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Scientific paper

Synthesis, Characterization and Thermal Degradation Kinetics of a New Pyrazole Derived Methacrylate Polymer, Poly(1,3-Diphenyl-1H-Pyrazol-5-Yl Methacrylate)

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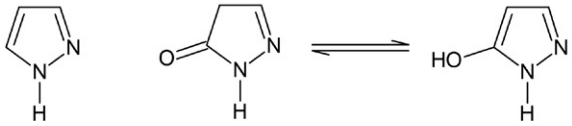
Abstract

Since the behavior and properties of macromolecular pyrazole derived polymers differ from their small molecules, such polymers are in the class of well-defined functional polymers due to the fact that the pyrazole ring contains two π-bonds as well as two hetero atoms in its structure, and this feature makes them important in the fields of scientific and technological applications. In present study, therefore, we synthesized a new pyrazole derived methacrylate monomer, 1,3-diphenyl-1H-pyrazol-5-yl methacrylate, from the reaction of 1,3-diphenyl-5-pyrazolone with methacryloyl chloride in the presence of triethylamine. After that, its homopolymerization was carried out by free radical polymerization method at 60 °C initiated with benzoyl peroxide. Spectral characterizations were achieved by ^{1}H-NMR and FTIR spectroscopies. The kinetics of thermal degradation of the new polymer, poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate), poly(DPPMA), were investigated by thermogravimetric analysis (TGA) at different heating rates. The initial decomposition temperature of the polymer changed from 216.3 °C to 243.5 °C depending on the increasing heating rate. The thermal decomposition activation energies in a conversion range of 7–19% were 79.45 kJ/mol and 81.56 kJ/mol by the Flynn–Wall–Ozawa and Kissinger methods, respectively. Thermodegradation mechanism of the poly(DPPMA) were investigated in detail by using different kinetic methods available in the literature such as Coats-Redfern, Tang, Madhusudanan and Van Krevelen. Among all these methods, the best result was obtained for Coats-Redfern method (E = 90.93 kJ/mol) at the optimum heating rate of 15 °C/min for D_1 mechanism that is a one-dimensional diffusion type deceleration mechanism.

Keywords: Pyrazole derived polymer; synthesis and characterization; thermal degradation kinetics; activation energy; reaction mechanism

1. Introduction

As is known, briefly, pyrazoles (or 1*H*-pyrazol) (1) are compounds in the class of heteroaromatic molecules containing two nitrogen atoms in the quintuple ring systems. When this five-membered lactam ring contains a ketonic group and two nitrogen atoms in its structure, it is called pyrazolone (or 1*H*-pyrazol-5(4*H*)-one) (2). There is also a tautomerization in the pyrazolone ring and, in that case, the resulting compound is named as pyrazolol (or 1*H*-pyrazol-5-ol) (3).[1,2]



(1) (2) (3)

The studies on the pyrazole/pyrazolones have gained importance recently, especially because of the broad pharmacological properties of these compounds. Some of these features are cytotoxic,[3] anti-inflammatory,[4] antimicrobial,[5] antioxidant,[6] antiviral,[7] oral hypoglycemic activity,[8] analgesic,[9] etc. In addition, these compounds are widely used in the preparation of herbicides,[10] liquid crystals,[11] dyes,[12] thermally stable polymers.[13,14] Since pyrazolones have different biochemical and physicochemical properties, new scientific research programs have been developed in the synthesis of these compounds.[1] In this context, pyrazolones are traditionally prepared from the reaction of beta-keto esters with hydrazine derivatives in an acidic environment at high temperatures.[15] In addition, the so-

lid-phase synthesis reaction,[16] two-step reaction of benzoyl hydrazones with silyl enolates in catalytic medium,[17] microwave synthesis method,[18] solvent-free medium reaction[14] are also available in literature.

Some of the features as above stated generally include the synthesis and application of these compounds in the form of small molecules. However, pyrazole/pyrazolone chemistry is also important for polymers. The behavior and properties of macromolecular pyrazole-derived polymers differ from these small molecules, and therefore, such polymers are in the class of well-defined functional polymers.[19] The most important factor causing this is that the pyrazole ring contains two π-bonds as well as two hetero atoms in its structure. Thus, the electro-optical properties and thermal properties of polymers containing pyrazole ring comes to the fore.[13,19–24] These polymers can be used in the semiconductor class thanks to their good optical properties such as refractive index, absorption, optical band gap, which are important for the electro-optical parts such as various diodes and transistors.[22–24] On the other hand, the presence of such a hetero ring in the polymer main chain, as well as the partial delocalization of the π -bonds, cause side group interactions between polymer chains and on the polymer main chains. This significantly restricts the movement of polymer chains and also delays the thermal degradation of polymers. Therefore, these structural behaviors allow the preparation of thermally stable polymers.[19–21] There are some studies in the literature investigating the thermal properties of pyrazole-derived polymers. One of these is reported by Connell et al, in that study, thermally stable polypyrazoles have been prepared by using the reactions of bis-hydrazines with acetylenic ketones and esters.[20] Moore and Mehta have developed a new way to synthesize polypyrazole by reacting bis-chloro vinylidene cyanides with diamines. They have succeeded in increasing the thermal stability of the synthesized polypyrazoles using the vinylic nucleophilic substitution reaction.[21]

Free radical addition polymerization is a well-known polymerization method that has been studied in detail. This method has been one of the most useful and beneficial areas of chemistry ever discovered. It is widely used in scientific and technological fields. It has been one of the most preferred polymerization methods in almost every period and platform. The free radical polymerization method is highly tolerant of functional groups in monomers and polymerization can occur in a wide variety of environments.[25] Free radical polymerization takes place in three different stages: initiation, propagation and termination.[26] In addition to chemical initiators such as organic peroxides, azo compounds, redox initiators as initiator system, radical polymerization can also be initiated with different physical factors such as heat, light, high energy, electrochemical method, etc.[27] In addition, radical polymerization is a very effective polymerization method in the polymerization of olefins, styrene and its derivatives, acrylamides, acrylates, methacrylates and their derivatives, and many other vinylic monomers, including unsaturated alkene chemistry.[28] On the other hand, there are different polymerization techniques in polymer chemistry and they are widely used for the purpose. Suspension and emulsion polymerizations have been used in important industrial processes for years. Apart from these, step growth polymerization techniques, ionic addition, coordination, ring opening, electrochemical polymerization etc. have been used for years.[25] In recent years, controlled polymerization techniques such as atom transfer radical polymerization (ATRP), degenerative transfer (DT), reversible addition fragmentation chain transfer processes (RAFT), nitroxide mediated polymerization (NMP), stable free radical polymerization (SFRP) have been developed to control the molecular weight distribution.[29] Generally, in these methods, since special reaction conditions and reagents are required, the application area is relatively limited, costly and mostly preferred in the synthesis of specific polymers. However, some factors such as ease of application, cheapness, low number of reagents (monomer and initiator), etc. make free radical polymerization more advantageous and common.[30]

As mentioned above, most of the reported studies on pyrazole/pyrazolone derivatives are for the synthesis of small molecules using different organic synthesis reactions and some applications. Within our knowledge of the literature, the studies on the synthesis of polymers derived from the pyrazole molecule, especially the methacrylate polymers containing it as a side group, is quite limited. Unfortunately, the study investigating the thermal degradation kinetics of pyrazole-derived methacrylate polymers is not seen in the literature. In order to fill this lack of literature, we aim the synthesis and spectral characterization of a new pyrazole-derived methacrylate polymer, poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate), poly(DPPMA), in the present study. The thermal behavior of the polymer is determined using the thermogravimetric analysis method (TGA). In addition, the thermal decomposition kinetics of the polymer have been investigated in detail by using different kinetic methods available in the literature. Kinetic parameters such as the activation energy and thermal decomposition mechanism are reported.

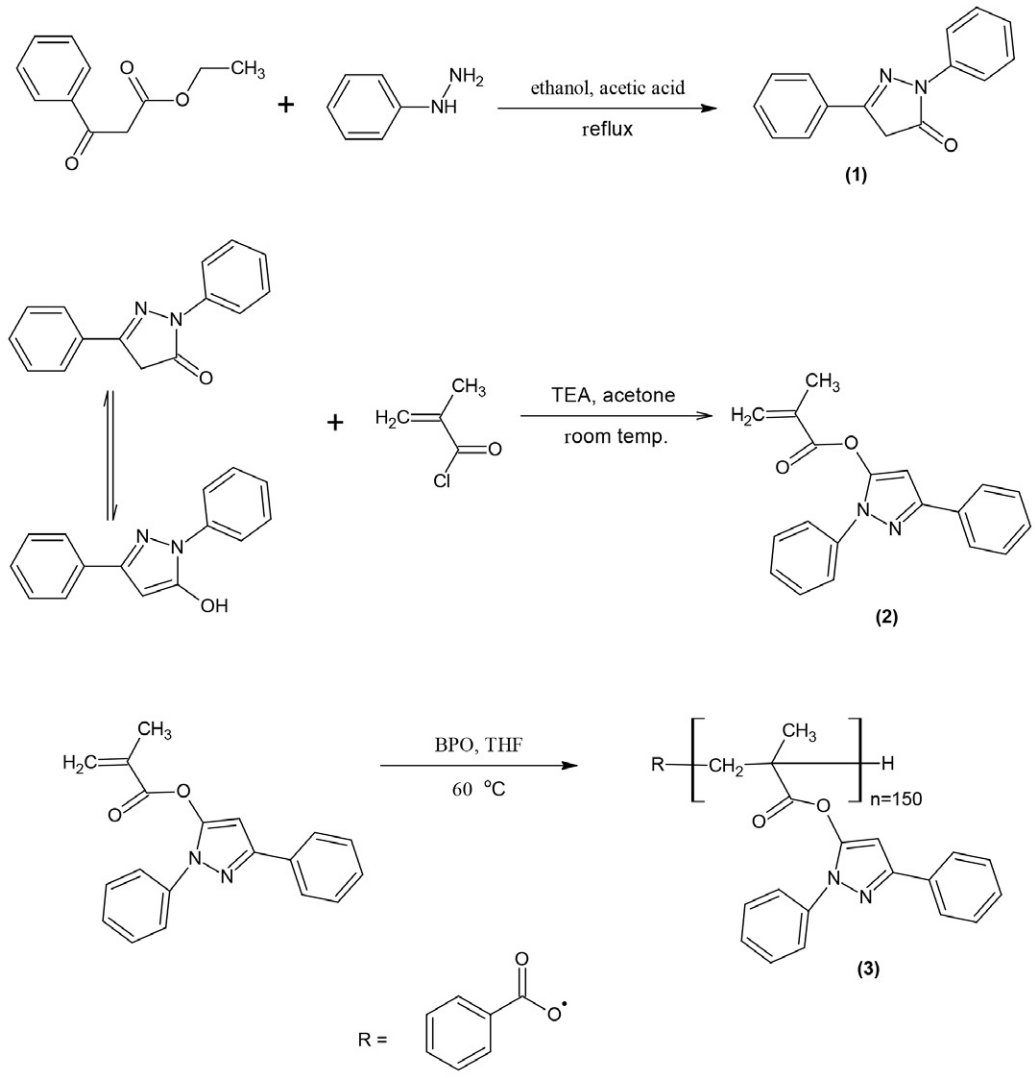
2. Experimental

2. 1. Materials

Ethyl benzoylacetate, phenylhydrazine, methacryloyl chloride, triethylamine (TEA), benzoyl peroxide (BPO), acetone, acetic acid, chloroform, ethyl alcohol and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Benzoyl peroxide before use in the polymerization as initiator was crystallized in ethanol.

2. 2. Synthesis of 1,3-diphenyl-5-pyrazolone

Ethyl benzoylacetate (1.921 g, 10 mmol), phenyl hydrazine (1.081 g, 10 mmol), ethanol (25 ml) and catalytic



Scheme 1. Homopolymerization of 1,3-diphenyl-1H-pyrazol-5-yl methacrylate monomer

amount of acetic acid were added into a 50 ml single-necked reaction flask and refluxed for 12 h on a magnetic stirrer using a method similar to that previously reported.[1] After the mixture was cooled to room temperature, it was precipitated in water. The product was then recrystallized in ethanol, and dried. The yield (1) was calculated as 94%.

FTIR (cm^{-1}): 3067–3044 (aromatic C-H stretching), 2956–2911 (aliphatic C-H stretching), 1699 (pyrazolone C=O stretching).

^{1}H-NMR (600MHz, $CDCl_3$):δ(ppm) = 7.4–8.1 (multiple, 10H, phenyl ring protons), 3.8 (singlet, 2H, pyrazolone ring protons)

2. 3. Synthesis of 1,3-diphenyl-1H-pyrazol-5-yl Methacrylate

1,3-diphenyl-5-pyrazolone (2.3627 g, 10 mmol), methacryloyl chloride (1.0453 g, 10 mmol), triethylamine (1.0119 g, 10 mmol) and acetone (50 ml) were added into a 100 ml single-necked reaction flask and stirred for 24 h at room temperature. The crude product was precipitated in water. It was crystallized again in ethanol. The yield (2) was calculated as 74%.

FTIR (cm^{-1}): 3085–3036 (aromatic C-H stretching), 2987–2903 (aliphatic C-H stretching), 1744 (methacrylate ester C=O stretching), 1635 (aliphatic C=C stretching), 1596 (aromatic C=C stretching), 1109 (-COC- stretching).

^{1}H-NMR (600MHz, $CDCl_3$):δ(ppm) = 7.4–8.0 (multiple, 10H, phenyl ring protons), 6.8 (singlet, 1H, pyrazol ring proton), 6.4 (singlet, 1H vinyl proton) 5.8 (singlet, 1 H, vinyl proton), 2.0 (singlet, 3H, methyl protons next to vinyl group)

2. 4. Synthesis of Poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate)

The homopolymerization of 1,3-diphenyl-1H-pyrazol-5-yl methacrylate monomer was carried out under

conventional free radical polymerization conditions. For this purpose, monomer (1.000 g), benzoyl peroxide (0.0100 g, 1% w/w of monomer) as initiator and THF (3 ml) as solvent were added into a polymerization tube, respectively, and the mixture was dissolved. It was then passed through argon gas for about 15 minutes. The tube was closed and immersed in an oil bath preheated to 60 °C. After a 21 h polymerization time, the polymer mixture was cooled to room temperature, and then precipitated twice in excess ethanol. The resulting polymer (3) was filtered, and dried under vacuum overnight. The appropriate scheme for this synthesis is shown in Scheme 1.

FTIR (cm^{-1}): 3095–3030 (aromatic C-H stretching), 2996–2909 (aliphatic C-H stretching), 1764 (methacrylate ester carbonyl stretching), 1595 (aromatic C=C stretching), 1072 (-COC- stretching)

^{1}H-NMR (300MHz, $CDCl_3$):δ(ppm) = 7.7–6.8 (phenyl ring protons), 6.6 (pyrazol ring proton), 1.8 and 0.8 (methylene and methyl protons in the polymer main chain, respectively).

2. 5. Characterization Techniques

The spectral characterizations were performed with a Perkin Elmer Spectrum 100 FTIR spectrometer with an attenuated total reflectance accessory and also with a high resolution Bruker Avance III HD 600 MHz NMR Spectrometer (its 300 MHz version used for homopolymer). NMR measurements were taken at room temperature using deuterated chloroform solvent and tetramethylsilane standard. Molecular weight and molecular weight distribution of polymer was determined by gel permeation chromatography (GPC) a Malvern Viscotek GPCmax system equipped with a refractive index detector. The eluting solvent was tetrahydrofuran (THF) and calibrated by using polystyrene as standard. A Perkin Elmer Differential Scanning Calorimeter (Pyris 6 DSC) was used to determine the glass transition temperature of poly(DPPMA) in the temperature range of 30–210 °C at a heating rate of 5 °C/min under a nitrogen atmosphere (100 ml/min). TGA analysis was performed on a Seiko SII 7300 TG/DTA thermobalance for obtaining the TG/DTG curves. Polymer samples were added to aluminum pans and then submitted to a controlled temperature program from ambient temperature to 500 °C in nitrogen flow of 25 mL/min. The samples were heated at various heating rates of 5, 10, 15 and 20 °C/min, respectively, in order to determine the kinetic parameters of the thermal decomposition of polymer.

3. Results and Discussion

Figure 1a shows the FTIR spectrum of 1,3-diphenyl-5-pyrazolone compound. The most characteristic absorption bands are observed at the frequencies of 3067–3044 cm^{-1} (aromatic C-H stretching), 2956–2911 cm^{-1} (aliphatic C-H stretching), 1699 cm^{-1} (pyrazolone C=O stretching). FTIR spectrum of 1,3-diphenyl-1H-pyrazol-5-yl methacrylate monomer is shown in Figure 1b where the aromatic and aliphatic C-H stretchings are absorbed at 3085–3036 cm^{-1} and 2987–2903 cm^{-1}, respectively. The other important bands are recorded at 1744 cm^{-1} for methacrylate ester C=O stretching, 1635 cm^{-1} for aliphatic C=C stretching, 1596 cm^{-1} for aromatic C=C stretching, 1109 cm^{-1} for -COC- stretching. Figure 1c shows the FTIR spectrum of poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate). In this figure, the most significant change is that the signal observed at 1635 cm^{-1} characteristic for C=C stretching in the vinyl group is lost due to polymerization. The disappearance of this signal is the most obvious evidence that polymerization has taken place, so it can be easily detected by FTIR.[31] The characteristic absorptions are also attributed to aromatic C-H stretching (3095–3030 cm^{-1}), aliphatic C-H stretching (2996–2909 cm^{-1}), methacrylate ester carbonyl stretching (1764 cm^{-1}), aromatic C=C stretching (1595 cm^{-1}) and -COC- stretching (1072 cm^{-1}).

^{1}H-NMR spectra of all compounds are shown in Figure 2. Among them, Figure 2a is recorded for 1,3-diphenyl-5-pyrazolone in which the multiple peaks in the range of 7.4–8.1 ppm are due to the phenyl ring protons. The singlet observed at 3.8 ppm is for the protons in the pyrazolone ring.

Figure 2b is also recorded for 1,3-diphenyl-1H-pyrazol-5-yl methacrylate monomer. As a result of tauterization in pyrazolone ring and then bonding of the methacryl group to it, the protons in the pyrazole ring decreased to one proton, which is resonated in the low chemical shift region at 6.8 ppm as a singlet. The location of the protons in the phenyl ring did not change significantly and signaled at 7.4–8.0 ppm. Two singlet at 5.8 and 6.4 ppm, which are new signals proving that the methacrylate group

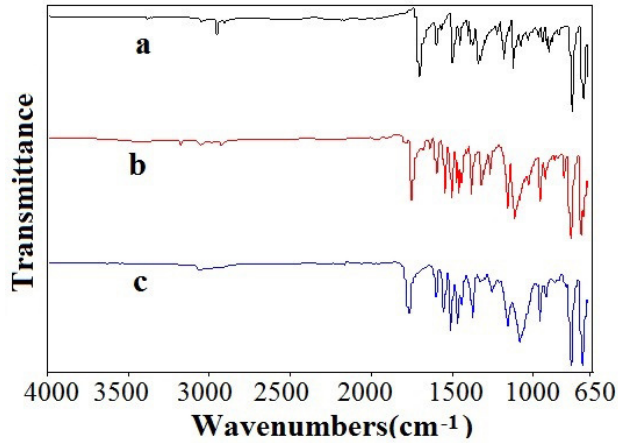


Figure 1. FTIR spectra: a) 1,3-diphenyl-5-pyrazolone, b) 1,3-diphenyl-1H-pyrazol-5-yl methacrylate, c) poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate)

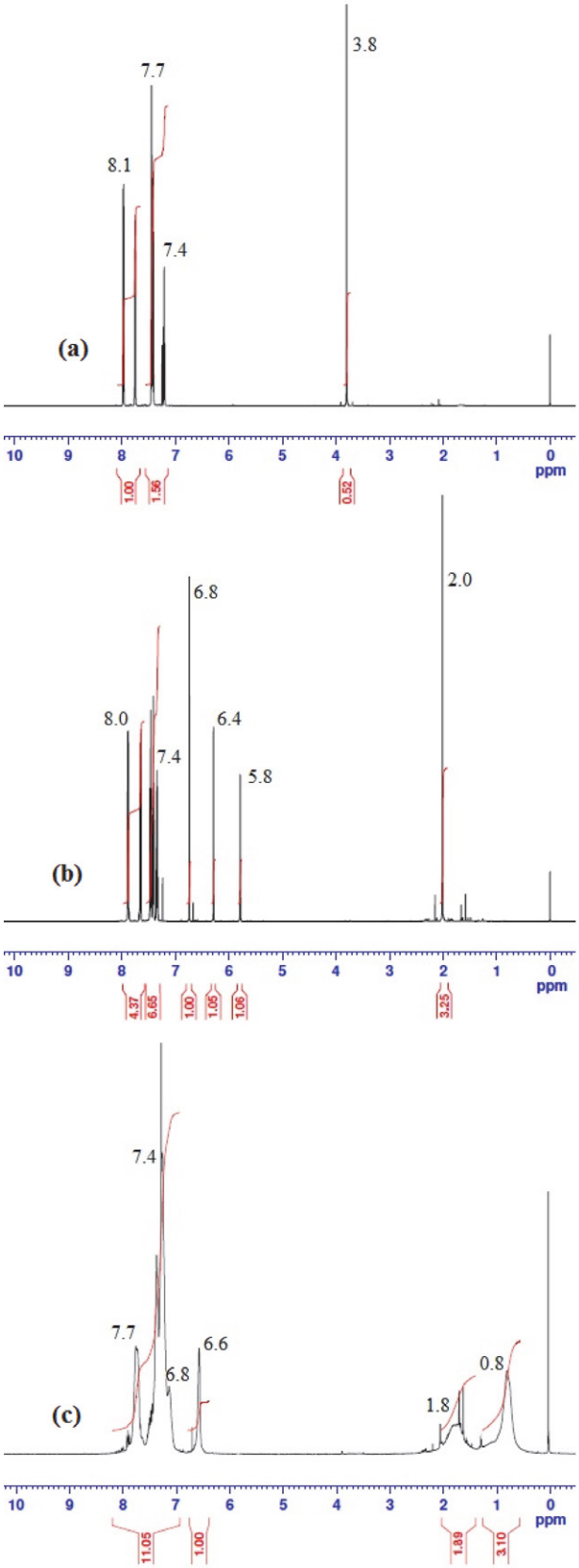


Figure 2. 1H-NMR spectra: a) 1,3-diphenyl-5-pyrazolone, b) 1,3-diphenyl-1H-pyrazol-5-yl methacrylate, c) poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate)

is in the structure, are attributed to methylene protons in the vinyl group. In addition, the singlet corresponding to 3 protons at 2.0 ppm is characteristic for the methyl protons adjacent to the vinyl group. ^{1}H-NMR spectrum of poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate) homopolymer is shown in Figure 2c. The 5.8 ppm and 6.4 pm signals, the two most important characteristic signals for the monomer, are disappeared due to polymerization. These signals are shifted to 1.8 ppm as a new signal group and appeared as methylene protons in the polymer main chain. Methacrylate methyl protons are also shifted to 0.8 ppm. The signal at 6.6 ppm is due to the proton in the pyrazol ring, and the 7.7–6.8 ppm signals are also due to the protons in the phenyl ring.

Figure 3 shows the chromatogram output of the gel permeation chromatography (GPC). The number – average molecular weight of the pyrazole derived poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate) polymer is measured to be 45800 and its molecular weight distribution (polydispersity) is 3.24. Since the free radical polymerization method is used, the measured polydispersity value is relatively moderate and in the acceptable range for this method. As seen in the literature, a precise molecular weight and distribution control cannot be achieved in the free radical polymerization process. This is because all polymer chains cannot be started at the same time, and undesirable events such as chain termination, chain transfers, etc. also occur simultaneously. Thus, very large and small chains may form during polymerization and the chain distribution may often wide (polydispersity ≥ 2).[32] In addition, the molecular mass of present DPPMA monomer is 304.342 g/mol, and thus the degree of polymerization (D_P) is calculated as 150.

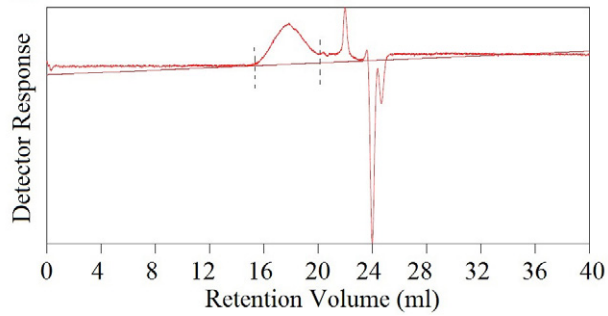


Figure 3. GPC chromatogram of poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate)

The glass transition temperature of poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate) was determined by using differential scanning calorimetry technique (DSC) and its thermogram is illustrated in Figure 4. As can be seen from that thermogram, the glass transition temperature of poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate) was measured to be 158.1 °C. Similar results to this measured value are seen in the literature for pyrazole derived hetero-

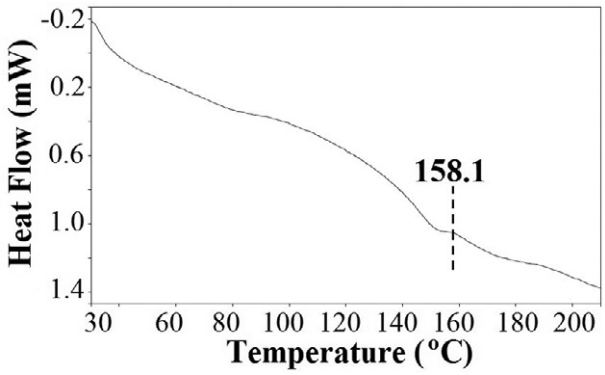


Figure 4. DSC thermogram of poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate)

cyclic polymers. Wang and Cheng synthesized a series of 3,5-disubstituted pyrazole polymers and found that the glass transition temperatures of these polymers varied in the range of 147 °C–158 °C.[33]

Thermal analysis of poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate) was performed by thermogravimetric analysis (TGA). The thermal decomposition process was followed on a temperature range of ~25–500 °C in nitrogen gas atmosphere in order to detect the possible data of decomposition phases. Therefore, a controlled heating program at different rates of 5, 10, 15 and 20 °C/min was applied to this process. TGA thermograms recorded from these heatings are given in Figure 5 comparatively.

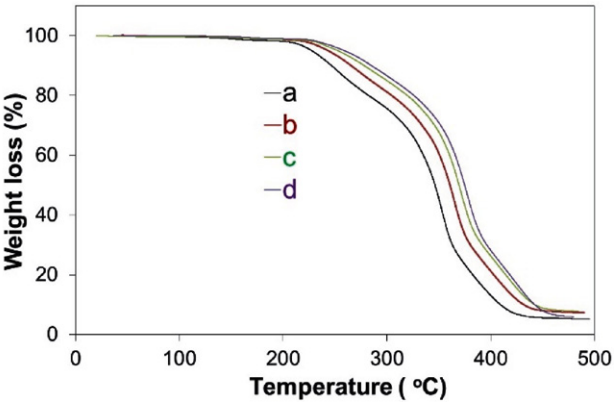


Figure 5. TGA curves of poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate) at different heating rates of a) 5, b) 10, c) 15 and d) 20 °C/min.

In general, at these heating conditions, the degradation of the poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate) took place in three stages. The first one, with up to 20% weight loss at ~215–300 °C usually caused by volatile hydrocarbons, the second decomposition stage is about between 300–380 °C *with* up to 70% weight loss, and the third one is ~ 380–450 °C with up to 93% weight loss (according to 10 °C/min used as reference). These results are in good agreement with the thermal behavior of pyrazole polymers. Wang and Cheng reported 3,5-disubstituted polypyrazoles synthesized by click polymerization procedure were decomposed at ~290 °C about 10% of their weight losses.[33] Some thermal data obtained in the thermal decomposition of the polymer, such as the initial decomposition temperature, the final decomposition temperature, the temperature at 50% mass loss, the % decomposition values at different temperatures, the % residual value, etc. are determined. These values are summarized in Table 1. As can be seen from the Table 1, the initial degradation temperatures of the polymer were calculated as 216.3, 230.9, 238.8 and 243.5 °C at heating rates of 5, 10, 15 and 20 °C/min. As expected, there is a positive correlation between heating rate increase and thermal stability. Similar results for thermal degradation of heterocyclic polymers have been reported in our previous publications and also by different researchers.[34–42] For example, Kurt et al.[37] reported the degradation temperatures of an isocoumarin derived polymer changed in a positive direction, which increased 256.6 °C to 286.1 °C by increasing heating rate from 5 to 20 °C/min. Meng and friends investigated the thermal degradation kinetics of a polyimide polymer containing 2,6-benzobisoxwwwwazole units and reported the onset decomposition temperatures increased with increase of heating rates.[40]

A typical kinetic process for thermal decomposition of polymeric materials can be given by the following equation:[43]

$$\frac{d\alpha}{dt} = A\, exp\left(-\frac{E}{RT}\right) f(\alpha) \qquad (1)$$

where f(α) is the differential function of a kinetic model, A is the pre-exponential factor, E is activation energy, R is the ideal gas constant (8.314 J/mol K), T is the absolute temperature (K), α is the extent of reaction and t is the time.

The integral function of a kinetic model, g(α), can be expressed as:

Table 1. Thermal data of poly(1.3-diphenyl-1H-pyrazol-5-yl methacrylate)

Reaction rate (°C/min)	$T_{initial}$ (°C)	T_{final} (°C)	$T_{\%50}$ (°C)	%Weight loss at 300 °C	%Weight loss at 350 °C	%Weight loss at 400 °C	%Residue at 500 °C
5	216.3	431.6	346.3	24.4	54.5	86.9	5.1
10	230.9	445.2	360.7	18.9	39.5	78.8	7.2
15	238.8	454.2	369.5	15.0	32.2	73.7	7.7
20	243.5	463.7	374.8	13.4	29.1	71.9	5.9

$$g(\alpha) = \int_0^{\alpha_p} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T_p} e^{-\frac{E}{RT}} dT \quad (2)$$

where β is the heating rate and T_p is the peak temperature (K). Thermal degradation of polymers mostly proceeds via a sigmoidal type mechanism or a deceleration type mechanism.[43] Different versions of these mechanisms are stated in Table 2. These g(α) functions allow the determination of thermal degradation mechanism of polymer by thermogravimetry method.[44] Besides, derivative thermogravimetry (DTG) method is also used to determine the thermal decomposition mechanisms of polymers and to determine the physical or chemical interaction types during decomposition. Therefore, kinetic parameters of thermal degradation can be determined based on TG/DTG data. These kinetic parameters are highly dependent on the calculation methods due to the different solutions of Equation 2. There are many methods in which the apparent activation energies are determined based on the data obtained from TGA curves recorded at different heating rates. Here, we used some kinetic methods namely, Flynn-Wall-Ozawa, Kissinger, Coats-Redfern, Tang, Madhusudanan and Van Krevelen method in order to determine kinetic parameters and decomposition mechanism for the degradation of poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate).

Of the kinetic methods mentioned, Flynn-Wall-Ozawa[45,46] and Kissinger[47] methods do not depend on the reaction mechanism and the degree of reaction. Therefore, it is used to calculate the thermal degradation activation energy of the polymer.[37,40,43] The Flynn-Wall-Ozawa equation is expressed as:

$$\log \beta = \log\left[\frac{AE}{g(\alpha)R}\right] - 2.315 - \frac{0.457\,E}{RT} \quad (3)$$

According to this equation, in order to calculate the activation energy, log β values versus (1000/T) values are plotted and the E value is calculated from the slope of the obtained line. For this, the decomposition temperatures corresponding to 7%, 9%, 11%, 13%, 15%, 17% and 19% conversions at different heating rates were measured and these values were plotted for each conversion as shown in Figure 6.

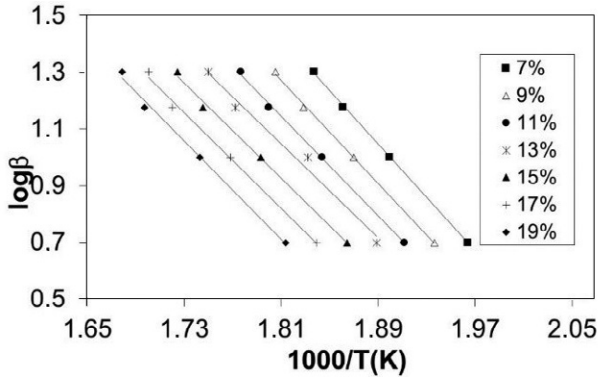


Figure 6. Flynn–Wall–Ozawa lines at different conversion values.

As can be seen from the figure, the lines of all conversions in an almost parallel order. In addition, the linear regression value of each line is also a high level. This increases the reliability of the calculations. The activation energy value corresponding to each conversion mentioned above was calculated separately. The results are given in Table 3. According to the table, activation energy values varied between the lowest value 75.43 kJ/mol and the highest 85.82 kJ/mol in the studied conversion range. The mean thermal decomposition activation energy value of poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate) according was calculated as 79.45 kJ/mol. The closest activation

Table 2. Algebraic expressions for g(α) for the most frequently used mechanisms of solid state processes

Symbol	g(α)	Solid state processes
Sigmoidal curves		
A_2	$[-\ln(1-\alpha)]^{1/2}$	Nucleation and growth (Avrami equation 1)
A_3	$[-\ln(1-\alpha)]^{1/3}$	Nucleation and growth (Avrami equation 2)
A_4	$[-\ln(1-\alpha)]^{1/4}$	Nucleation and growth (Avrami equation 3)
Deceleration curves		
R_1	α	Phase boundary controlled reaction (One-dimensional movement)
R_2	$[1-(1-\alpha)^{1/2}]$	Phase boundary controlled reaction (contraction area)
R_3	$[1-(1-\alpha)^{1/3}]$	Phase boundary controlled reaction (contraction volume)
D_1	α^2	One-dimensional diffusion
D_2	$(1-\alpha)\ln(1-\alpha)+\alpha$	Two-dimensional diffusion
D_3	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion (Jander equation)
D_4	$(1-2/3\alpha)\ (1-\alpha)^{2/3}$	Three-dimensional diffusion (Ginstling-Brounshtein equation)
F_1	$-\ln(1-\alpha)$	Random nucleation with one nucleus on the individual particle
F_2	$1/(1-\alpha)$	Random nucleation with two nuclei on the individual particle
F_3	$1/(1-\alpha)^2$	Random nucleation with three nuclei on the individual particle

Table 3. Activation energies of poly(1.3-diphenyl-1H-pyrazol-5-yl methacrylate) obtained by Flynn-Wall-Ozawa method

α (%)	*E* (kJ/mol)	*R*
7	85.82	0.9996
9	82.71	0.9990
11	80.16	0.9985
13	75.43	0.9840
15	76.23	0.9965
17	76.75	0.9956
19	79.06	0.9951
Mean	79.45	

energy value to that was reached at a conversion of 19%, with a value of 79.06 kJ/mol.

The activation energy of thermal decomposition of poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate) was also determined by the Kissinger method. This method, like the Flynn-Wall-Ozawa method, does not depend on the reaction mechanism and order. This method is expressed by following equation:

$$\ln\left(\frac{\beta}{T_{max}^2}\right) = \left\{\ln\frac{AR}{E} + \ln\left[n(1-\alpha_{max})^{n-1}\right]\right\} - \frac{E}{RT_{max}} \quad (4)$$

where n is the reaction order, T_{max} is the temperature at the maximum reaction rate, α_{max} is the maximum conversion at T_{max}. According to this method, $\ln(\beta/T^2_{max})$ versus $1000/T_{max}$ values are plotted and the activation energy is determined from the slope of this line. Figure 7 shows these plots. The T_{max} values required to determine the activation energy according to the Kissinger method were measured from the DTG curves. These temperatures were 245.12, 262.04, 273.98 and 281.59 °C for the rates of 5, 10, 15 and 20 °C/min, respectively. Accordingly, the activation energy value was determined as 81.56 kJ/mol with a high linear regression (R = 0.9990) using the Kissinger method. When the results are examined, an energy difference of only 2.11 kJ/mol is detected among the energy values of these integral methods. This result also shows that there is a very good agreement between the methods used and the reliability of the results is high.

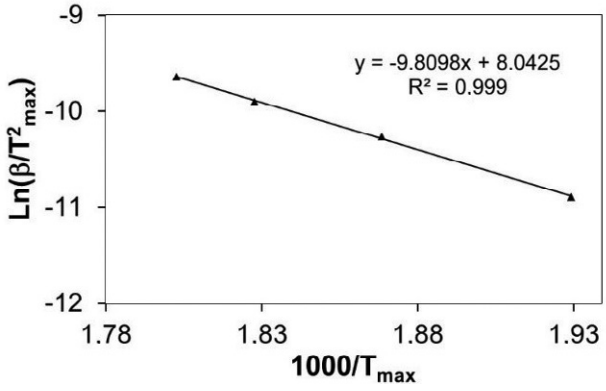


Figure 7. $\ln(\beta/T^2_{max})$ versus $1000/T_{max}$ plots obtained from Kissinger method.

There are some kinetic methods in which the different sigmoidal and deceleration type g(α) functions given in Table2 are analyzed with different approaches in determining the thermal degradation mechanism of the polymer. One of these methods is the Coats-Redfern method.[48] This method is used the below equation:

$$\ln\frac{g(\alpha)}{T^2} = \ln\frac{AR}{\beta E} - \frac{E}{RT} \quad (5)$$

From the fitting $\ln[g(\alpha)/T^2]$ vs. 1000/T plots, the activation energy corresponding to different g(α) functions is obtained at constant heating rates. Another method to determine thermodegradation mechanism is Tang method,[49] and which used:

$$\ln\left[\frac{g(\alpha)}{T^{1.89466100}}\right] = \left[\ln\frac{AE}{\beta R} + 3.63504095 - 1.89466100\ln E\right] - 1.00145033\frac{E}{RT} \quad (6)$$

The plots of $\ln[g(\alpha)/T^{1.89466100}]$ vs. 1000/T give a straight line and from its slope, E can be calculated for each g(α) function. Madhusudanan method[50] is another one, and which is expressed as:

$$\ln\left[\frac{g(\alpha)}{T^{1.921503}}\right] = \left[\ln\frac{AE}{\beta R} + 3.772050 - 1.921503\ln E\right] - 1.000955716\frac{E}{RT} \quad (7)$$

E values for each g(α) mechanisms can be calculated from the slope of $\ln[g(\alpha)/T^{1.921503}]$ vs. 1000/T plots. As a final method, the Van Krevelen method[51] is proposed by the following equation:

$$\log g(\alpha) = \log B + \left(\frac{E}{RT_r} + 1\right)\log T \quad (8)$$

where T_r corresponds the reference temperature which is taken as the temperature of the maximum reaction rate obtained by derivative thermogravimetry. E is defined from a linear fitting of log g(α) vs. logT plots for every g(α) mechanisms.

In general, each activation energy value calculated for the g(α) mechanisms in different states and for the heating rates is compared with the Flynn-Wall-Ozawa and Kissinger methods to determine the thermal degradation mechanism of the polymer. Because, as is known, these two methods are independent of the reaction mechanism and order. The activation energies, obtained from the other methods, closest to Flynn-Wall-Ozawa and Kissinger methods are determined. The corresponding g(α) mechanism is accepted as the thermal decomposition mechanism of the pro-

Table 4. Activation energies of poly(1.3-diphenyl-1H-pyrazol-5-yl methacrylate using Coats-Redfern Method

Mechanism	Heating Rate							
	5 °C/min		10 °C/min		15 °C/min		20 °C/min	
	E (kJ/mol)	R	E (kJ/mol)	R	E (kJ/mol)	R	E (kJ/mol)	R
A_2	20.57	0.9659	19.02	0.9719	17.43	0.9825	18.22	0.9858
A_3	10.78	0.9445	9.63	0.9506	8.50	0.9661	8.99	0.9730
A_4	5.88	0.8977	4.94	0.8968	4.04	0.9157	4.38	0.9351
R_1	46.17	0.9729	43.56	0.9783	40.79	0.9866	42.39	0.9888
R_2	48.04	0.9751	45.34	0.9803	42.48	0.9882	44.13	0.9902
R_3	48.67	0.9758	45.95	0.9809	43.05	0.9887	44.72	0.9907
D_1	101.16	0.9776	96.26	0.9824	90.93	0.9894	94.24	0.9912
D_2	103.61	0.9787	98.60	0.9834	93.15	0.9902	96.54	0.9919
D_3	106.15	0.9799	101.03	0.9845	95.45	0.9910	98.91	0.9926
D_4	104.46	0.9791	99.41	0.9838	93.92	0.9905	97.33	0.9921
F_1	49.95	0.9772	47.17	0.9822	44.20	0.9896	45.92	0.9915
F_2	−1.08	0.9731	−1.75	0.9845	−2.35	0.9744	−2.24	0.9603
F_3	6.66	0.9961	5.65	0.9908	4.65	0.9648	4.99	0.9590

cess. The heating rate corresponds to the optimum heating rate.[37,43] The activation energy values calculated for each g(α) function for different heating rates using the above kinetic methods are given in Tables 4–7. Conversion percentages for this process are between 7% and 19%. When these tables were analyzed in detail, it was determined that the degradation of polymer progressed through the D_n mechanism, which is a common degradation mechanism for all methods. Because, the activation energy values calculated for the D_n mechanisms (deceleration-type dimensional diffusions) are the closest to the Flynn-Wall-Ozawa and Kissinger methods. In addition, linear regression values determined for D_n mechanisms are relatively high. In order to see the results more clearly, the activation energy values corresponding to the D_n mechanisms calculated for all methods are also summarized in Table 8.

Table 4 shows the results obtained for the Coats Redfern method. Compared to other methods and their D_n mechanisms, especially for the D_1 mechanism, the activation energy value at the heating rate of 15 °C is 90.93 kJ/mol. This value is very close to the values obtained from Flynn-Wall-Ozawa (E = 79.45 kJ/mol) and Kissinger (E = 81.56 kJ/mol) methods, and the results are quite compatible. According to the results calculated by the Coats Redfern method, it can be said that the thermal degradation mechanism of poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate) proceeds strongly through the D_1 mechanism, deceleration type one-dimensional diffusion mechanism.

Activation energy and linear regression values calculated according to the Tang method are given in Table 5. As can be seen from this table, the closest result to Flynn-Wall-Ozawa and Kissinger methods among all g(α) mechanisms is obtained for D_1 mechanism at 15 °C heating rate, which is E = 91.29 kJ/mol. The results obtained from Tang method also support the Coats Redfern method and increase the reliability of their results.

Table 5. Activation energies of poly(1.3-diphenyl-1H-pyrazol-5-yl methacrylate using Tang Method

Mechanism	Heating Rate							
	5 °C/min		10 °C/min		15 °C/min		20 °C/min	
	E (kJ/mol)	R	E (kJ/mol)	R	E (kJ/mol)	R	E (kJ/mol)	R
A_2	20.57	0.9659	19.02	0.9719	17.43	0.9825	18.22	0.9858
A_3	10.78	0.9445	9.63	0.9506	8.50	0.9661	8.99	0.9730
A_4	5.88	0.8977	4.94	0.8968	4.04	0.9157	4.38	0.9351
R_1	46.17	0.9729	43.56	0.9783	40.79	0.9866	42.39	0.9888
R_2	48.04	0.9751	45.34	0.9803	42.48	0.9882	44.13	0.9902
R_3	48.67	0.9758	45.95	0.9809	43.05	0.9887	44.72	0.9907
D_1	101.16	0.9776	96.26	0.9824	90.93	0.9894	94.24	0.9912
D_2	103.61	0.9787	98.60	0.9834	93.15	0.9902	96.54	0.9919
D_3	106.15	0.9799	101.03	0.9845	95.45	0.9910	98.91	0.9926
D_4	104.46	0.9791	99.41	0.9838	93.92	0.9905	97.33	0.9921
F_1	49.95	0.9772	47.17	0.9822	44.20	0.9896	45.92	0.9915
F_2	−1.08	0.9731	−1.75	0.9845	−2.35	0.9744	−2.24	0.9603
F_3	6.66	0.9961	5.65	0.9908	4.65	0.9648	4.99	0.9590

Table 6. Activation energies of poly(1.3-diphenyl-1H-pyrazol-5-yl methacrylate using Madhusudanan Method

Mechanism	Heating Rate							
	5 °C/min		10 °C/min		15 °C/min		20 °C/min	
	E (kJ/mol)	R	E (kJ/mol)	R	E (kJ/mol)	R	E (kJ/mol)	R
A_2	20.90	0.9670	19.36	0.9729	17.78	0.9833	18.58	0.9864
A_3	11.11	0.9479	9.98	0.9541	8.86	0.9690	9.36	0.9752
A_4	6.22	0.9081	5.29	0.9096	4.40	0.9287	4.75	0.9447
R_1	46.47	0.9733	43.88	0.9786	41.11	0.9868	42.72	0.9890
R_2	48.34	0.9755	45.66	0.9806	42.80	0.9884	44.46	0.9904
R_3	48.97	0.9762	46.26	0.9812	43.37	0.9889	45.05	0.9908
D_1	101.40	0.9778	96.52	0.9826	91.21	0.9895	94.52	0.9912
D_2	103.86	0.9789	98.87	0.9836	93.43	0.9903	96.81	0.9919
D_3	106.39	0.9800	101.29	0.9846	95.72	0.9911	99.18	0.9926
D_4	104.70	0.9793	99.68	0.9839	94.19	0.9906	97.60	0.9922
F_1	50.25	0.9775	47.48	0.9825	44.53	0.9898	46.24	0.9917
F_2	−0.73	0.9423	−1.39	0.9747	−1.99	0.9635	−1.86	0.9427
F_3	6.99	0.9965	6.00	0.9918	5.01	0.9693	5.36	0.9640

Table 7. Activation energies of poly(1.3-diphenyl-1H-pyrazol-5-yl methacrylate using Van Krevelen Method

Mechanism	Heating Rate							
	5 °C/min		10 °C/min		15 °C/min		20 °C/min	
	E (kJ/mol)	R	E (kJ/mol)	R	E (kJ/mol)	R	E (kJ/mol)	R
A_2	24.39	0.9808	22.93	0.9849	21.46	0.9910	22.34	0.9924
A_3	14.82	0.9808	13.80	0.9849	12.79	0.9910	13.36	0.9924
A_4	10.04	0.9808	9.24	0.9849	8.46	0.9910	8.86	0.9924
R_1	49.40	0.9779	46.79	0.9824	44.15	0.9889	45.85	0.9906
R_2	51.22	0.9794	48.53	0.9837	45.79	0.9900	47.55	0.9915
R_3	51.84	0.9798	49.12	0.9841	46.35	0.9903	48.13	0.9918
D_1	103.11	0.9779	98.04	0.9824	92.85	0.9889	96.31	0.9906
D_2	105.51	0.9789	100.33	0.9833	95.02	0.9896	98.55	0.9912
D_3	107.99	0.9798	102.69	0.9841	97.25	0.9903	100.87	0.9918
D_4	106.34	0.9792	101.11	0.9836	95.76	0.9899	99.32	0.9914
F_1	53.09	0.9808	50.31	0.9849	47.48	0.9910	49.29	0.9924
F_2	3.26	0.9994	2.75	0.9990	2.26	0.9965	2.44	0.9956
F_3	10.82	0.9994	9.95	0.9990	9.08	0.9965	9.49	0.9956

Table 8. Activation energies for Dn mechanisms of all methods

Method	Mechanism	5 °C/min *E (kJ/mol)*	10 °C/min *E (kJ/mol*	15 °C/min *E (kJ/mol*	20 °C/min *E (kJ/mol*
Coats-Redfern	D_1	101,16	96,26	90,93	94,24
	D_2	103,61	98,60	93,15	96,54
	D_3	106,15	101,03	95,45	98,91
	D_4	104,46	99,41	93,92	97,33
Tang	D_1	101,47	96,60	91,29	94,60
	D_2	103,93	98,94	93,51	96,89
	D_3	106,46	101,36	95,80	99,26
	D_4	104,77	99,75	94,27	97,68
Madhusudanan	D_1	101,40	96,52	91,21	94,52
	D_2	103,86	98,87	93,43	96,81
	D_3	106,39	101,29	95,72	99,18
	D_4	104,70	99,68	94,19	97,60
Van Krevelen	D_1	103,11	98,04	92,85	96,31
	D_2	105,51	100,33	95,02	98,55
	D_3	107,99	102,69	97,25	100,87
	D_4	106,34	101,11	95,76	99,32

Table 6 shows the results obtained by the Madhusudanan method in which activation energy is found to be E = 91.21 kJ/mol and linear regression is R = 0.9895 for the D_1 mechanism at a heating rate of 15 °C/min. These values are also in good agreement with the Flynn-Wall-Ozawa and Kissinger methods. In addition to the results obtained from the above kinetic methods, the latest Van Krevelen method is used. The results determined by this method are summarized in Table 7. Similar results to other methods are also available for this method. Accordingly, the activation energy (E = 92.85 kJ/mol) value and linear regression (R = 0.9889) value are close to Flynn-Wall-Ozawa (E = 79.45 kJ/mol) and Kissinger (E = 81.56 kJ/mol) methods. These results show that there is a very good agreement between all the kinetic methods used and also the degradation mechanism proceeds through the D_1 mechanism, one-dimensional diffusion-type deceleration mechanism.

4. Conclusions

A new pyrazole derived methacrylate polymer poly(1,3-diphenyl-1H-pyrazol-5-yl methacrylate) poly(DPPMA) was synthesized and spectrally characterized. Then, it was tested for determining the thermal characteristics by TGA method at various heating rates. The initial decomposition temperature of the polymer changed from 216.3 °C to 243.5 °C depending on the increasing heating rate. The thermal decomposition activation energies in a conversion range of 7–19% were 79.45 and 81.56 kJ/mol by the Flynn–Wall–Ozawa and Kissinger methods, respectively. Thermodegradation mechanism of the poly(DPPMA) were investigated in detail by using different kinetic methods available in the literature. The best result was obtained for Coats-Redfern method (E = 90.93 kJ/mol) at the optimum heating rate of 15 °C/min for D_1 mechanism, one-dimensional diffusion type deceleration mechanism.

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Povzetek

Obnašanje in lastnosti polimerov, pridobljenih iz makromolekularnega pirazola, se razlikujejo od njihovih osnovnih molekul. Temu ustrezno takšni polimeri spadajo v razred dobro opredeljenih funkcionalnih polimerov zaradi dejstva, da pirazolni obroč vsebuje dve π-vezi in dva heteroatoma v svoji strukturi, kar jih dela pomembne na področju znanstvenih in tehnoloških aplikacij. V tej študiji je bil tako sintetiziran nov metakrilatni monomer, pridobljen iz pirazola, 1,3-difenil-1*H*-pirazol-5-il metakrilata, prek reakcije 1,3-difenil-5-pirazolona z metakriloil kloridom v prisotnosti trietilamina. Za tem je bila izvedena njegova homopolimerizacija z metodo polimerizacije prostih radikalov pri 60 °C, začeta z benzoil peroksidom. Produkt je bil okarakteriziran z ^{1}H-NMR in FTIR spektroskopijo. Kinetika termične razgradnje novega polimera, poli(1,3-difenil-1*H*-pirazol-5-il metakrilata), poli(DPPMA), je bila raziskana s termogravimetrično analizo (TGA) pri različnih hitrostih segrevanja. Začetna temperatura razgradnje polimera je v območju od 216,3 °C do 243,5 °C, odvisno od naraščajoče hitrosti segrevanja. Aktivacijski energiji termičnega razpada v območju pretvorbe 7–19 % sta bili 79,45 kJ/mol po Flynn–Wall–Ozawa in 81,56 kJ/mol po Kissingerjevi metodi. Mehanizem termičnega razpada poli(DPPMA) je bil podrobno raziskan z različnimi kinetičnimi metodami, ki so na voljo v literaturi, kot so Coats-Redfern, Tang, Madhusudanan in Van Krevelen. Med vsemi omenjenimi metodami je bil najboljši rezultat dosežen pri Coats-Redfernovi metodi (E = 90,93 kJ/mol) pri optimalni hitrosti segrevanja 15 °C/min za mehanizem D_1, opredeljen kot enodimenzionalni zaviralni mehanizem difuzijskega tipa.