

Infrared Spectroscopic Studies on Some Thermally Degraded Poly(methyl methacrylate) Doped with N,N,N',N'- tetraoxaloyl Para Sulphanilamide

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INFRARED (IR) spectroscopic studies were performed for some poly (methyl methacrylate)(PMMA) samples prepared in absence and presence of N,N,N',N'-tetraoxaloyl-p-sulphanilamide after the extraction of the dopant during thermal treatment. There were no drastic changes in the IR absorption bands position, but noticeable changes in the band intensities were found. The relative transmission of IR absorption bands, such as those at 1070, 1242, 1444 and 1730 cm^{-1} , were measured with respect to the transmission of the methyl group band at 1388 cm^{-1} (the most stable band during thermal treatment). By using the combined technique of transmission data of C-C skeletal vibration C-O, CH_2 and C=O bands with respect to the transmission band of methyl group and measuring the area under the curve for the degradation and recombination zones, the protection efficiency of the organic dopant in the PMMA matrix against thermal degradation could be explained.

The protection mechanism of the organic dopant was confirmed by measuring the mass spectrum of the organic dopant for determination of different organic radicals that could be produced during thermolysis. Measuring ^{13}C -NMR of the PMMA-organic dopant after the extraction of the dopant confirms the presence of phenyl moieties in the polymeric chains.

The degradation and recombination mechanism of different groups in the polymeric chain units or backbone scission during thermal treatment could be explained by the behavior of the relative transmission data with increasing temperature. The protection efficiency of the organic dopant was found to be the maximum in presence of 7% of the organic dopant in the PMMA matrix.

Keywords: Poly (methyl methacrylate), Thermal degradation, Protection efficiency and Organic ligand.

The infrared (IR) absorption spectrum of poly (methyl methacrylate) (PMMA) has been the subject of several investigations⁽¹⁻⁵⁾. The object of most of these investigations was to describe the stereo-regular nature of the polymeric chains.

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Sayyah *et al.*⁽⁶⁾ studied the IR spectra of PMMA samples doped with some luminescent materials. They concluded that there was no interaction between the dopant and PMMA with most of the investigated materials, whereas it was observed with β -naphthol, hydrogen bonding between adjacent molecules in the polymer matrix.

Thermal degradation of the polymers is highly complex. It refers to overall exothermic reactions, usually of oxidative nature, having the ability to propagate throughout the phase⁽⁷⁻¹¹⁾. Chemical reactions may take place in three regions: within the condensed phase, at the interface between the condensed phase and the gas phase and in the gas phase. The balance between the different chemical reactions involved, appearing as a net energy flux throughout the system was given by different authors⁽¹²⁻¹⁴⁾.

The methacrylate ester monomer was of particular interest since it allows studying the effects of radical reactivity on the chemical structure changes. But precisely the same radical takes part in chain depolymerization reactions which are typical for this type of polymers⁽¹⁵⁻¹⁷⁾.

Thermal degradation of a sample prepared by free radical polymerization and therefore containing terminal (C=C) was studied in absence⁽¹⁸⁻²²⁾ and presence of oxygen⁽²³⁻²⁵⁾ by weight loss technique.

For PMMA prepared by free radical polymerization, the depolymerization is initiated at relatively low temperature⁽²⁶⁻³⁰⁾ by the cleavage of weak double bonds at the chain end; PMMA is regarded as a polymer that depropagates to monomer as a result of thermal degradations up to 550°C⁽³¹⁻³⁵⁾. It has also been reported⁽³⁶⁻⁴²⁾ that some degradations occur by side-group elimination, leading to the production of unsaturated products. It has also been claimed that side group elimination is a more dominant process than chain scission initiation, due to the possibility of efficient recombination of the caged radical chain ends.

The degradation occurs in two main stages⁽⁴³⁻⁵¹⁾. In the first stage, the radical chain unzipping reaction is initiated at unsaturated chain-ends. In the second stage, initiation occurs randomly along the polymer chain.

Kashiwagi *et al.*⁽¹²⁾ have pointed out that additional small peaks which are observed at much lower temperatures (around 160°C) in non-isothermal differential thermogravimetry (DTG) or thermal volatilization analysis (TVA) experiments for some PMMA samples are due to a degradation initiated at head-to-head linkage.

In the present work, we intend to investigate the fundamental changes of the absorption bands in FTIR spectra of PMMA samples doped with sulphur containing organic ligand during thermal treatment after the extraction of the dopant material. Also, the mechanism of degradation, recombination and protection of PMMA during thermolysis under nitrogen atmosphere would be

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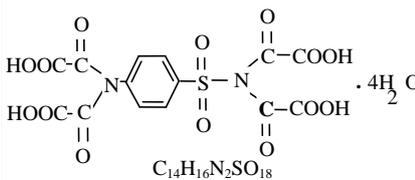
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studied.

Experimental

Materials

The MMA monomer was a product of Merck-Schuchardt(Germany) (99% yield) and was stabilized with 100 ppm hydroquinone. It was purified as described⁽⁶⁾. All chemicals used in this work were of the available purest analytical grade. A Dean-Stark apparatus was used for the preparation of the sulphur containing organic dopant, as previously described by Sabbah *et al.*⁽⁵²⁾. The structures and some analytical data of the prepared dopant are given in Table1.

TABLE 1. Some analytical data of the prepared ligand.

Molecular formula	Elemental analysis (Calc./ Found)				MWt. C/F.	Acid value C/ F	pK ₁ - pK ₄ Value
	C%	H %	N %	S %			
 <chem>C14H16N2SO18</chem>	31.67 32.40	3.01 3.50	5.26 6.00	6.01 6.80	532 539	421.8 430.5	1.86 2.13 6.92 9.70

Determination of molecular weight and water of crystallization of the organic dopant

Molecular weight of the prepared organic dopant was determined using Ebullioscopic method. The principal of the method depends upon Raoult's law and the clauses clapeyron equation

$$\ln P^0/P = \Delta H_v / R [(T - T_0) / TT_0] \quad (1)$$

where P is vapor pressure of the solution at T₀, while P⁰ is the vapor pressure at T, ΔH_v is taken as the heat of vaporization per mole of solvent from the solution when the solution is dilute, ΔH_v is taken as the heat of vaporization of pure solvent and T is not much different from T₀ and therefore we may write T.T₀ = T₀². Consequently equation (1) becomes

$$\ln P^0/P = - \ln P/P^0 = (\Delta H_v / R)(\Delta T_b / T_0^2) \quad (2)$$

and from Raoult's law

$$\ln (1 - X_B) = - (\Delta H_v / R)(\Delta T_b / T_0^2) \quad (3)$$

but,

$$\ln (1 - X_B) = - X_B - (X_B^2 / 2) - (X_B^3 / 3)$$

since the solution is dilute, X_B is very small, thus

$$\ln (1 - X_B) = - X_B$$

substitution into equation (3)

$$-X_B = (RT_o^2 / \Delta H_v) X_B \quad (4)$$

and therefore

$$\Delta T_b = (RT_o / \Delta H_v) X_B \quad (5)$$

Equation (5) gives the boiling point elevation of a solution in terms of boiling point, heat of vaporization of pure solvent and the mole fraction of the solute.

The common practice in boiling point elevation work is to express the concentration not in mole fractions but in molality, *m*. If we now let n_1 , be the number of moles of solvent in 1000 g then

$$X_B = m / (n_1 + m) = m/n_1 \quad (6)$$

Therefore, equation (5) will be

$$\Delta T_b = [RT_o^2 / \Delta H_v n_1] m \quad (7)$$

Finally, equation (7) reduces to

$$\Delta T_b = K_b m \quad (8)$$

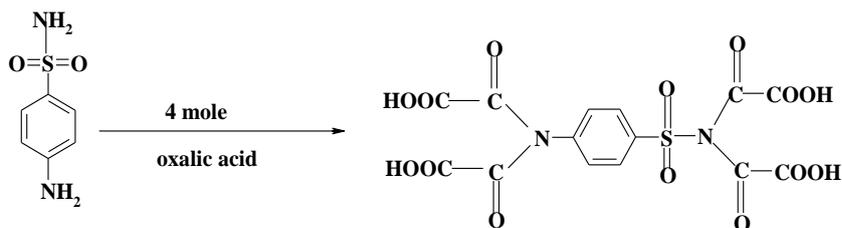
where K_b is called the molal boiling point elevation. If we let ΔT_b the boiling point elevation for solution containing W_2 g of solute (its molecular weight M_2) dissolved in W_1 g solvent, then the weight of solute per 1000 g solvent is $((W_2 \times 1000) / W_1)$ and hence, the molality of solution is

$$m = ((W_2 \times 1000) / (W_1 \times M_2)) \quad (9)$$

Knowing K_b , (12.2) in case of water and a determination of the boiling point elevation of a solution, one can calculate the molecular weight of the solute.

Preparation of organic ligand

The organic chelating agent was prepared by condensation of sulphanilamide (0.1 mole) and oxalic acid (0.4 mole) in xylene medium, using Dean and Stark apparatus. The theoretical amount of water was removed to produce N,N,N',N' -tetraoxaloyl sulphanilamide, which has a melting point 210°C . After crystallization from distilled water the yield percentage was found to be 82.5%.



Neutralization curves and determination of acid value

The experimental neutralization curve of 20ml (0.1 mole) of the prepared ligand (dopant) with 0.1N sodium hydroxide was determined by electrometric titration. The structure of the prepared dopant was confirmed to be tetrabasic. The acid dissociation constants for each proton in the prepared ligand (dopant) are given in Table 1.

The acid value of the prepared dopant was measured by dissolving a known

weight of the dopant in 25ml ethyl alcohol, then titrating the dopant solution with 0.1N ethanolic KOH solution. The acid value can be determined by applying the following equation

$$\text{Acid value} = (N \times V \times 56.1) / W \quad (10)$$

where N= Normality of KOH, V= volume in ml of KOH solution and W= weight of sample.

The acid value for the prepared dopant given in Table 1 is in good agreement with the suggested structure.

Preparation of pure PMMA and PMMA doped with the organic dopant

The pure PMMA samples and PMMA doped with ligand were prepared by mixing the monomer with benzoyl peroxide as a free radical initiator (8.264×10^{-3}) and the calculated amount of the ligand (1, 3, 5, 7, 10 and 15% with respect to the weight of MMA) in a soda glass tube (2.2 cm in diameter and 30cm length). The tubes were flushed with pure nitrogen gas and then sealed. The sealed tubes were put into an automatically controlled water bath at 60°C for several days. Finally, hard plastic samples were obtained for PMMA-ligand composite samples or pure PMMA.

Thermal treatment of the PMMA samples

The pure PMMA samples and PMMA doped with different percentages of the prepared organic dopant were thermally treated by using Muffle Furnace (Model CLF-M25.DAIHAN Scientific, Co. Ltd) under nitrogen atmosphere, taking into consideration the concepts of Cowley *et al.* ⁽⁵³⁾ experiment during the PMMA thermal treatment. The thin films of PMMA which had a thickness of 500 µm are subjected to thermal treatment between two plates of Aluminum connected to thermocouple at the required temperature to avoid temperature ingredient in the tested samples.

Measuring the area under the curve

For the calculation of the area under the curve; an aluminum foil sheet was cut into different pieces, which had different areas of 1-400 cm². Each aluminum foil piece was weighed then a calibration curve between the weight (g) and foil piece area (Cm²) was plotted. A straight line was obtained with Microsoft Excel5. The equation for this was as follows:

$$Y = 0.0077X + 0.0019 \quad (11)$$

where Y is the area and X is the weight.

Instrumentation

The IR spectra were obtained with a Shimazu FTIR 430 Jasco spectrophotometer (Japan) under conditions yielding the maximum resolution. All IR measurements were carried out at room temperature. The IR spectra of the PMMA/organic dopant composite samples before and after thermal treatment

were measured after the extraction of the organic dopant. This was carried by dissolving the PMMA in benzene thiophene free but the dopant was not dissolved in this solvent. After casting of the PMMA solution in petri-dish and complete drying of the film in vacuum oven at 60°C, the polymer films, which had the same thickness(100µm), were subjected to infrared measurements against air. The thicknesses of the PMMA films were measured by micrometer or optical method before and after thermal treatment with different temperatures and the extraction of the dopant material.

The ¹³C-NMR spectrum was recorded on a Varian Mercury VX-300 NMR spectrometer, running at 75.46 MHz in deuterated chloroform.

Carbon, Hydrogen, Nitrogen and Sulphur were determined by elemental analysis for the prepared organic dopant in the micro-analytical laboratory by oxygen flask combustion and dosmat E415 Titrator (Metrohm) at Cairo University.

Results and Discussion

IR spectrum of pure PMMA

The IR absorption bands of PMMA are summarized in Table 2. The most prominent absorption bands in the IR spectrum of PMMA are listed as C-H, C-O and C-C modes^(4, 54-61).

TABLE 2. The absorption infrared bands and their assignments for pure PMMA.

Wave number (Cm ⁻¹)	Assignments ^(4, 58, 70, 71)
747 ^m	CH ₂ skeletal stretching
843 ^m	CH ₃ Rocking vibration
966 ^m	Rocking deformation for α-CH ₃ group
989 ^m	∃ a C-O-C combined with OCH ₃ group
1070 ^m	Symmetric vibration for C-C skeletal mode
1193 ^b	Asymmetric vibration for C-O-C group with internal CH deformation
1242 ^b	Symmetric vibration for C-C-O combined with CH deformation
1388 ^m	Symmetric bending deformation for CH in α-CH ₃ group
1436 ^m	Symmetric bending deformation for CH in OCH ₃ group
1444 ^s	Symmetric bending deformation for CH in CH ₂ group
1730 ^s	Symmetric stretching vibration for C=O group
2850 ^m	Asymmetric stretching vibration for CH in aliphatic group
2950 ^b	Combination band involving ∃ CH and CH ₃ group

Effect of thermal treatment on the IR absorption bands of pure PMMA

Thermal degradation mechanism of PMMA has been studied extensively⁽⁶⁰⁻⁶⁴⁾. But, to our knowledge, the investigation of the mechanism of degradation and recombination which take place during thermal degradation of PMMA using FTIR method is not given in the literature. Sayyah *et al.* used the IR studies for investigation of the effect of gamma ray on the PMMA samples prepared in absence and presence of organic ligands and their cobalt (II) complex. They were successfully used for confirming the mechanism of degradation during gamma radiolysis^(65,66). The IR spectra of pure PMMA before and after thermal treatments are shown in Fig.1.

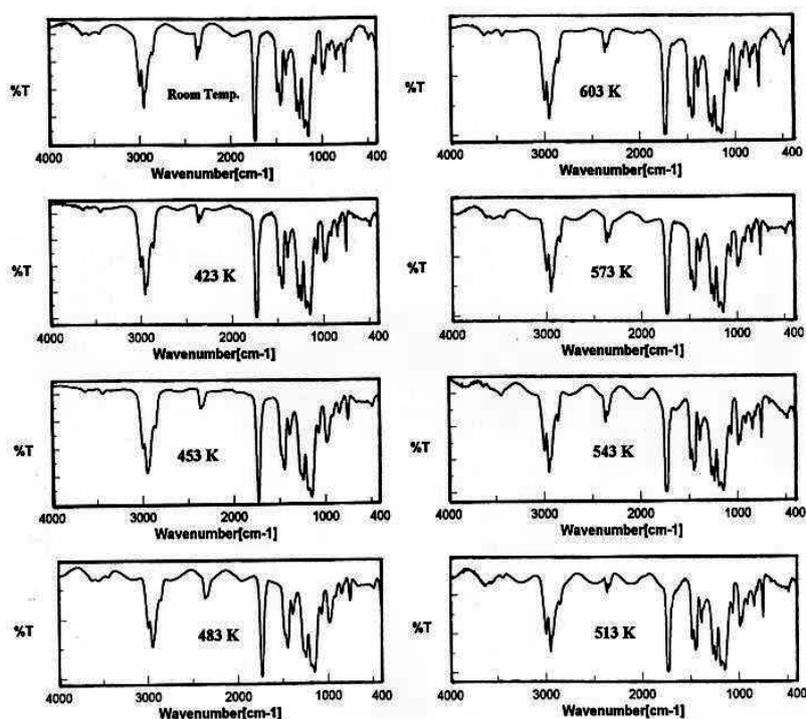


Fig.1. The IR spectra of pure PMMA before and after thermal treatment.

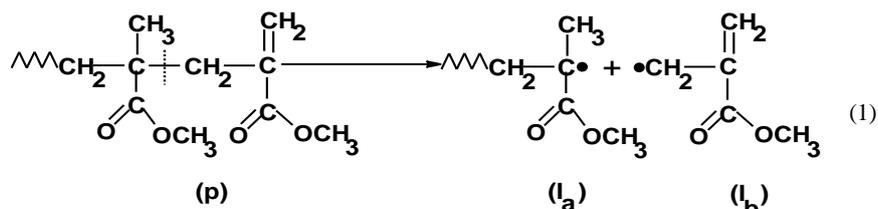
There are no drastic changes in the band positions, but some changes in the band intensities are observed. The variation of the band intensities with the increasing of temperature for absorption bands appearing at 1070, 1242, 1388, 1444 and 1730 cm^{-1} are graphically represented in Fig. 2. The changes in the band intensities for each absorption band are summarized as follows:

- (1) The changes in C-C modes along the polymeric chains appearing at 1070 cm^{-1} ^(12,37,46-47) with the increasing of temperature are as follows: The band intensity decrease from 423 K to 453 K, increase from 453 K to 543 K and

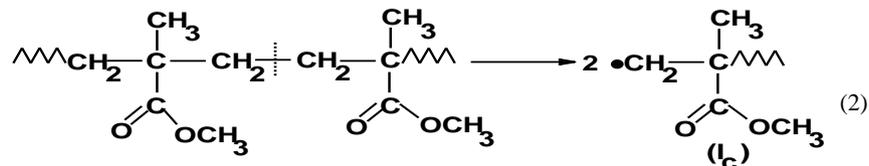
finally decrease from 543 to 603 K. The decrease in the band intensity can be explained by the following equations:

(i) At temperature lower than 473 K,

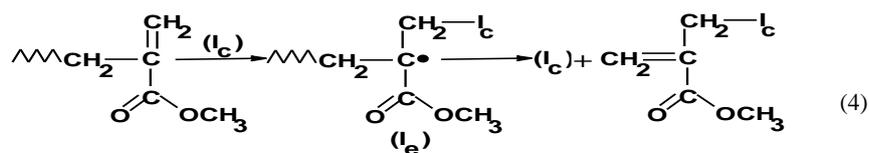
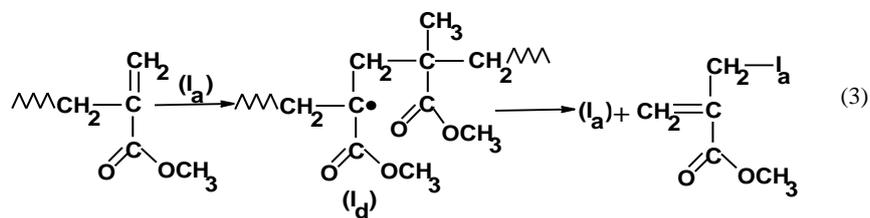
(a) PMMA degrades by scission at C-CH₂ as follows



(b) At the linkage of the small amount of head-to-head linkages generated during the preparation of radically polymerized PMMA are unstable and will decompose as shown in the following equation:

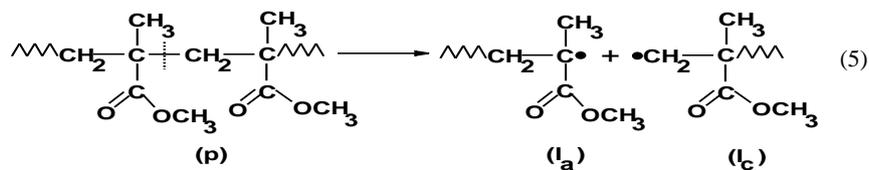


(c) PMMA(C=C) will decompose by chain transfer process

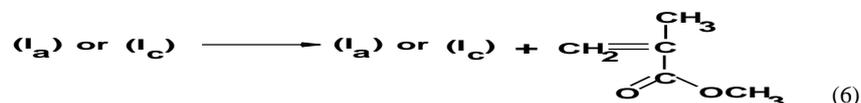


(ii) At temperature higher than 473 K by

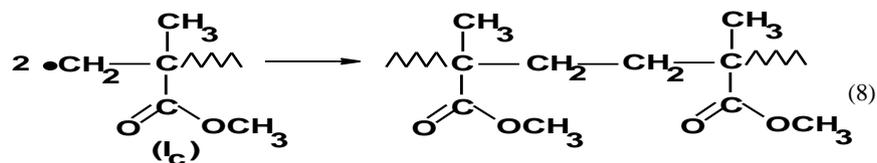
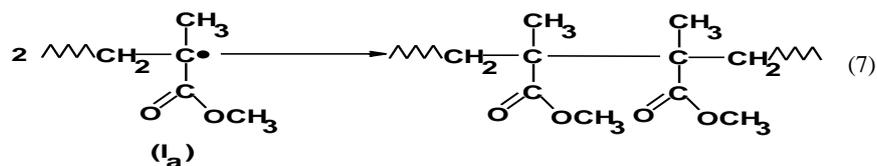
(a) random C-C scission:



(b) The intermediate products (I_a) and (I_c) further decompose to generate monomer:

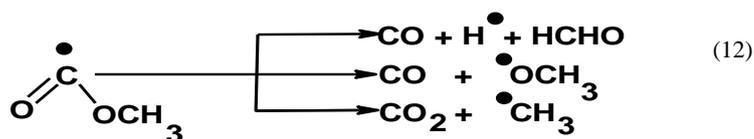
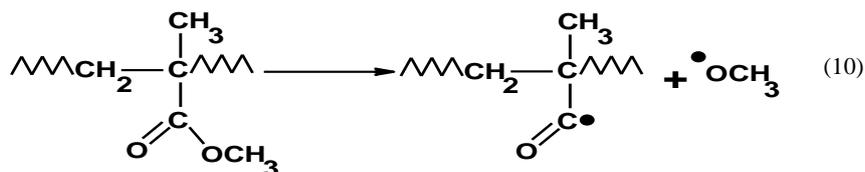


The increase in the band intensity from 453 K to 543 K can be explained by equations number 7 and 8:

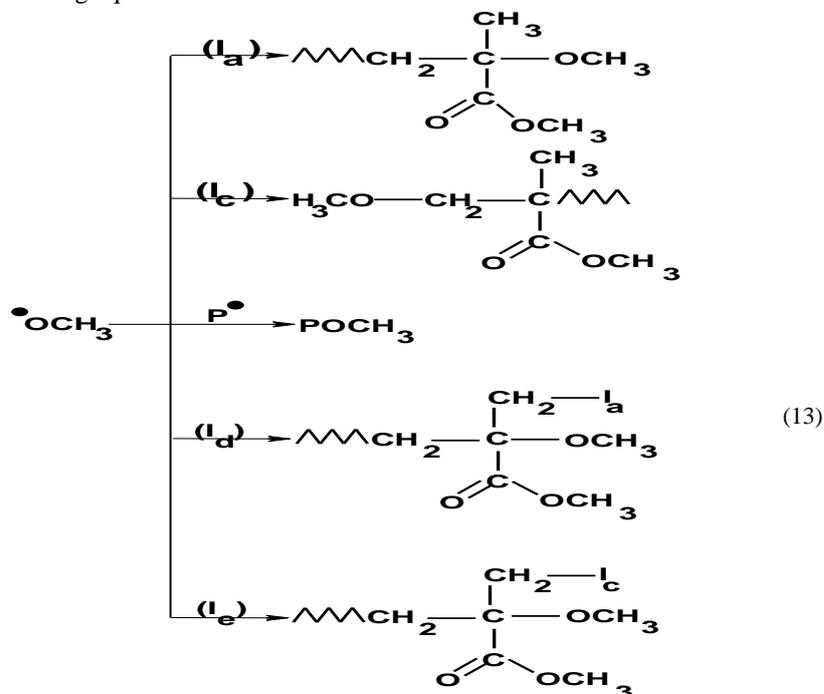


(2) For the absorption band appearing at 1242 cm⁻¹, which could be attributed to C-O stretching vibration in PMMA chain. The intensity decreases from 423K to 453K, increases from 453 K to 543 K and finally decreases from 543 K to 603 K.

The decrease in the band intensity from 423 K to 453 K and from 543 K to 603 K can be explained by the following equations:



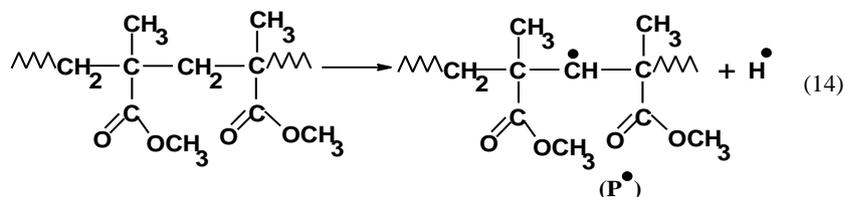
The increase in the band intensity from 453K to 543K can be explained by the following equations:



(3) For the absorption band appearing at 1388 cm^{-1} , which could be attributed to the deformation of methyl group, there were no drastic changes and it remained approximately constant with the increase of temperature.

(4) The changes of the band intensities of C-H modes ⁽¹²⁾ which appear at 1444 cm^{-1} are as follows: For the absorption band appearing at 1444 cm^{-1} , which could be attributed to the scissoring deformation in methylene group, the band intensity decreases from 423K to 453K, increases from 453K to 543K and finally decreases from 543K to 603K. The decrease in band intensity from 423K to 453K and from 543K to 603K could be explained by the following equations:

By abstraction of hydrogen from the PMMA chain,



The increase in the band intensity from 453K to 543K can be explained by the following equation:

$$P + I_c = P - I_c \quad (15)$$

- (5) The changes in C-O modes⁽⁶⁷⁻⁶⁹⁾ appearing at 1730 cm^{-1} , could be attributed to the stretching vibration in carbonyl group, where the band intensity decreases from 423K to 453K, increases from 453K to 543K and finally decreases from 543K to 603K.

The decrease in the band intensities from 423 K to 453 K and from 453K to 603K can be explained by the equations 11 and 12.

The increase in the band intensity from 453K and 543 K can be explained by equations 7 and 8.

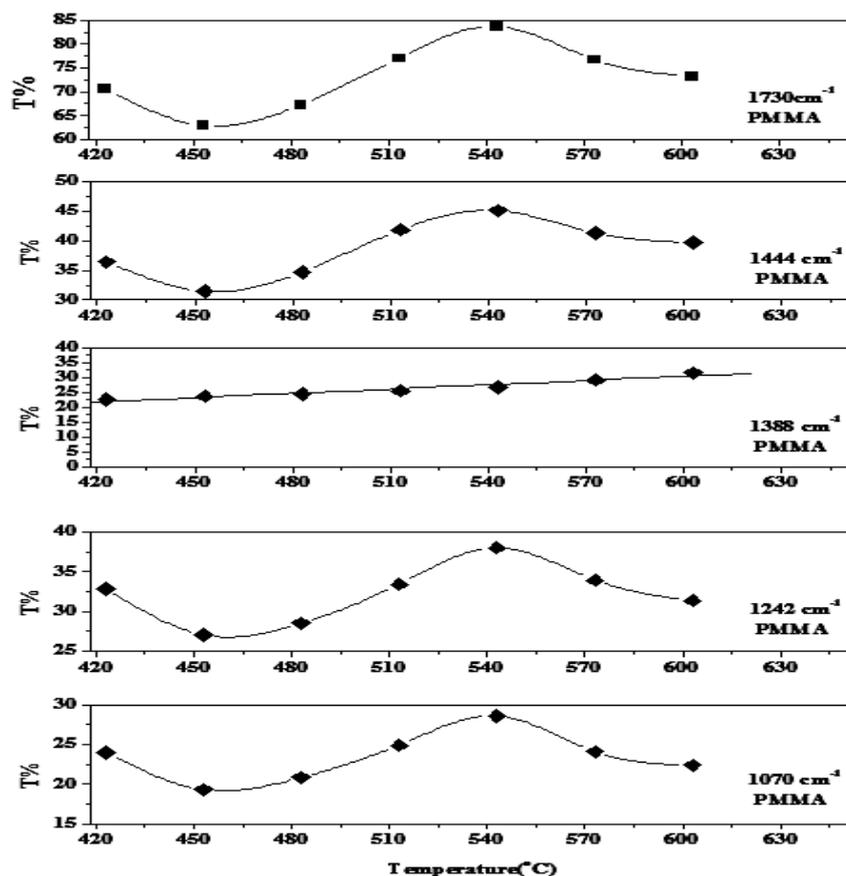


Fig. 2. Relation between band intensity and the temperature for the bands appearing at 1070, 1242, 1388, 1444 and 1730 cm^{-1} in case of pure PMMA.

The variation in the relative transmission data for the other groups can be explained by equations (10-15), as mentioned previously, in the case of band intensity behavior of pure PMMA with the increasing of the temperature.

The scission in the polymeric chain could also take place in side groups, such as the ester group. This affects the relative transmission of different groups present in the polymeric structure. The scission of the backbone chain was more predominant and had a marked effect in the case of pure PMMA. However, a lower effect was observed in case of the presence of the prepared organic dopant (*c.f.* Fig. 4).

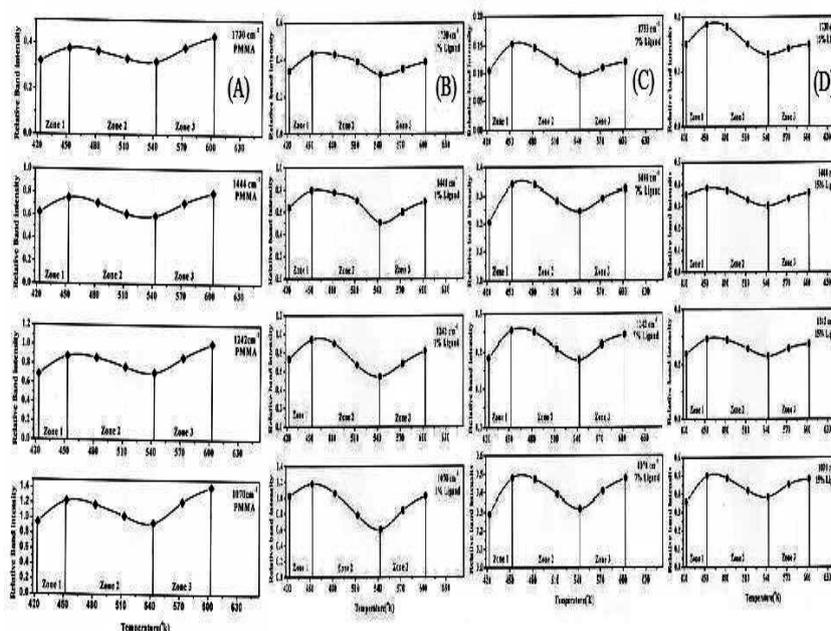


Fig. 4. Relation between different relative band intensity for PMMA samples and treatment temperature for :
 (A) Pure PMMA (B) 1% ligand (C) 7% Ligand (D) 15% Ligand.

As shown by the forementioned relations between the relative transmissions of the T_{1070} / T_{1388} , T_{1242} / T_{1388} , T_{1444} / T_{1388} and T_{1730} / T_{1388} and temperature, the area under the curve could be divided into three zones. Two zones were for the degradation process between 423-453K and 543-603K. The other zone was an indication of the recombination process from 453- 543K. The area under the curve was calculated for each zone and the data are summarized in Table 3. By cutting the curves represented in Fig. 4, taking into consideration the three zones, and weighing each aluminum foil piece, each is equal to a degradation zone and the recombination one. By using an appropriate computer program giving the weight, we obtained the area under the curve for each zone.

The area under the curve is also calculated by fitting procedures and the obtained data are in good agreement with what was found by the weight method.

From Table 3, it is clear that during the thermal treatment of pure PMMA, the degradation process predominated. The presence of the prepared organic dopant leads to the protection of PMMA against thermal degradation. The order of the thermal degradation process in the different polymeric samples was as follows: Pure PMMA > PMMA_{dopant15%} > PMMA_{dopant1%} > PMMA_{dopant7%}. This means that the most protective additive was the dopant that had 7% concentration in the polymeric matrix

TABLE 3. Area under the curves for the degradation and recombination processes in the absence and presence of different additives.

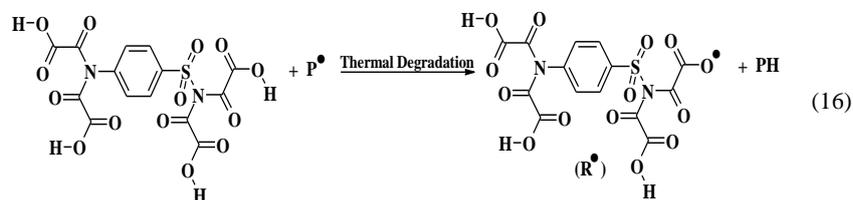
Area type corresponding to the different zones	Area in cm ²			
	Additives type			
	Pure PMMA	PMMA with dopant (1%)	PMMA with dopant (7%)	PMMA with dopant(15%)
Degradation (423 – 453) + (543 – 603) K	240.125 ^D	229.5 ^D	229.5 ^D	244.375 ^D
Recombination (453 – 543) K	234 ^R	247.625 ^R	250.625 ^R	256.625 ^R
Net area	6.125 ^D	18.125 ^R	21.125 ^R	12.25 ^R

where, D = Degradation process and R= Recombination process.

Protection mechanism of the prepared dopant

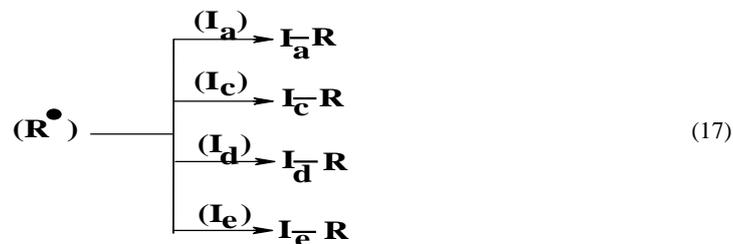
The prepared organic dopant (ligand) has one sulphur atom, one phenyl ring and four carboxylic groups in the structure. The radicals that can be formed during thermal treatments are listed in Table 4. Thermal degradation protection by the prepared additives may be considered to operate through the following two alternative mechanisms:

- 1) Some form of energy transfer may take place from PMMA to the additive, with the polymer being chemically unsaturated. The additive may either dissipate the energy without having any permanent chemical changes or may itself be modified or ceased to be active. In the latter case, the protection will cease when all the additives are destroyed or modified.
- 2) The additive may repair the damage caused by thermal treatment. In PMMA polymers, the major reaction is the loss of hydrogen atom leaving a polymer radical (P^{*}). Protection against further reactions can occur if the additive itself can furnish a hydrogen atom and remain a radical with a new activity as shown in the following equation:

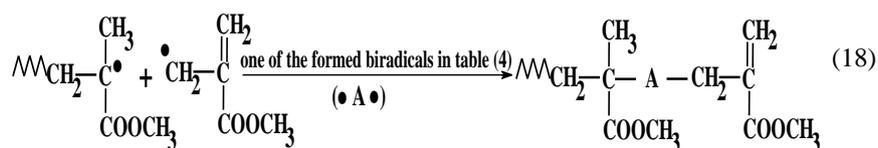

TABLE 4. Different radicals that can form during thermal degradation.

Radical formula and number	Z/M	Radical formula and number	Z/M	Radical formula and number	Z/M
$ \begin{array}{c} \text{O} \\ \parallel \\ \bullet \text{N} \text{---} \text{C} \text{---} \text{COOH} \\ \parallel \\ \text{O} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{O} \\ \parallel \\ \text{H-O} \end{array} $	160	$ \text{C}_6\text{H}_5^\bullet $	78	$ \bullet \text{COOH} $	45
$ \begin{array}{c} \text{O} \\ \parallel \\ \bullet \text{C} \text{---} \text{COOH} \end{array} $	73	$ \text{C}_6\text{H}_4 \text{---} \text{S} \text{---} \text{O}^\bullet $	140	$ \begin{array}{c} \text{O} \\ \parallel \\ \bullet \text{S} \bullet \\ \parallel \\ \text{O} \end{array} $	64

In the case of the degradation of PMMA by main chain fracture as shown in eq. (10), a protective additive molecule may combine with these radicals to form a stable side chain or less reactive radical as shown in the following equations:



The protective additive may link the two polymer radicals together and thereby heal a temperature-induced fracture. This means that there will be no significant change in the average molecular weight. These radicals are the biradicals listed in Table 4.



The forementioned mechanisms were confirmed by the appearance of absorption bands at 3200-3500 cm^{-1} for different groups combined with PMMA chains during thermal treatment.

Other absorption bands of these groups may be superimposed with the PMMA absorption bands. Also, the ^{13}C -NMR spectrum, represented in Fig. 5, shows two singlet signals in the region of $\delta = 120$ ppm, which indicates the presence of a benzene ring from the organic ligand in the PMMA chains, which heal a thermal degradation fracture.

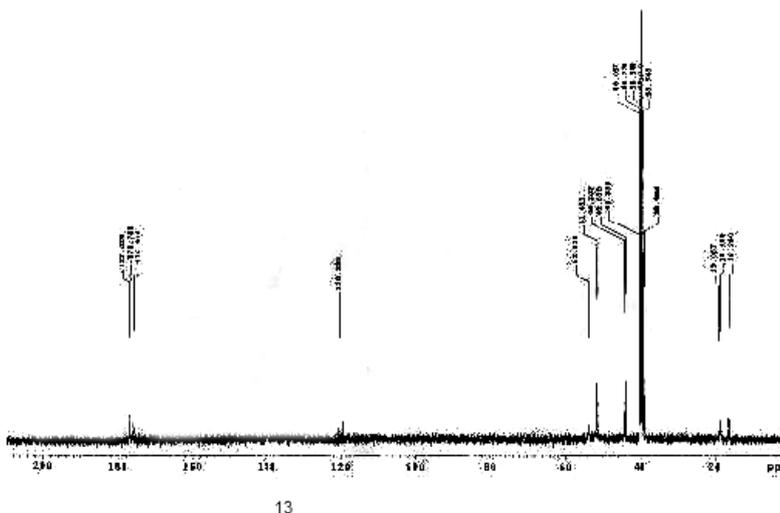


Fig. 5. C-NMR for PMMA samples.

Conclusion

In conclusion, the thermal degradation and recombination data reveal the following:

- Infrared measurements can be used as a successful method for the determination of the degradation and recombination of different group bands of PMMA such as CH_2 , C-O, C=O and C-C with raising the temperature.
- The following up of the degradation and recombination of different groups in PMMA chain segments with raising the temperature can also be given.
- The use of the combined technique of transmission data of C-C skeletal vibration, C-O, CH_2 and C=O bands with respect to the transmission band of methyl group and measurements of the area under the curve for the degradation and recombination zones is a good technique for obtaining an idea about the protection efficiency of the organic dopant.
- The presence of different thermolysis radicals in the PMMA chain segments was confirmed by ^{13}C NMR and mass spectroscopy.

- e) The most protective amount of the organic dopant in the PMMA matrix was found to be 7% of the polymer weight.

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دراسات لطيف الامتصاص في الأشعة تحت الحمراء لبعض عينات البولي ميثيل ميسكرليت المطعمة بمركب اوكسالوويل بارا سافاتيلايميد أثناء التعرض للحرارة

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لقد تم قياس طيف الامتصاص في الأشعة تحت الحمراء لبعض عينات البولي ميثيل ميسكرليت في وجود وغياب رباعي اوكسالوويل بارا سافاتيلايميد. كما تم دراسة التغيرات الطارئة على طيف الامتصاص في الأشعة تحت الحمراء و لأماكن منحنيات طيف الامتصاص ووجد أنه لا يوجد تغيرات ملحوظة في أماكن منحنيات الامتصاص ولكن هناك تغيرات في كثافة المنحنيات ، واستخدمت النفاذية النسبية لطيف الامتصاص عند الأطوال الموجية 1070 ، 1242 ، 1444 ، 1730 سم⁻¹ وقياسها بالنسبة إلى مجموعة المثيل الخاصة بمجموعة ميثيل ميسكرليت عند 1388 سم⁻¹ وهي الأكثر ثباتا أثناء التعرض للحرارة وباستخدام هذا التكنيك المترابك من الأطياف والنفاذة للتردد الهيكلي لمجموعات C=O,CH₂, C-O, C-C بالنسبة لنفاذية الضوء لمجموعة المثيل وقياس مساحة المنحنى لهذه القياسات لنطاقات التحطيم والاتحاد يمكن حساب قدرة حماية Ligand المحضر لبوليمر البولي ميثيل ميسكرليت أثناء التعرض للتأثير الحرارى.

ولقد تم تأكيد ميكانيكية الحماية لهذه المادة المحضرة لقياس طيف الكتلة للمادة العضوية المطعم بها البوليمر لمعرفة أنواع الشقوق العضوية التي يمكن أن تتكون أثناء التثبيح الحراري أو التعرض للحرارة وبقياس مطياف الكتلة للكربون 13 لعينات البولي ميثيل ميسكرليت مع المادة العضوية المحضرة بعد استخلاص المادة العضوية من العينات و التي تؤكد وجود شقوق الفينيل في سلاسل البوليمر بما يؤكد الميكانيكية المقترحة للحماية.

ولقد تم إثبات أن الحماية العظمى ضد التفسير الحراري للبولي ميثيل ميسكرليت وقد تم التوصل إليها عند تطعيم البولي ميثيل ميسكرليت بنسبة 7% من المركب العضوي المحضر (Ligand).