 400 MHz Bruker and on a Mattson 1000 FT-IR spectrometer, respectively. The infrared spectra of polymer and other products were recorded on NaCl windows. The TGA and differential scanning calorimetry (DSC) measurements of polymers were recorded using a Shimadzu TGA-50 (by heating rate of $10^\circ\text{C min}^{-1}$) and Shimadzu DSC-50 (by heating rate of $20^\circ\text{C min}^{-1}$) under a nitrogen flow, respectively. TGA measurements were carried out on approximately 5 mg samples at a heating rate of $10^\circ\text{C min}^{-1}$ under conditions of nitrogen flow ($10\text{ cm}^3\text{ min}^{-1}$). The GPC measurements were carried out using a silica gel column with an Agilent 1100 system having a refractive index detector by means of tetrahydrofuran (THF) as eluting solvent and the flow rate in 1 mL min^{-1} . The dielectric measurements of the polymer were carried out by sandwiching under four tons of pressure into disk-shaped. The measurements were recorded using a QuadTech 7600 LRC impedance analyzer between the frequency range 10–4000 Hz. The products of degradation formed to 500 °C were analyzed by GC-MS having Agilent Technologies 6890N Network GC System and Agilent Technologies 5973 Inert Mass Selective Detector.

RESULTS AND DISCUSSION

Structure Characterization

Poly(HNPPMA) was prepared according to FRP procedure in the presence of AIBN at 60 °C. The $^1\text{H-NMR}$ spectrum of monomer was illustrated in Figure 1(a), and it showed the important signals such as ortho protons aromatic ring according to NO_2 group at 8.21 ppm, meta protons aromatic ring according to NO_2 group at 7.01 ppm, at 6.17 and 5.64 ppm cis and trans protons on vinyl group, respectively, —OH proton at 2.84 ppm, CH_3 protons at 1.97 ppm. The $^{13}\text{C-NMR}$ spectrum of monomer was illustrated at Figure 1(b), and it showed the important signals at 18.23 ppm (CH_3), 65.44 ppm ($-\text{OCH}_2$ next to ester group), 163.57 ppm (ipso carbon on aromatic ring), 142 ppm ipso carbon next to NO_2 group), and 135.71 ppm ($\text{C}=\text{CCH}_3$), 167.79 ppm (ester $\text{C}=\text{O}$). The infrared spectrum of poly(HNPPMA) showed characteristic bands at 1728 cm^{-1} ($-\text{C}=\text{O}$ in ester), at 1550 and 1350 cm^{-1} ($-\text{NO}_2$ symmetrical stretching, $-\text{NO}_2$ asymmetrical stretching, respectively), 3435 cm^{-1} (O–H stretching). The $^1\text{H-NMR}$ spectrum of poly(HNPPMA) showed the most characteristic signals at 7.9–8.3 ppm (protons next to nitro group on aromatic ring), 6.8–7.3 ppm (protons next to ether group on aromatic ring), 4.3 ppm (CH_2 adjacent to ester oxygene). The $^{13}\text{C-NMR}$ spectrum of polymer showed the most characteristic signals at 177.0 ppm ($\text{C}=\text{O}$), 154 ppm (ipso carbon on aromatic ring), 44 ppm (quaternary carbon on main backbone). The number average-molecular weights of poly(HNPPMA) synthesized by FRP



Scheme 1. General synthetic procedures of HNPPMA monomer and poly(HNPPMA) and the formation mechanism of the epoxide and methacrylic acid structures begins at temp > 300°C during the degradation of poly(HNPPMA).

system is $18,800 \text{ g mol}^{-1}$ and its polydispersity (M_w/M_n) is 1.69. The PDI values of degraded polymer are decreased with increasing temperature. This phenomenon implies that a decrease in molecular weight of polymer is because of shorting length of the polymer chains. A DSC thermogram of poly(HNPPMA) was generated using a DSC-50. The measurements were carried out by sample amounts of about 5-6 mg under a nitrogen flow from room temperature to 200 °C by heating rate of 20 °C min^{-1} . The T_g 's of poly(HNPPMA) was taken as mid-point of transition region on DSC curve. The DSC curves of poly(HNPPMA) are displayed in Figure 2. The T_g of poly(HNPPMA) synthesized in this study is 110 °C. The T_g 's of some polymers having hydroxyl side group such as poly

(2-hydroxyethyl methacrylate) and poly(2-hydroxypropyl methacrylate) have been recorded as 100 °C and 95 °C in the literature, respectively.^{14,15} That T_g of poly(HNPPMA) is more high than that of PHEMA and PHPMA is because of an aromatic ring with rigid property containing nitro group. The glass transition temperature (T_g) of amorphous polymers is directly related with chain flexibility. It is characteristic for these polymers and this temperature (T_g) is a good way to understand the segmental mobility of polymer.

Dielectric Measurements of Poly(HNPPMA)

The dielectric properties are observed to be governed by dipolar polarization fully and interfacial polarization partially. So the

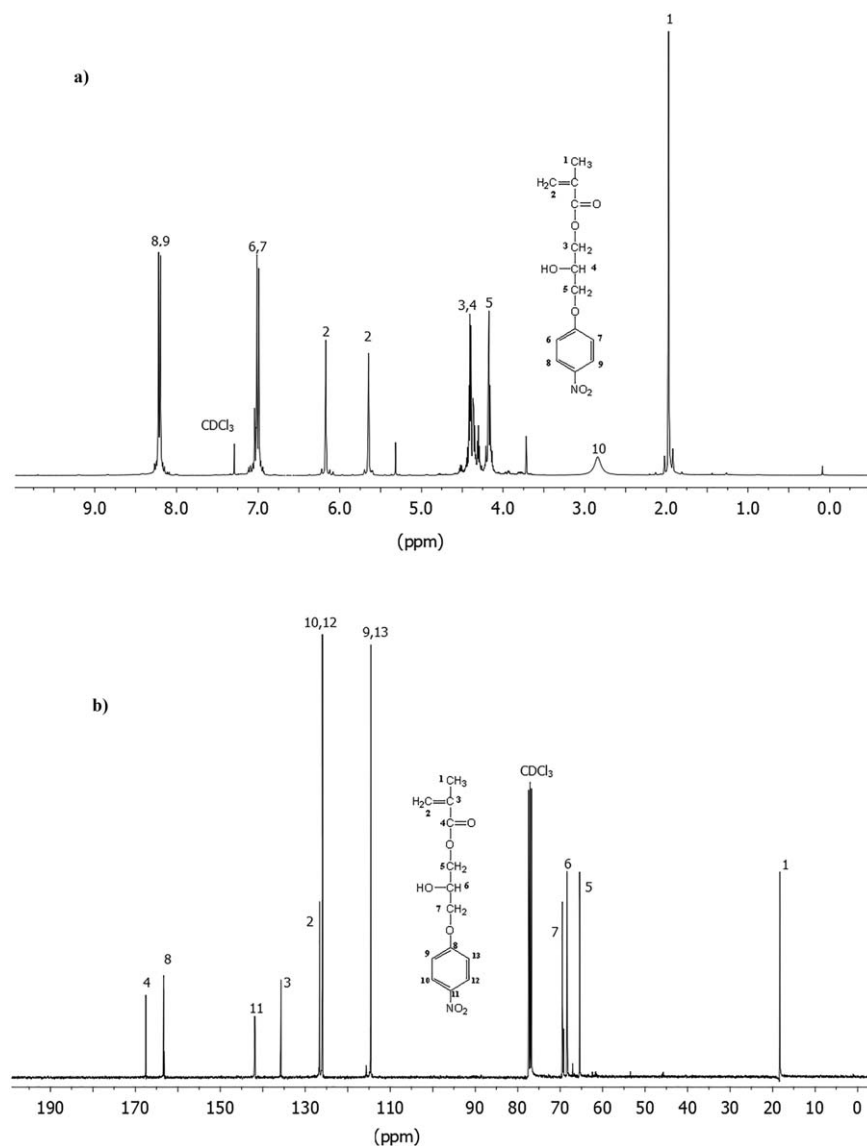


Figure 1. (a) ¹H NMR and (b) ¹³C-NMR spectra of monomer (HNPPMA).

effects of the thermal degradation on the dielectric constant for the poly(HNPPMA) is associated with their action on the polarization process. It is determined from parallel capacitance measurements by using an equation, which is $\epsilon' = C_p d / \epsilon_0 A$. Where,

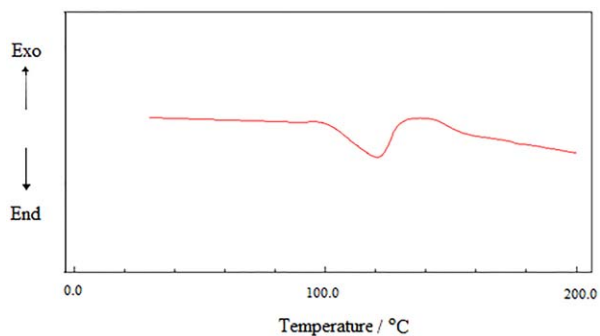


Figure 2. DSC curve of poly(HNPPMA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

C_p is parallel capacitance, ϵ_0 is the permittivity of free space ($\epsilon_0 = 8.85 \times 10^{-12}$ F/m), disc thickness of the polymer.¹⁶ The poly(HNPPMA) initiating to decomposition at 246 °C, as was summarized in Scheme 1 or others, is comprehensively changing its chemical structure with increasing temperature. The value of the dielectric constant increases with increase in temperature and it is a maximum at 340 °C at 1 kHz. The anhydride band given is maximum in polymer structure at 340 °C. Poly(HNPPMA) degraded becomes polarized when an electric field was imposed, and the amount of accumulated charge depends on the polarity of the polymer. The plot of dielectric constant versus frequency at room temperature and versus temperature at 1 kHz for polymer of residue are shown in Figure 3(a,b), respectively. The dielectric constant value of poly(HNPPMA) measured at room temperature is 5.66. When the temperature increased, the dielectric constant decreased to 1.76 at 673 K. Our results show that dielectric constant rises with increasing temperature and this increasing is greater at higher

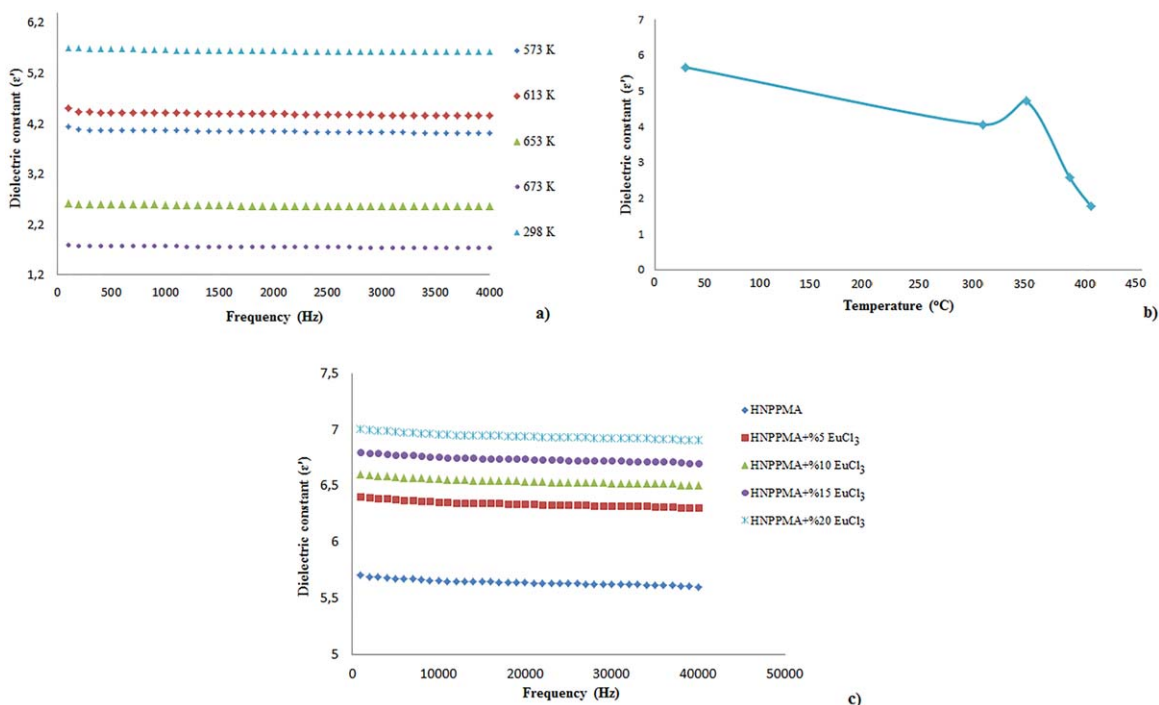


Figure 3. (a) The plot of dielectric constant versus frequency for poly(HNPPMA) at room temperature, (b) the plot of dielectric constant versus temperature for residue polymer at 1 kHz, and (c) the plot of dielectric constant versus frequency doped with EuCl_3 at different ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperatures. This conduct is a characteristic of the polar dielectric substances and the dielectric constant (ϵ') increased to enable orientation of the dipoles in the polar substance with increasing temperature. The increase of ϵ' with increase in temperature is generally associated with decrease in bond energies.¹⁷ While the ϵ' is increasing as temperature increases, it decreases depending on decomposition of polymer at progressive temperature. The effect of temperature may show two effects on the polarization of dipolar. The first effect, it weakens the intermolecular forces and hereby rises the orientational vibration. The second effect, it increases thermal mobility and therefore the orientational vibration strongly affects.¹⁸ The plot is showing a

maximum at 347 $^{\circ}\text{C}$ that anhydride band concentration is high. This means that increases the thermal agitation and strongly disturbs the orientational vibrations. Figure 3(c) shows the behavior of the dielectric constant with frequency at room temperature for pure poly(HNPPMA) and polymer composites doped with 5 wt % EuCl_3 , 10 wt % EuCl_3 , 15 wt % EuCl_3 , and 20 wt % EuCl_3 . Figure 3(c) reveals that are significant changes in dielectric constant of poly(HNPPMA) depending on doping EuCl_3 . So, the value of dielectric constant (ϵ') for composites with increasing dopant concentration was higher than that of pure poly(HNPPMA), and their dielectric constants were measured as 6.4, 6.6, 6.8, 7.0 depending on doping EuCl_3 at 1 kHz

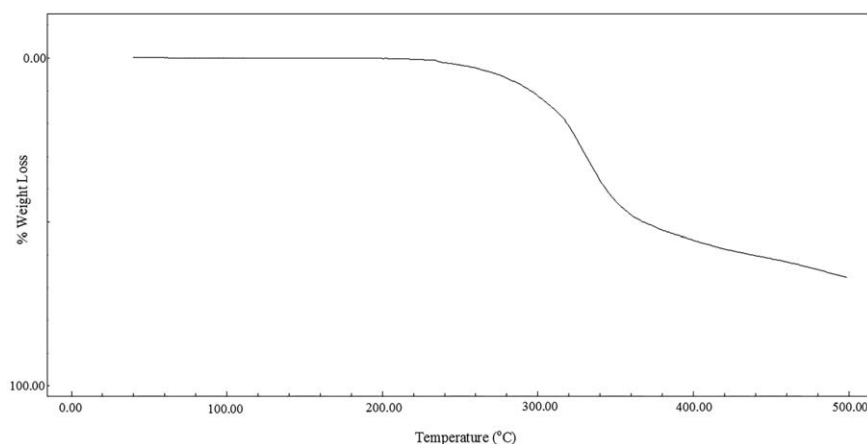


Figure 4. TG curve of poly(HNPPMA) heated at $10^{\circ}\text{C min}^{-1}$ under flow of argon gas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. TGA Data for Poly(HNPPMA) and Some Polymers Bearing Hydroxy Side Group as Compared

Polymer	IDT _a (°C)	T _{max} (°C)	Residue (%) at 340 (°C)	Residue (%) at 450 (°C)
Poly[HNPPMA]	246	378	63	37
Poly(NOPMA)	187	220 and 370	58	21
Poly(HPMA) [24]	196	275	15	7
Poly(HEMA) [25]	195	272	10	2

IDT: Initial decomposition temperature.

T_{max}: Temperature at maximum rate of decomposition.

for polymer composites, respectively. This behavior may find an interpretation in terms of mainly increasing number of dipoles which contribute to the polarization.

Thermogravimetric Measurements and Thermal Decomposition Kinetics

The thermogravimetric curve of poly(HNPPMA), which was obtained from ambient temperature to 500 °C at a heating rate of 10 °C min⁻¹ under nitrogen flow, has been given in Figure 4. The TG measurements were carried out by amount of 5 mg

constant samples. Under nitrogen flow, in comparison to the TGA curves revealed some differences in the mass loss and residue behavior of poly(HNPPMA), poly(2-hydroxyethyl methacrylate) [poly(HEMA)], poly(2-hydroxypropyl methacrylate) [poly(PHEMA)], and poly[(2-hydroxy,3-(1-naphtyloxy)propyl] methacrylate [poly(NOPMA)] for some polymers bearing hydroxyl side group. All the polymers appear to undergo only one significant mass loss step in an inert environment. The poly(HNPPMA) is thermally stable up to about 246 °C and gives 71% mass loss and occurs in a single step up to about 500 °C.

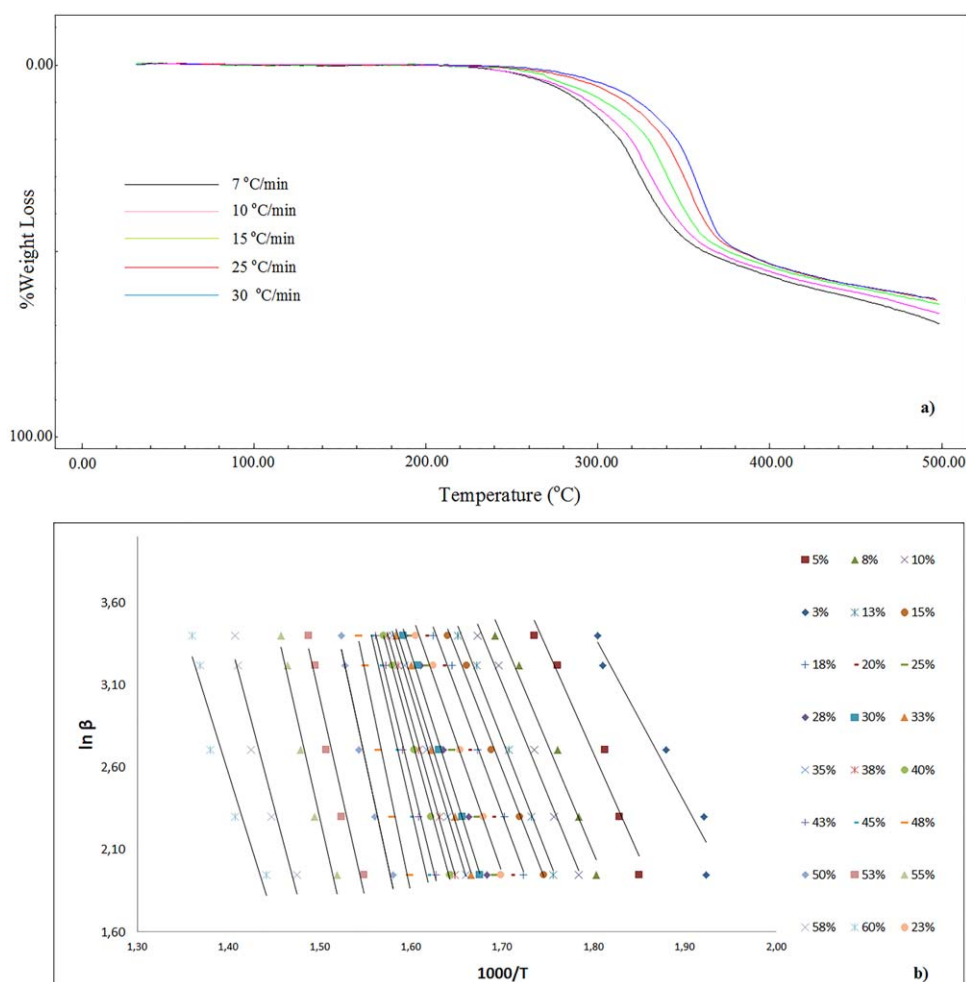


Figure 5. (a) TGA curves in different heating rates of poly(HNPPMA), (b) five experimental for alpha-temperature curves for the thermal decomposition of poly(HBPPMA) in nitrogen, obtained at different heating rates (7.0, 10.0, 15.0, 25, and 30 °C min⁻¹). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

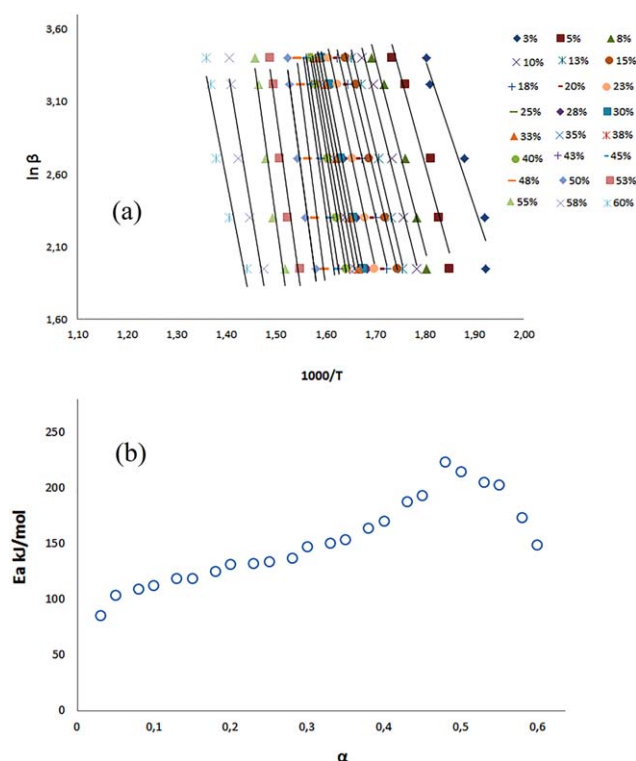


Figure 6. (a) The results of Flynn Wall Ozawa analysis ($\ln \beta$ versus $10^3/T$), (b) dependences $E-\alpha$ computed from the data simulated as a function of T for the decomposition of poly(HNPPMA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Whereas, the decomposition temperatures from TGA curves of poly(HEMA), poly(PHEMA), and poly(NOPMA) had been measured as 195 °C, 196 °C, and 187 °C, respectively. The major mass loss of poly(HNPPMA) occurs between 246 °C and 500 °C. A slowing mass loss follows a residue with 37% or 63% weight loss to 450 °C. The TG results of poly(HNPPMA) and those of the others are summarized in comparison with that of poly(HNPPMA) in Table I.

The effect of thermal activation on nonisothermal decomposition kinetics was investigated using TGA according to Flynn–Wall–Ozawa method. The weight loss versus temperature curves of dynamic thermal degradation of poly(HNPPMA) using heating rates at 7, 10, 15, 25, and 30 °C min⁻¹ were shown in Figure 5(a). The apparent activation energies (E_α) for the thermal decomposition of the polymers, which were calculated from the results of TG experiments, were determined by Flynn–Wall–Ozawa method widely used. In this study, the activation energy value was investigated by using TGA measurements and all measurements were performed according to literature.¹⁹ The variables, such as carrier gas and flow rate, the powder or solid form of samples directly affect these kinetic parameters. The results of Flynn–Wall–Ozawa analysis (curves of $\ln \beta$ versus $1/T$) obtained from a series of experiment performed at several heating rates for the conversion values, ranging from 3% to 60% were determined for poly(HNPPMA) and were shown in Figure 6(a). These results revealed that the straight lines are approximately parallel for different heating rates and different samples.

The E_a corresponding to the different conversions calculated from the slope of the lines are illustrated in Figure 6(a) for all samples. The isoconversional method of Flynn–Wall–Ozawa is a “model-free” method involves measuring the temperatures corresponding to fixed values of α from experimental at different heating rates, β , and plotting $\ln(\beta)$ against $1/T$.²⁰

$$\ln \beta = \ln \left(\frac{AE_a}{R \cdot g(\alpha)} \right) - 5.331 - 1.052 \frac{E_a}{R} \frac{1}{T} \quad (1)$$

The $-E_a/R$ determines the slopes of plots.

The curves ($\ln \beta$ versus $1/T$) obtained from a series of experiment performed at different heating rates should be a straight line whose slope allows evaluation of the activation energy:

Where β is the heating rate (°C min⁻¹) and R (8.314 J mol⁻¹K⁻¹) is a constant, the values of α have been determined from the TGA data as partial mass losses. According to eq. (1) above mentioned, the E_a (activation energy) of thermal decomposition can be calculated from the slope of the linear relationship between $\ln \beta$ and the reciprocal of the temperature, as was shown in Figure 6(a). The activation energy results were found for weight loss to %60. It should be mentioned that the dependence of E_α on α is a source of additional kinetic information of process.²¹ For this purpose, the curves of five experimental α –temperature for the decomposition of poly(HNPPMA) in nitrogen flow were obtained at different heating rates (7.0, 10.0, 15.0, 25.0, and 30 °C min⁻¹). The application of the advanced isoconversional method to the TGA data decomposition of P(HNPPMA) of results in obtaining the E_α dependencies was shown in Figure 6(b). The progress of degradation is accompanied by an increase in E_α that reaches a maximum at E_α around 225 kJ mol⁻¹, which gives a maximum to $\alpha=0.485$. But, E_α value decreases to 148.6 kJ mol⁻¹ at $\alpha=0.6$. In the P(HNPPMA) the plateau value is reached above $\alpha=0.2$. The occurrence of the decreasing E_a after $\alpha=0.485$ dependence clearly suggests that the examined anhydride cure follows multi-step kinetics. It should be given that E_a of degradation determined from mass loss in the thermogravimetric curves are based on mass loss and not on the individual products formed throughout degradation. The diversity of E_α versus transformation is an proof of the complicated degradation mechanism (likely parallel or consecutive reactions).^{22,23} The thermal degradation initiation temperature in polymer is decreased with the conversion values in the range of 3–60% increment. The kinetic model determines only one single activation energy, for the whole conversion range depending on formation of all degradation products. Therefore, the model-free methods (Flynn–Wall–Ozawa analysis) could be used for determining the dependency of activation energy on conversion.²⁴ Some sets of kinetic data on Thermal Analysis and Calorimetry (ICTAC) recommendations in 1996 had been recorded. One of them was record of α –temperature curves in nitrogen at different heating rates.²⁵ For this aim, the conversional curves (α – T) for nonisothermal decomposition of samples to be milled for nominal heating rates of 7.0, 10.0, 15.0, 25.0, and 30.0 °C min⁻¹ are indicated in Figure 5(b). As seen in Figure 5(b), these conversional curves exhibited the sigmoid profile, and by increasing heating rate, the curves shifted toward the higher temperature.

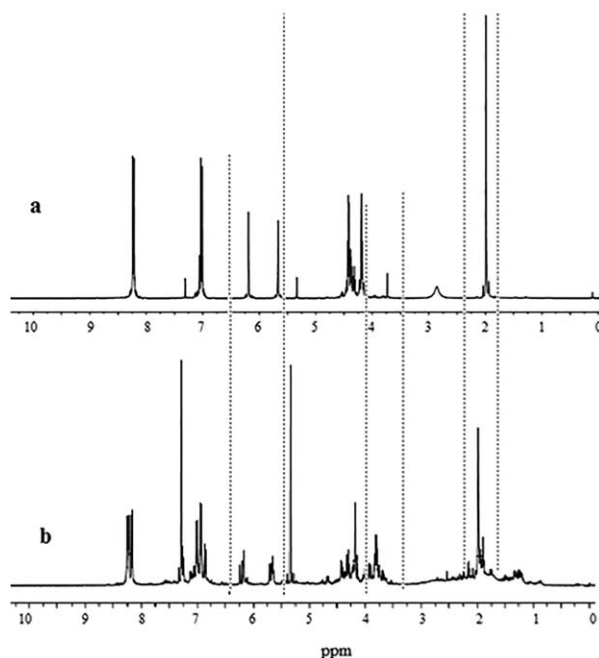


Figure 7. ^1H -NMR spectra of (a) monomer and (b) CRF product assignments of degradation.

As heating rate increases the conversion curve was shifted to a lower temperature range for an identical heating rate.

Product Identification Studies

The thermal degradation of poly(HNPPMA) in a glass ampoules tube having a condenser, product collection ring, and a vacuum pump, about 400 mg poly(HNPPMA) was degraded from room temperature to 500 °C. The cold ring fraction (CRF), which contains degradation products having high boiling point condensable at room temperature and resulted from degradation of the poly(HNPPMA) to 500 °C were consist of a mixture of a yellow colored liquid. The liquid mixture was dissolved in a number of other common laboratory solvents with success. The CRF was examined by ^1H -NMR, ^{13}C -NMR FT-IR spectroscopies, and GC-MS technique, and the changes of structural in the residue for the route of degradation were also investigated. Products of the most beneficial volatile characterized as result of degradation provide important information required to determine mechanism of degradation. The most volatile components can be trapped at -196°C for a trap containing the mixture of products in this fraction. The less volatile components can be characterized by techniques such as FT-IR, ^{13}C -NMR, ^1H -NMR, GC-MS methods. In most respects, these spectra are partially similar to original HNPPMA (monomer). The monomer is one of the major products of degradation. The cause of monomer formation rather than side group elimination at temperatures above initiation decomposition temperature is probably because of initiation at unsaturated chain ends.

The CRF of products obtained from thermal degradation of poly(HNPPMA) to 500 °C were investigated by the FT-IR, ^1H and ^{13}C -NMR. ^1H -NMR spectra of monomer and CRF were showed in Figure 7. ^1H -NMR (ppm): the signals at 5.65 (cis-proton according to $\text{C}=\text{O}$ in $\text{CH}_2=\text{C}$), 6.17 (trans proton according to $\text{C}=\text{O}$ in $\text{CH}_2=\text{C}$), 4.4 ($-\text{CH}_2\text{O}-$ adjacent to ester

oxygen), 1.97 ($=\text{CCH}_3$), 8.2 (ortho protons next NO_2 group on aromatic ring), 6.99 (meta protons next NO_2 group on aromatic ring) are characteristic for monomer structure. The peak intensities at 1.91 ppm ($\text{CH}_3-\text{C}=\text{C}$), 5.68, and 6.18 ppm ($\text{CH}_2=\text{C}$) are the important signals showing the presence of the monomer as the important product in the CRF. The CRF spectrum showed additional peaks at 3.5–4.0, 1.0–1.5, 5.6–6.2, and 6.8–7.3 ppm. The FT-IR and ^{13}C -NMR spectra of CRF are similar to that of original monomer in most respects as shown in Figure 7(a,b). The presence of O–H band at 3400 cm^{-1} in FT-IR spectrum of CRF illustrated in Figure 8(a) is an important evidence for formation of 4-nitrophenol as a result of side group elimination during degradation of poly(HNPPMA). The ^{13}C -NMR of CRF was illustrated in Figure 8(b) and the important signals were summarized in Table II. From characterization of CRF, HNPPMA (monomer) is exactly formed as a liquid product during the degradation of HNPPMA, but the presence of small amount implies that decomposition in the side groups is much more important. Table II displays the ^{13}C -NMR signals observed at analysis of the cold ring fraction with the general assignment for each resonance signal. The FT-IR, ^1H and ^{13}C -NMR results presented highlight the presence of a mixture of species within cold ring fraction containing ester, allyl, epoxide, ketone, phenol, and carboxyl functionalities. The GC-MS investigation of CRF showed that the major products was monomer about 19% by mole [m/e : 281, 195, 177, 143, (69, base peak)], 4-nitrophenol 24% by mole [157(M+), (139, base peak), 109, 93, 81, 65, 39]. The other product assignments of degradation were summarized in Table III. There is a distinct different in formation of monomer during degradation of poly(HNPPMA) in this study and that of poly(NOPMA) in our previous study.²⁶ That is, poly(HNPPMA) depolymerizes to about 19%, whereas poly(NOPMA) does not undergo any depolymerization. This phenomenon may be depended on that shows more acidic behavior

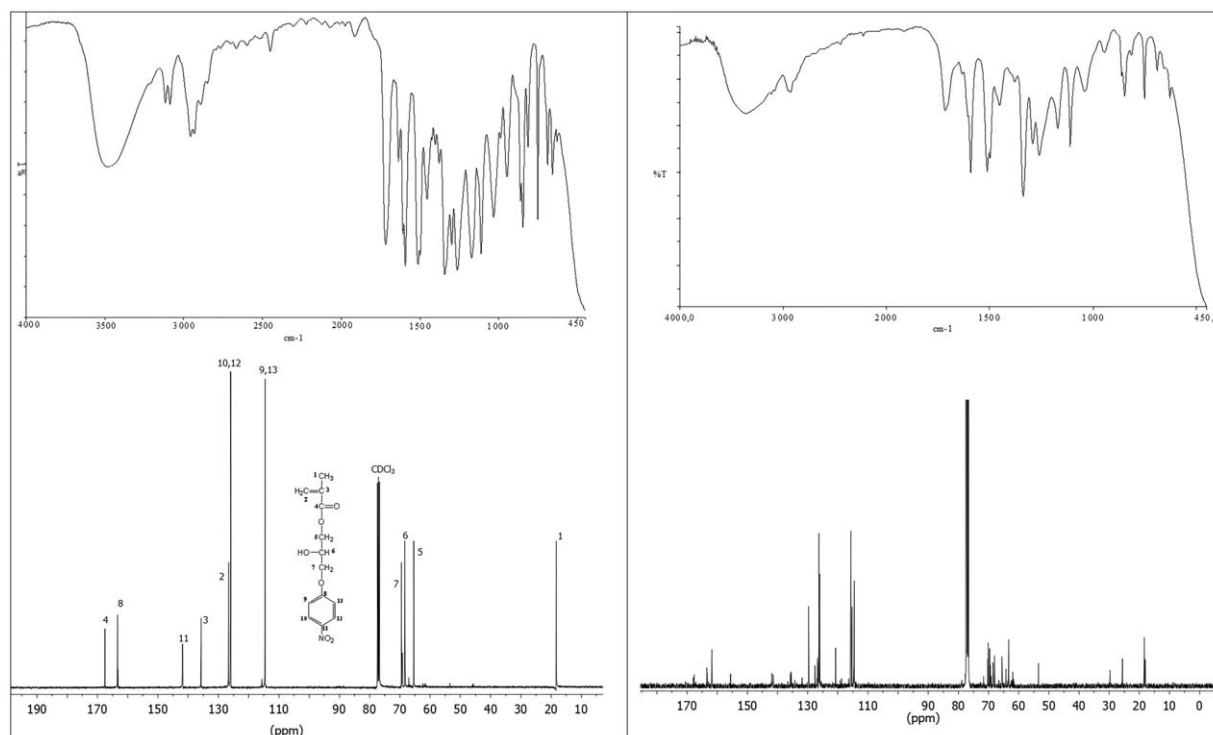


Figure 8. (a) FT-IR and (b) ^{13}C -NMR spectra of CRF product assignments of degradation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

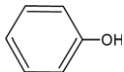
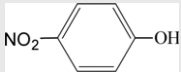
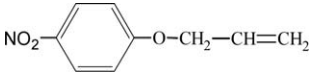
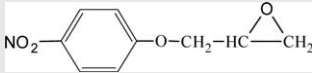
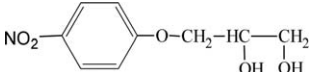
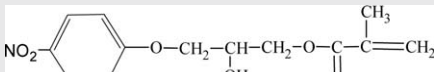
of proton on hydroxyl group because of the electron drawing NO_2 group on aromatic ring (Scheme 1). But, in case of poly[2-hydroxy,3-(1-naphthoxy)propyl] methacrylate, because α -naphthoxy group is a more basic group, α -naphthol forms by taking a proton from hydroxyl group and cannot be degraded to monomer.²⁶ The side group decomposition without main chain breaking can occur in various methacrylate ester polymers: for it to take place, H-abstraction from the carbon having hydrogen in the β position in the ester alkyl group

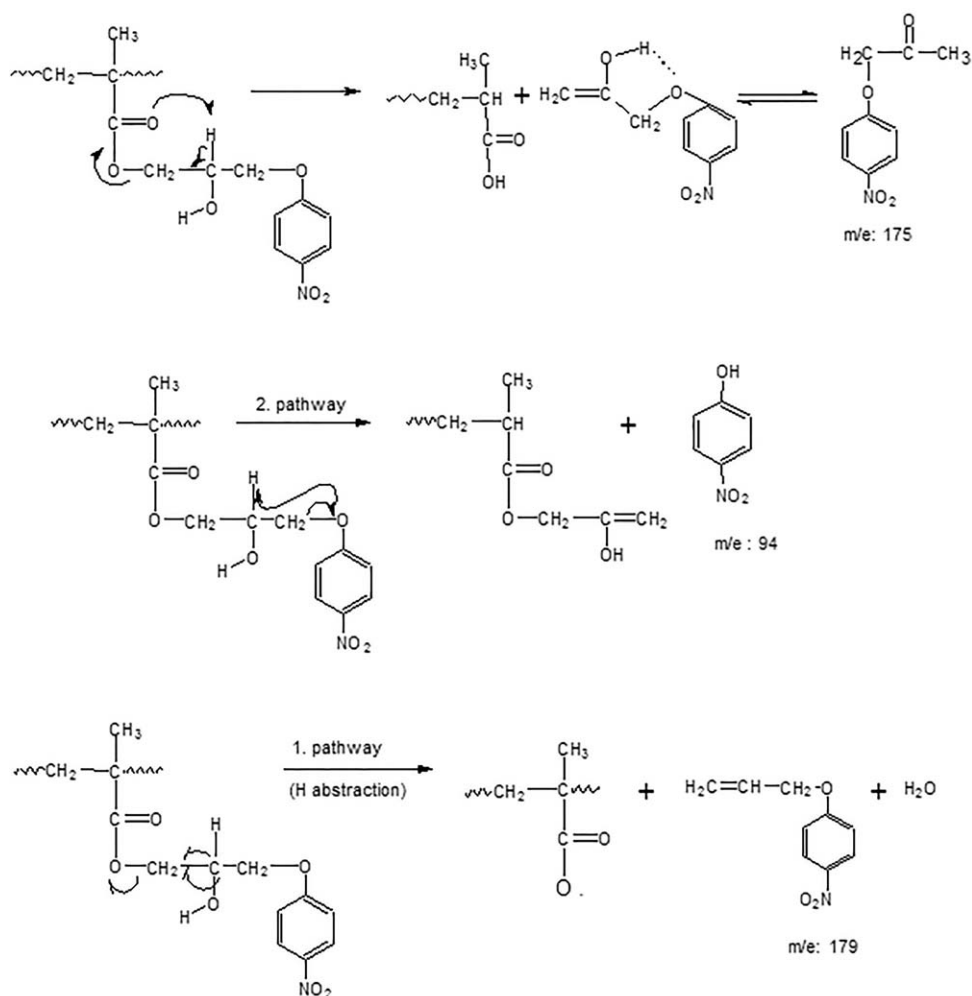
must be possible. The identification of products such as 4-nitrophenol, 3-(4-nitrophenoxy)propene, 3-(4-nitrophenoxy)-2-oxo propane and its tautomer analog in CRF shows side group decomposition without main chain breaking during degradation of poly(HNPPMA) as indicated in Scheme 2. The fragments, which result in elimination of side group are more abundant around 390°C . This phenomenon may find interpretation that thermal degradation by random chain scissions becomes more effective at high temperatures.

Table II. The Important ^{13}C -NMR Signals of CRF

^{13}C -NMR signals of CRFs δ (ppm)	Position of carbons
167,9; 167,4	C=O in various positions
163,2; 161,7	ipso carbon being adjacent to allyloxy carbon, characteristic for 4 numbered product in Table III
141,9; 141,1	ipso carbon adjacent to NO_2 group on aromatic ring
155,5	ipso carbon being adjacent to ether group, characteristic for 5 numbered product in Table III
135,6; 135,5; 125.; 124.0	Various olefinic carbons for allyl and vinyl groups
129,6; 114,6	sp^2 -hybridized carbons on aromatic ring
71,9-62,7	sp^3 -hybridized carbons adjacent to oxygen
53,0-35,0	CH, CH_2 in various positions
70,1-63,3	sp^3 -hybridized carbons adjacent to ether or alcohol oxygen
53,47	CH_2 adjacent to etheric oxygen
29,7; 25,6	CH, CH_2 in various positions
18,0-18,3	CH_3

Table III. Structure and Mass Spectra Results of CRF

GC peak No	Retention time/min	Degradation products	m/e of major peaks
1	3.9	CH ₃ COOH	41, 69, 86
2	8.2		39, 55, 66, 77, 94
3	27.2		31, 39, 46, 53, 66, 74, 81, 93, 109, 123, 139
4	27.8		41, 69, 154, 179
5	28.1		41, 69, 129, 142, 200
6	41.0		43, 61, 75, 93, 109, 123, 139, 153, 213
7	46.9		53, 41, 69, 87, 109, 0, 165, 250, 281
8	51.8	Unknown	342, 289, 211, 177, 152, 131, 107, 69, 41



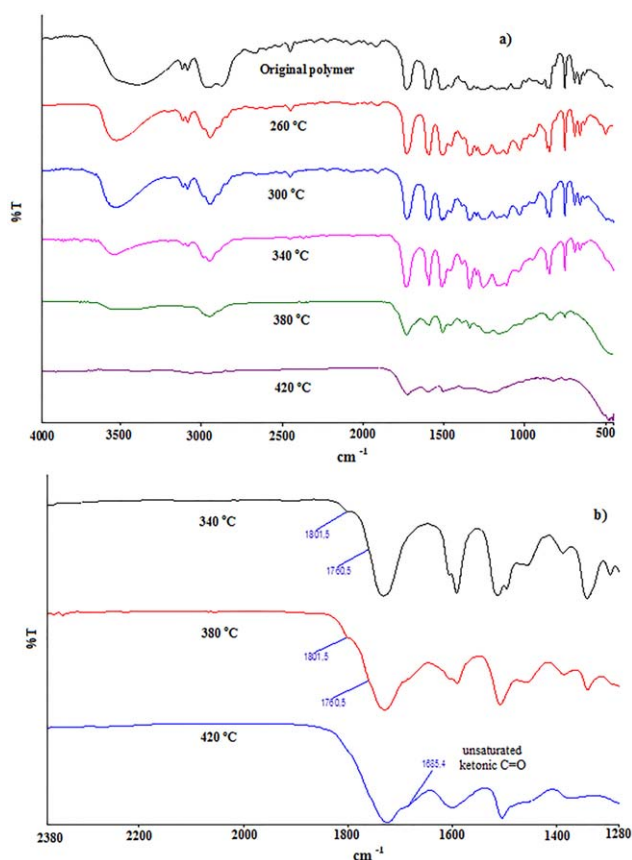


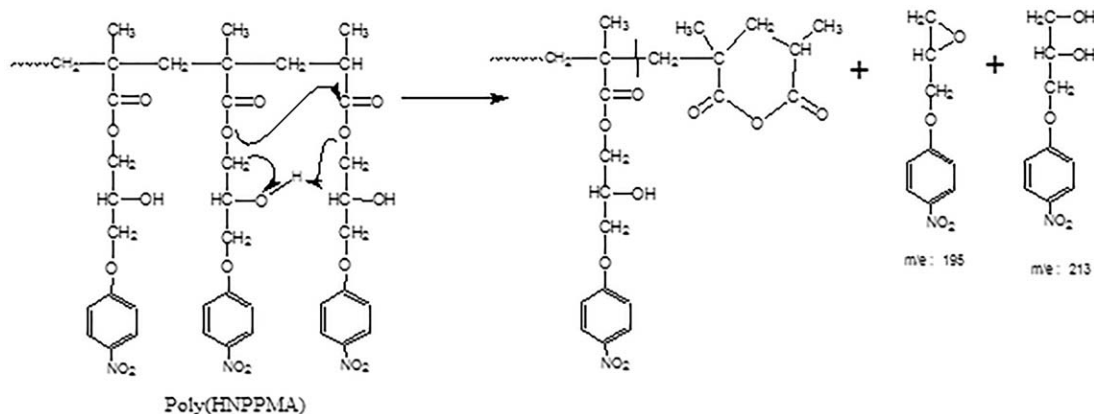
Figure 9. FT-IR spectra of residue at various temperatures during the degradation of poly(HNPPMA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The Mechanism of Degradation

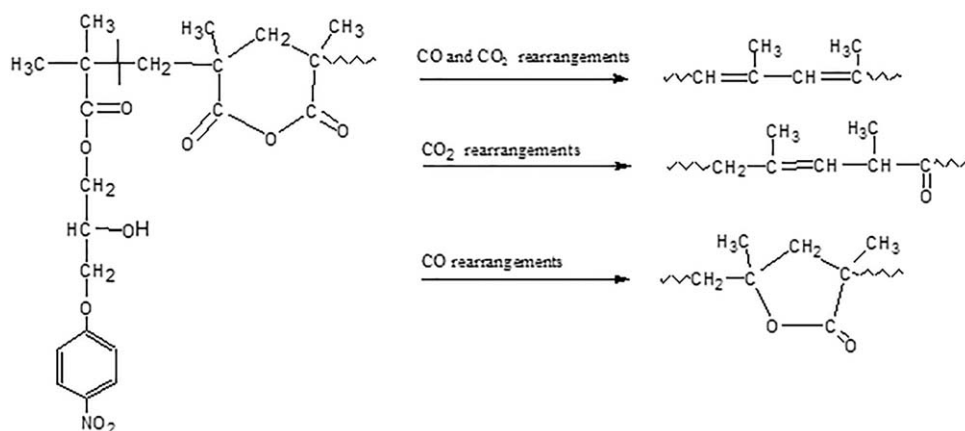
In the thermal degradation of poly(HNPPMA), there are two main patterns of breakdown consisting of depolymerization and side group reactions. The GC-MS and spectroscopic analysis on the CRF indicated that depolymerization was an important process in thermal degradation of poly(HNPPMA). An important evidence of the main chain breakdown or depolymerization is a decline in molecular weight with increasing temperature. So,

the number-average molecular weight of poly(HNPPMA) is 9300 g/mol. Whereas that of polymer heated to 260 °C is 4600 g/mol. Although TG of poly(HNPPMA) shows 8% weight loss to 300 °C, the FT-IR spectrum of the polymer heated at the same temperature is quite similar to that of original polymer as shown in Figure 9(a). During degradation of poly(HNPPMA) proceeds only depolymerization as a result of main chain breakdown up to 300 °C, and then it forms both depolymerization and substitution reactions (Scheme 3) leading to a more complex pattern of degradation. In general, the FRP of methacrylate monomers terminates with unsaturated ends, and these ends are known that are the weakest bonds of a polymer backbone. But the different end-groups may lead to different thermal behavior. Many researchers concur that the formed termination with disproportionate during polymerization and because of degradation of $-\text{CH}=\text{CH}_2$ group containing the unsaturated bonds at a lower temperature leads to instability at the ends of the polymer chains.

In the degradation of polymer, there are two main patterns of behavior, one of them is elimination of the side group, which is characteristic for formation of products such as water, 4-nitrophenol, 3-(4-nitrophenoxy)propene, the other is cyclization neighboring side groups with the elimination of a small molecule because of formation of a six-membered anhydride ring between methacrylic acid moieties and other repeating unit (Scheme 3). The formation of methacrylic acid and anhydride rings in the partially degraded polymer at 340 °C according to FT-IR spectra illustrated in Figure 9 have been observed, and the CRF indicates that an cyclization of side groups in adjacent moieties is also possible. A suggested route involving a six-center transition state is shown in Scheme 3. The partially degraded poly(HNPPMA) residue also showed increase in anhydride absorption bands at 1765 and 1801 cm^{-1} along with a progressive decrease in ester absorption. Those bands were maximum at 390 °C. Anhydride rings formed, however, reduce the zip length of depolymerization to monomer. Besides depolymerization, ester breakdown in side groups becomes more important with increasing temperature. The identical homolytic scission reactions are thought to occur during the thermal degradation of poly(HNPPMA) depending on the formation of degradation



Scheme 3. The formation mechanism of the cyclic anhydride, epoxide and diol structures begins at temp > 330 °C during the degradation of poly(HNPPMA).



Scheme 4. Formation of unsaturated ketone and lactone products by chain scission.

products having high molar mass such as 4-nitro phenol, methacrylic acid, 3-(4-nitrophenoxy) propene, 2-hydroxy-3-(4-nitrophenoxy)propyl methacrylate, 2-hydroxy-3-(4-nitrophenoxy)propane, 1,2-epoxy-3-(4-nitrophenoxy)propane, 1,2-dihydroxy-3-(4-nitrophenoxy)propane. A mechanism to account for the observed pattern of degradation products is displayed in Schemes 1–4. The mechanism summarizes the homolytic bond scissions likely to occur during the thermal degradation of poly(HNPPMA). The FT-IR results of partially degraded poly(HNPPMA) showed that were the important changes in carbonyl bands at 1801 and 1765 cm^{-1} after heating the polymer to 420 °C. Anhydride ring structures have been also found in many cases in the degradation of many homo- and co-polymethacrylate esters.^{27–31} Many polymethacrylates, polystyrenes and their derivatives undergoes scission to radicals which depropagate to monomer, if they do not bear a strained ring or an easily breaking group in their side chain.^{31,32} For example, poly(methyl methacrylate) is formed in almost 100% yield, polystyrene gives monomer 50% by weight, poly(2-hydroxypropyl methacrylate) gives monomer about 35% (to 300 °C).³⁴ The FT-IR, ¹H-NMR data all suggest that depoly-

merization does contribute significantly to degradation of poly(HNPPMA) to 320 °C. So, the main product during degradation of poly(HNPPMA) is monomer [HNPPMA]. The FT-IR, GC-MS and NMR data for all of degradation products suggest that degradation of poly(HNPPMA) up to high temperatures does generate monomer. This may be because of the absence of β -hydrogen atoms adjacent to the ester oxygen or CH next to OH in HNPPMA moieties.

Analysis of Residue

The GPC measurements of residue polymer by depending on two different temperatures (260 °C, 300 °C) were investigated. The GPC chromatograms of original poly(HNPPMA) and its residue polymer after heating to 260 °C, 300 °C was illustrated as comparison in Figure 10. The number-average molecular weight of poly(HNPPMA) was 9300 g/mol but that of heated to 300 °C was 4400 g/mol and its polydispersity was decreased to $M_w/M_n = 1.34$. The residue polymer heated to this temperature was dissolved in most of the common organic solvents. Dissolution of the residue polymer until this temperature is one of the

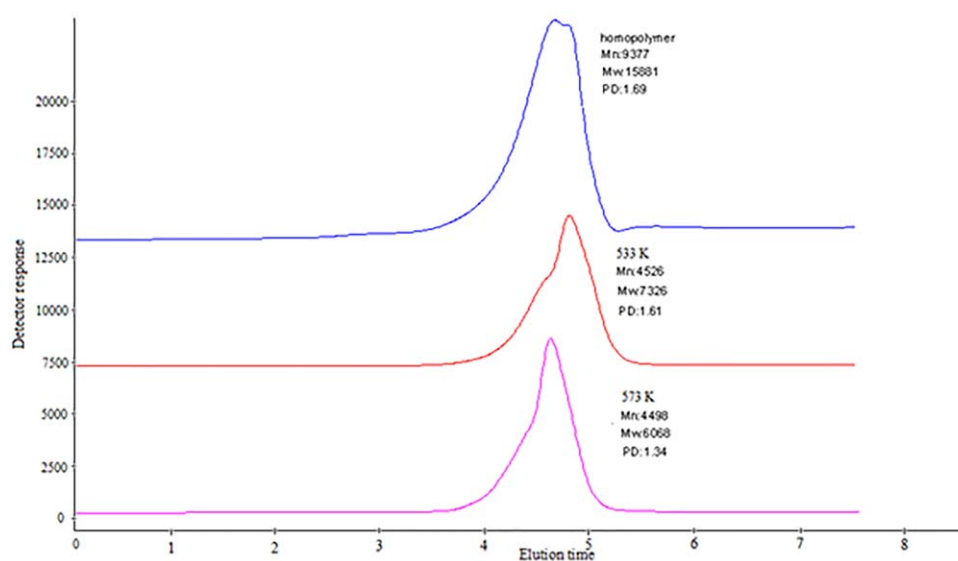


Figure 10. GPC chromatograms of original poly(HNPPMA) and its residue polymer after heating to 260 °C, 300 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

important evidences for depolymerization. But when the temperature increases the residue polymer either partially dissolves or do not dissolve in the laboratory common solvents. This phenomenon shows that degradation reactions at high processing temperatures will occur. These decomposition reactions will lead to a drop in molar mass, loss of crucial polymer properties. The structural changes induced by partial degradation were examined by FT-IR spectroscopy. FT-IR spectra of residue recorded for each heating stages at 260 °C, 300 °C, 340 °C, 380 °C, and 420 °C temperatures during the degradation of poly(HNPPMA) were illustrated in Figure 9. Poly(HNPPMA) heated to 300 °C at 10 °C min⁻¹ produced a light yellow residue which was soluble in common organic solvents. But poly(HNPPMA) heated to 330 °C at 10 °C min⁻¹ was insoluble within any organic solvents and as the temperature increases polymer is produced to a light yellow residue. Poly(HNPPMA) degraded forms some complex structures by breakup of the polymer chain in the temperature region between 330 °C and 500 °C. The most complex processes at high temperature can be summarized reactions such as eliminating CO, CO₂, lactone ring forming, and ketone structures on the chain as was seen in Scheme 4. The C=O band, which is the characteristics for a five-membered lactone group appeared as a shoulder at 1778 cm⁻¹. The bands which characterize ester C=O (at 1727 cm⁻¹) and NO₂ groups (at 1511, 1592 cm⁻¹) are still observed as a band in low intensity. As illustrated in Figure 9, the FT-IR spectrum of the polymer degraded to 340 °C showed significantly peaks at 1026 cm⁻¹ (C—O stretching), 1765 cm⁻¹ (asymmetric C=O stretching), and 1801 cm⁻¹ (symmetric C=O stretching) of anhydride structures.^{33–35} The residue with a light yellow which was insoluble in common organic solvents produced cross-linked structures bearing anhydride functionality as was shown in Scheme 3.

The FT-IR spectrum of brown tar examined after heating the polymer to 420 °C was illustrated in Figure 9(b). As was illustrated in Figure 9(b), a new C=O peak was observed at 1685 cm⁻¹ with an overtone above 3382 cm⁻¹ and a band at 1160 cm⁻¹ which suggests the formation of an aliphatic ketone as the predominant carbonyl groups in the vicinity of unsaturation. The black residue after degradation to 500 °C showed new bands C=C between 1640 and 1560 cm⁻¹. These bands (1640 and 1560 cm⁻¹) observed according to FT-IR spectrum of residue at 500 °C mean that is significantly mass of carbonaceous residue remaining from the degradation of poly(HNPPMA).

CONCLUSIONS

The dielectric measurements of poly(HNPPMA) prepared by FRP method were measured by means of an impedance analyzer as a function of temperature and frequency. The value of the dielectric constant is a maximum at 340 °C at 1 kHz. The anhydride band given is maximum in polymer structure at 340 °C. The dielectric constants of pure poly(HNPPMA) and those of doped with EuCl₃ were observed that increased significantly with the increasing concentration of EuCl₃. The thermal degradation data of poly(HNPPMA) presented in this manuscript highlight different behavior in the degradation pathway. Also, poly(HNPPMA) has demonstrated partial similarity to that of

its methacrylate analogous with OH side group only undergo one major thermal decomposition pathway. This primary thermal degradation reaction is thought to be identical for poly(HNPPMA) prepared in this study and the other polymers involve depolymerization resulting in C—C bond scission in the polymer main backbone, scission of the ester bonds in the side group resulting in the formation of ketone, epoxide ring, carboxylic acid. Poly(HNPPMA) was found to be slightly more stable than those of poly(propyl methacrylate) with the other hydroxyl side group, and the presence of nitrophenyl group results in significant differences in product composition, although HNPPMA (monomer) and 3-(4-nitrophenoxy) propene remain the predominant products. The residue and CRF studies on the thermal degradation of poly(HNPPMA) up to 500 °C revealed that degradation was likely to proceed via radical-based degradation mechanism. The action of homolytic bond scission occurring in the polymer backbone throughout the temperature of decomposition accounts not only depolymerization reaction but the variety of additional degradation products detected by GC-MS. In the degradation of poly(HNPPMA), condensable volatile degradation species, formation of cyclic anhydride, depolymerization and ketone structures have been proposed as the dominant degradation. So, an identical reaction mechanism depending on formation of products has been suggested.

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