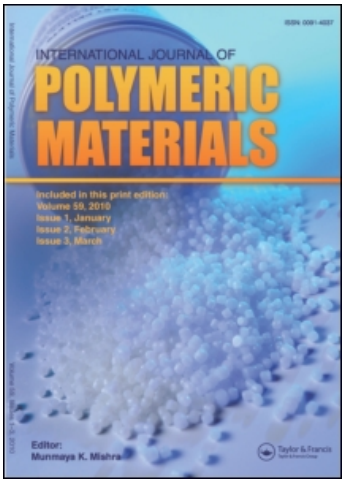

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Copolymerization of Benzylidene malononitrile with methyl methacrylate and spectroscopic studies before and after irradiation with gamma rays of the obtained copolymer

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COPOLYMERIZATION OF BENZYLIDENE MALONONITRILE WITH METHYL METHACRYLATE AND SPECTROSCOPIC STUDIES BEFORE AND AFTER IRRADIATION WITH GAMMA RAYS OF THE OBTAINED COPOLYMER

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Benzylidene malononitrile (BMN) monomer was prepared from the condensation of benzaldehyde with malononitrile in absolute ethanol as a reaction medium using few drops of piperidine as a catalyst at the reflux temperature for one hour. This monomer (BMN) was copolymerized with methyl methacrylate (MMA) by solution polymerization technique in the presence of benzoyl peroxide as a free radical initiator using dimethyl formamide as a reaction medium in a sealed tube under a nitrogen atmosphere at 65°C.

The Kelen–Tudös and Fineman–Ross methods were used to determine the copolymerization parameters of MMA (M_1) and BMN (M_2) monomers. It was found that, the reactivity ratios r_1 and r_2 for MMA and BMN are equal to 2.45, 0.12 ± 0.05 respectively. Alfrey Price (Q) and (e) values were calculated and the obtained data indicated that the copolymer structure is a block system.

Also, infrared, ^{1}H-NMR and UV-visible spectroscopic studies for the obtained copolymer were performed. Further UV-visible studies of the PMMA film blended with 1% by weight of the prepared MMA-BMN copolymer were carried out before and after irradiation with different gamma doses in the range from 0–100 KGy.

Keywords: Copolymerization; Gamma-rays irradiation; Benzylidene malononitrile; Methyl methacrylate; Spectroscopy

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1. INTRODUCTION

Cis- and *trans*-cinnamonitrile were polymerized in the presence of various anionic catalysts such as grignard reagent, alkali metal naphthalenes and calcium zinc tetraethyl [1]. But the study of copolymerization reaction of benzylidene malononitrile (BMN) with some vinyl monomers such as methyl methacrylate (MMA), to the best of our knowledge, have not been investigated. Benzalacetophenone, does not homopolymerize, but copolymerizes with styrene to form copolymers with benzalacetophenone units incorporated separately in the main chain. Such copolymer has excellent photodegradability. Although benzalacetophenone copolymerizes with styrene in the presence of radical initiator such as azobisisobutyronitrile, it was reported that benzalacetophenone does not copolymerize with MMA. Since the copolymer of MMA with benzalacetophenone would also be of interest as a photodegradable polymer, successful attempt was obtained by using $SnCl_4$ [2]. Benzalacetophenone was copolymerized with styrene by radical polymerization in bulk or suspension [3], but benzalacetone was copolymerized by emulsion polymerization [4]. Copolymerization of the substituted aldehydes, crotonaldehyde, Cinnamaldehyde, 2-methyl-3-phenylacrylaldehyde, 3-(2-furyl) acrylaldehyde and 3-(2-furyl)-2-methacrylaldehyde with styrene was affected by steric hindrance and by transfer reactions, and the polymerization rate decreases in the presence of even small proportions of aldehyde in the monomer feed, especially, for the furyl derivatives [5].

Radical polymerization of styrene with substituted vinyl cinnamates was investigated at 60°C [6–10], while benzylidene malononitrile was copolymerized with vinyl acetate or *N*-vinyl pyrrolidone. Highly photoreactive polymers containing benzylidene or cinnamate units have been synthesized [11–20].

One of the most successfully applied in dosimetry is poly(methyl methacrylate) PMMA [21, 22]. Gamma ray dosimeter was also reported by using styrene – methacrylic acid polymer and converting the carboxyl pendant groups along the polymer chain to polar—COOK or—COONa groups resulting in electrically conducting products which lost electric conductivity after exposure to gamma radiation [23]. Some PMMA films doped with some amine derivatives were investigated as gamma ray dosimeter by Sayyah *et al.* [24, 25].

In the present study we intend to examine the behavior of BMN in copolymerization with MMA monomer. Also, this work describes the reactivity ratio determinations by two methods, Fireman–Ross [26] and Kelen–Tudös [27]. The Alfery and Price [28] (Q) and (e) values were calculated and the characterization of the obtained copolymer by ^{1}H-NMR,IR and UV-visible spectroscopy was carried out. The

potential use of the produced copolymer as gamma dosimeter was also investigated.

2. EXPERIMENTAL

2.1. Materials

Methyl methacrylate (MMA) monomer was a product of Merck-Schuchardt, yield 99%, stabilized with 100 ppm hydroquinone, specific gravity (20/4°C) 0.942 to 0.944 g/cm^3. It was purified as described in a previous article [28]. The pure and blended PMMA film samples are prepared by casting technique as previously described by Sayyah *et al.* [30].

Benzaldehyde was a product of Prolabo Chemical Company (England). Absolute ethanol (b.p = 78°C), dimethyl formamide (DMF) (b.p = 143°C) were of chemically pure grade from El-Nasr Pharmaceutical Chemical Company, Egypt. Malononitrile was a product of B.D.H Chemical Company (England). Benzoyl Peroxide as a free radical initiator was of chemically pure grade from El-Nasr Pharmaceutical Chemical Company, Germany. Other solvents used in this work were of analytical pure grade and twice distilled over the suitable drying agent.

2.2. Methods of Preparation and Characterization

2.2.1. Preparation of Benzylidene Malononitrile Monomer

Benzylidene malononitrile (BMN) was prepared from the condensation of benzaldehyde with malononitrile in absolute ethanol as a medium and a few drops of pipridene as catalyst at the reflux temperature for one hour. Recrystallization of the product from absolute ethanol was carried out to obtain faint yellow crystalline product, which has melting point = 80°C, the yield of the product was 90%.

2.2.2. Instrumental Analysis

The carbon hydrogen and nitrogen contents of the prepared polymer samples were determined in the micro analytical laboratory, Cairo University, Egypt. The ultraviolet-visible absorption spectra of the prepared polymers were measured using Varian 634 spectrophotometer at room temperature in the region 200–750 nm. The PMMA films were adjusted to constant thickness (500 μm) and concentration (1% of benzylidene polymers) as a blended material based on the PMMA weight. Infrared measurements were carried out using Pye-Unicam Sp 2000 spectrophotometer.

The ^{1}H-NMR measurements were carried out using Perkin–Elmer R32, 90 MHZ, NMR spectrophotometer. The NMR proton signals of the

prepared polymers have been recorded in dimethyl sulfoxide with tetramethylsilane as internal reference.

2.2.3. γ-Irradiation of the PMMA Films

Egypt's Mega gamma I, supplied as type J-6300 by Canada Ltd., of the atomic Energy and situated at the National Center for Radiation and Technology, was used. The ^{60}Co source having an activity of 137000 Ci was used for γ-irradiation of the PMMA films. The radiation doses 5, 15, 25, 35, 50, 75 and 100 KGy were measured by radiochromic dye film on prespex. The overall error in the dose measurements did not exceed $\pm$ 4%.

3. RESULTS AND DISCUSSION

3.1. Copolymerization Reaction between Methyl Methacrylate (MMA) and Benzylidene Malononitrile (BMN)

The monomer reactivity ratios of the copolymerization system (r_1 and r_2) involving methyl methacrylate and nitrogen containing monomer were determined on the basis of comonomer composition – copolymer composition relationship. The copolymer composition of each sample was calculated according to its nitrogen content as follows:

$$\frac{\text{Nitrogen percentage of copolymer}}{\text{Nitrogen percentage of } M2} = \frac{\text{molecular weight of } M2}{\text{molecular weight of } M2 + \text{molecular weight of } M1/b(1)}$$

where M_2 is the nitrogen containing monomer (BMN) and $b = m_2/m_1$ is the molar ratio of copolymer composition. The monomer reactivity ratios of each system were calculated according to Fineman–Ross [26] and Kelen–Tudös [27] methods.

3.1.1. Fineman–Ross Method

The copolymerization reaction between MMA and BMN was carried out in a round bottom flask equipped with reflux condenser in the presence of benzoyl peroxide as free radical initiator using dimethyl formamide as a medium under nitrogen atmosphere at 65°C. The total concentration of the two monomers was 1M. The copolymerization reaction was stopped by adding small quantity of hydroquinone and precipitated by water/methanol mixture (60:40 v/v), steam distilled to remove the unreacted MMA and solvent, and dried in a vacuum oven for 6 hours at 60°C. The two monomers are incorporated into the copolymer chains depending on their relative concentrations and reactivities.

The composition of the copolymer was quantitatively determined by nitrogen analysis of the copolymer samples at conversion percentage between 5 and 10%. The initial monomer concentrations, copolymer composition and conversion percentage are summarized in Table 1.

The monomer reactivity ratios r_1 and r_2 of this copolymer was calculated from the data of Table 1 by application of the Fineman–Ross equation:

$$F/f\,(f-1) = r_1(F^2/f) - r_2$$

where

$F = M_1/M_2$ (molar ratio for monomer composition) and
$f = m_1/m_2$ (molar ratio for copolymer composition)

The values of $F/f\,(f-1)$ and (F^2/f) are calculated and a plot relating them is given in Figure 1. The slope and intercept of the diagram represented in Figure 1 are equal to $r_1 = 2.4$ and $r_2 = 0.12$ respectively.

3.1.2. Kelen–Tudös Method

The values of Y_1, Y_2, X and Y are summarized in Table 2. From X and Y values, η and ζ are calculated. The plot between η and ζ is represented in Figure 2, from which r_1 and r_2 can be calculated. Where $-r_2/\alpha =$ intercept with η coordinate, but $r_1 =$ value of η when $\zeta = 1$.

TABLE 1 Reactivity ratio data for MMA (M_1) and BMN (M_2) copolymerization system

	Initial monomer concentration									
	Molar fraction		*Weight*				*Produced copolymer*		*Copolymer*	
	M_1	M_2	M_1	M_2	*Reaction time*		*Conv.*	*N*	*composition*	
No.	*MMA*	*BMN*	(g)	(g)	*Hours*	*Min*	(%)	(%)	m_1	m_2
1	0.8	0.2	0.722	0.278	11	–	52.30	2.40	–	–
					–	3	2.87	2.30	0.873	0.082
2	0.7	0.3	0.603	0.397	18	–	32.60	3.70	–	–
					–	5	7.63	3.60	0.802	0.129
3	0.6	0.4	0.494	0.506	16	–	21.70	4.80	–	–
					–	10	9.18	4.90	0.730	0.175
4	0.5	0.5	0.394	0.606	16	–	18.76	5.80	–	–
					–	15	5.67	5.90	0.675	0.211
5	0.4	0.6	0.302	0.698	20	–	29.40	7.00	–	–
					1	–	6.63	7.10	0.609	0.254
6	0.3	0.7	0.218	0.782	20	–	15.28	8.20	–	–
					4	–	7.49	8.30	0.543	0.296

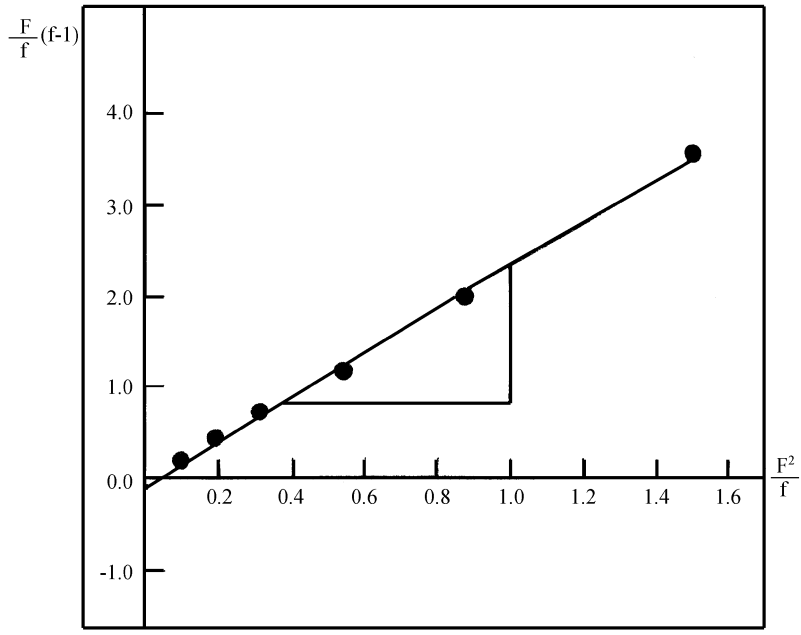


FIGURE 1 Fineman – Ross plot; determination of the monomer reactivity ratios of MMA-BMN copolymer system.

TABLE 2 Kelen – Tudös parameters for MMA-BMN copolymer system

	Molar ratio in monomer feed		M_1/M_2	*Molar fraction of m_1 in copolymer*	*Molar fraction of m_2 in copolymer*	Y_1/Y_2		
No.	M_1	M_2	(X)	(Y_1)	(Y_2)	(Y)	η	ζ
1	0.8	0.2	4.00	0.914	0.086	10.628	1.912	0.794
2	0.7	0.3	2.33	0.861	0.139	6.194	1.543	0.692
3	0.6	0.4	1.50	0.807	0.193	4.181	1.229	0.580
4	0.5	0.5	1.00	0.762	0.238	3.202	0.979	0.445
5	0.4	0.6	0.67	0.706	0.294	2.401	0.678	0.324
6	0.3	0.7	0.43	0.647	0.353	1.833	0.361	0.206

The calculated monomer reactivity ratios according to the two methods (*i.e.*, Fineman – Ross and Kelen – Tudös) are summarized in Table 3. From Table 3 it is clear that the values of r_1 and r_2 calculated by the Finman – Ross are in good agreement with those calculated by Kelen – Tudös.

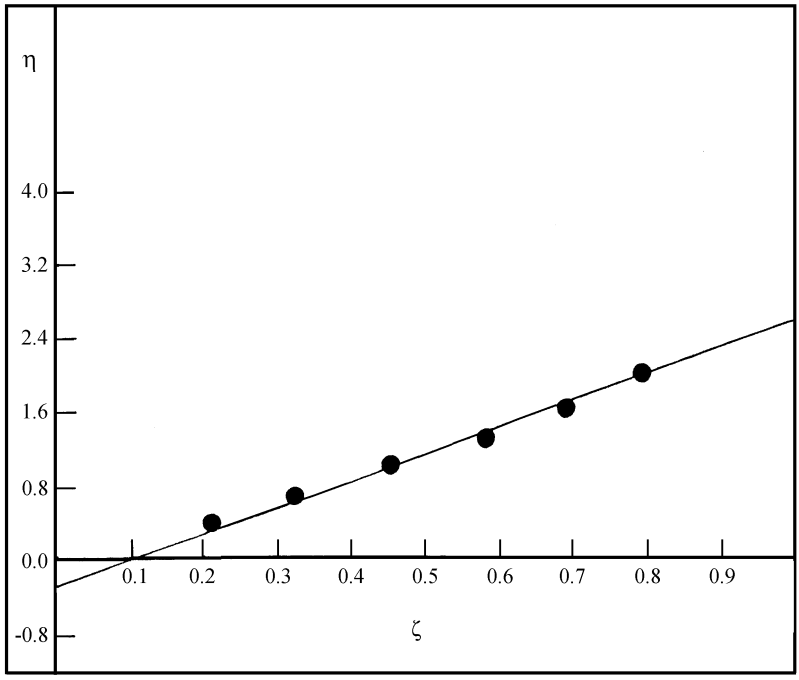


FIGURE 2 Kelen–Tudös plot: determination of the monomer reactivity ratios of MMA-BMN copolymer system.

TABLE 3 Monomer reactivity ratios for MMA-BMN copolymerization system

Copolymer system	*Fineman–Ross (I)*		*Kelen–Tudös (II)*		r_1r_2							
M_1-M_2	r_1	r_2	r_1	r_2	(*I*)	(*II*)	r_1^*	r_2^*	Q_1	e_1	Q_2	e_2
MMA-BMN	2.4	0.12	2.5	0.12	0.3	0.39	2.45 ± 0.05	0.12 ± 0.00	0.74	0.4	0.19	− 0.71

r_1^* and r_2^* are the mean values of the obtained experimental results of the two methods (Fineman–Ross and Kelen–Tudös).

Table 3 shows that the value of r_1 is more than one and r_2 is less than one. In this case the propagation reaction type 11 and 21 will be preferred than the type 12 and 22, hence the probability of M_1 entering into the copolymer chain is higher as compared to M_2. The copolymer formed will, therefore be richer in M_1. If r_1 and r_2 differ very widely, the copolymer

formed will comprise almost entirely M_1 and it will be very difficult to incorporate any appreciable quantity of M_2 in the copolymer chain. The copolymer composition data for the investigated system is calculated and the relation between mole fraction of M_1 in the copolymer formed (n_1) and the mole fraction of M_1 in the monomer feed (N_1) is represented in Figure 3. From this figure, it is clear that all points are lied on the left side of the azeotropic line, which means that the copolymer compositions are richer in M_1 in their chains. From the above obtained data, it is also clear that the copolymer structure is a block structure.

Therefore, the copolymerization mechanism can be represented as shown in Scheme (1).

The (Q), (e) values were calculated from the monomer reactivity ratio by using Alfrey–Price equations.

$$e_1 = e_2 \pm (-\ln r_1 r_2)^{0.5}$$

$$Q_1 = (Q_2/r_2) \exp .^{(-e(e-e))}_{2\ 2\ 1}$$

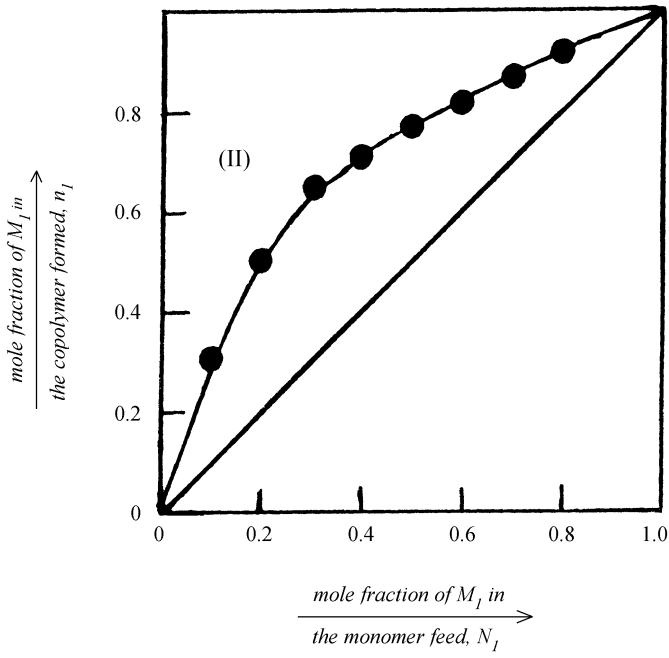
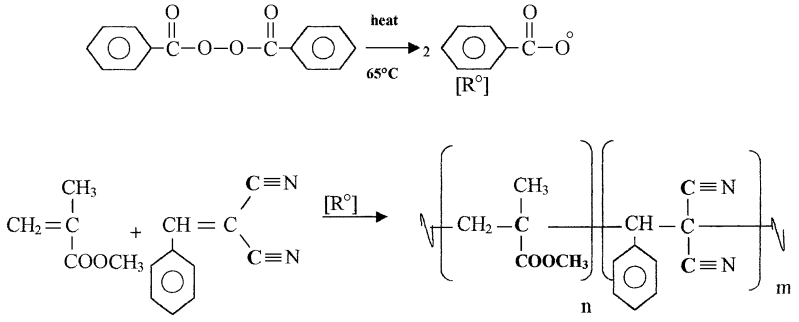


FIGURE 3 Composition curve for the copolymerization reaction between MMA and BMN.



SCHEME 1.

The (Q) and (e) values which represent the extent of resonance stabilization and the polarity of the double bond, respectively, in a monomer and its radical are extensively tabulated by young [31] from earlier copolymerization data. Thus, the average (Q), (e) values for the investigated system by using the monomer reactivity ratios for the investigated monomer pair, were calculated and given in Table 3. The obtained data show that the monomer pair is block copolymer. The negative value of e_2 indicate that the double bond in the benzylidene malononitrile is more stabilized than that present in MMA.

3.2. Infrared Spectroscopic Studies on the MMA-BMN Copolymer

Infrared spectra of polymethyl methacrylate, polybenzylidene malononitrile and benzylidene malononitrile-methyl methacrylate-copolymer are represented in Figure 4. The infrared spectrum of PMMA shows absorption bands in the region (1300 ····1050 cm^{-1}) instead of one single band in simple ester, which is in good agreement with what found by Krimm *et al.* [32]. In case MMA-BMN copolymer sample, the methyl acetate group shows large broadening of these bands which could be attributed to the superimposed of the bands characteristics for the aliphatic and aromatic CH deformation of BMN unit in this region. The sharp band appearing at 1731 cm^{-1} could be assigned to the carbonyl group frequency in the ester group of PMMA sample (Fig. 4a). In case of the copolymer sample, a broad splitted band appears at 1724 cm^{-1} and 1672 cm^{-1}, which could be attributed to the carbonyl group frequency and the stretching vibration of C=C in aromatic ring of BMN unit in this region. This leads to a slight shift of the two bands and slight broadening. For the PMMA sample, bands at 2996, 2951 and 2848 cm^{-1} were observed. These bands are all associated with the C—H stretching vibration. The intensities of the first two bands were found to be

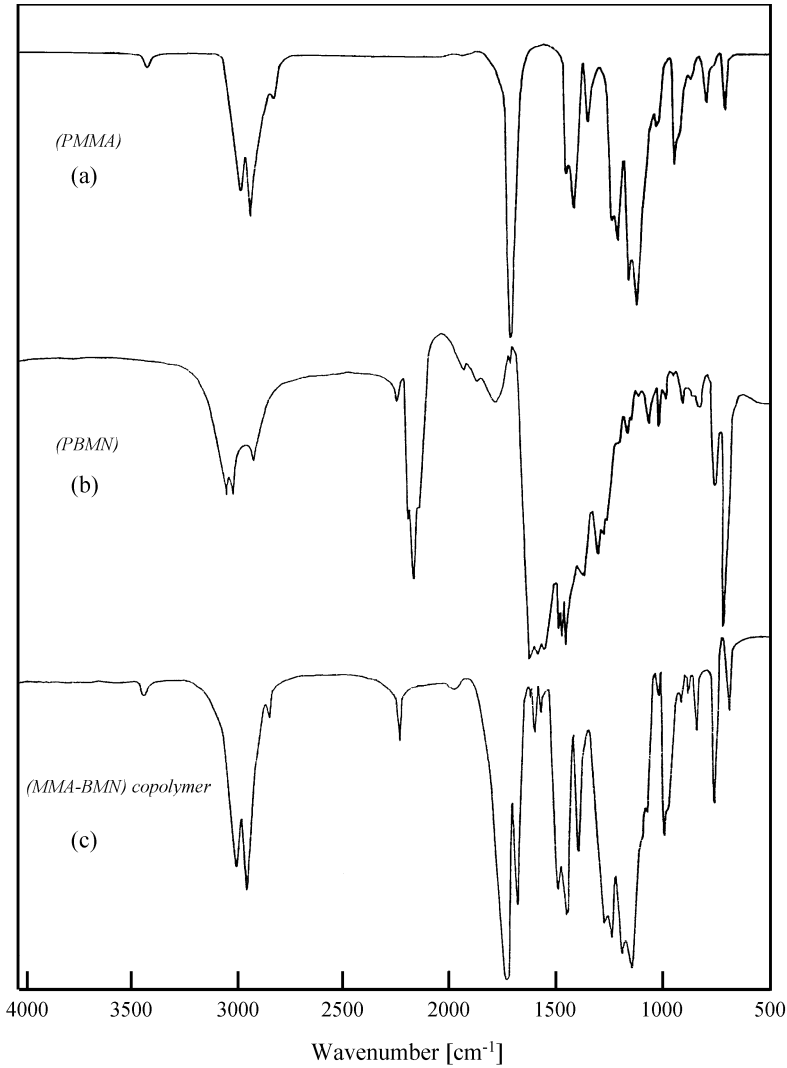


FIGURE 4 Infrared spectra of the prepared PMMA, PBMN and MMA-BMN copolymer samples.

larger than that of the latter. This could be explained in terms of different stretching vibrations of the two methyl groups in PMMA sample. The bands at 2996 and 2951 cm^{-1} are attributed to the fundamental vibrations of the ester methyl group. The third band at 2848 cm^{-1} is referred to the methyl

group attached to the carbon atom [33]. In case of BMN homopolymer only one weak band appears at 2930 cm^{-1} due to the asymmetric stretching vibration of C—H in methine group. But in case of copolymer, this band became sharp and shifted to higher wave number (*i.e.*, 2948 cm^{-1}) which could be attributed to the superimposed of the C—H band of methine group in BMN unit and CH stretching vibration of ester methyl group of MMA unit.

The investigated PMMA sample shows three bands at 1484, 1449 and 1387 cm^{-1}, respectively, which are attributed to C—H deformation. These bands appear also in case of the copolymer but at lower wave number (at 1479, 1438 and 1386 cm^{-1} respectively). The increase of the intensity of these bands are due to the superimposed of the characteristic bands for CH deformation in case of MMA unit and the C=C stretching vibration in aromatic system in case of BMN unit.

The infrared spectrum of the BMN-MMA copolymer shows some variations from the infrared spectra of both homopolymer samples, which can be summarized as follows:

(1) The band appears at 3445 cm^{-1} for overtone and combination of C=O group, appears only in case of PMMA sample and in case of copolymer.
(2) Instead of three absorption bands in the region 2275–2161 cm^{-1}, only one band appears in case of the copolymer at 2231 cm^{-1} which could be attributed to the nitrile group.
(3) In the region 1672–1492 cm^{-1}, the absorption bands which are characteristic for C=C in aromatic system in case of BMN homopolymer but with a slight shift to a higher wave number, but disappear in case of PMMA sample.
(4) The bands, which appear in case of PMMA at 1242 and 1271 cm^{-1} appears also in case of copolymer at 1238 and 1269 cm^{-1} which, could be attributed to C—O stretching vibration. These two bands disappear in case of BMN homopolymer.
(5) In the region 983–686 cm^{-1}, only two bands appear in case of PMMA and seven bands appear in case of BMN-MMA copolymer (*cf.* Tab. 4).

3.3. ^{1}H-NMR Studies of MMA-BMN Copolymer

The proton MNR spectrum of MMA-BMN copolymer, is represented in Figure 5. The spectrum shows the following observations:

(i) The singlet signal appears at $\delta = 0.8$ ppm, is due to the —CH_3 proton in MMA unit.

TABLE 4 Absorption bands and their assignments in the infrared spectra of the prepared benzylidene malononitrile – methyl methacrylate co-polymer

Wave Number (cm^{-1})			
Name			
PMMA	*Homo.*	*Copoly.*	*Assignment*
–	700^{s}	686^{m}	Out of plane C—H def. showing monosubstituted benzene ring in PBMN and its copolymer or CH_2 rocking in MMA unit
751^{m}	756^{m}	745^{s}	
849^{m}	–	838^{m}	C—H def. in ketones or CH_3 rocking vibration
–	–	876^{w}	
–	–	907^{w}	
925^{w}	–	–	$\gamma(\alpha\text{-}CH_3)$ in MMA unit
967^{sh}	–	$959^{sh(9)}$	
989^{m}	–	$983^{s(9)}$	δ_a(C—O—C) combined with CH_3O
–	1021^{w}	1010^{w}	δ C—H aromatic in PBMN and its copolymer or intramolecular interation C—C skeletal mode in MMA unit
1065^{w}	1070^{w}	1062^{sh}	
–	–	1086^{sh}	
$1150^{s(1)}$	1154^{sh}	$1141^{s(10)}$	δ C—H aromatic in PBMN and its copolymer or C—O str. with internal C—H def. in MMA unit
$1193^{s(1)}$	1176^{w}	$1186^{s(10)}$	
–	1218^{sh}	–	
$1242^{s(2)}$	–	$1238^{(11)}$	δ CH_2 (external deformation) or C—O str.
$1271^{s(2)}$	–	$1269^{(11)}$	C—O str. combined with C—H def.
–	1288^{sh}	–	δ C—H aromatic
–	1316^{m}	–	δ CH_2 def. aliphatic in PBMN and its copolymer or CH_3, CH_3—CH_2 Str. in MMA unit
1387^{m}	1388^{sh}	1386^{s}	
$1449^{s(3)}$	$1450^{s(5)}$	$1438^{s(12)}$	[C=C aromatic ring of PBMN and its copolymer] or [δ CH_2 (internal def.) or α-CH_3 in MMA unit]
$1484^{s(3)}$	$1471^{(5)}$	$1479^{(12)}$	

–	1492[(5)]	–	
–	1556[(6)]	1569[w]	
–	1588[(6)]	1590[m]	C═C aromatic ring
–	1634[(6)]	1614[w]	
–	–	1672[s]	
1731[s]	–	1724[s]	C═O str.
–	1803[b]	–	Combination and overtone bands of monosubstituted aromatic ring
–	1887	–	
–	1950	1966[w]	
–	2161[sh(7)]	–	
–	2190[s(7)]	–	C≡N stretching
–	2218[sh(7)]	2231[w]	
–	2275[w]	–	
2849[w]	–	2845[sh]	CH asym. str. aliphatic in mithine group
2951[s(4)]	2930[m]	2948[s(13)]	CH asym. str. aliphatic in methylene group
2996[s(4)]	–	2997[s(13)]	CH asym. str. aliphatic in mithine group
–	3028[m(8)]	–	
–	3063[m(8)]	–	CH str. aromatic
–	3088[sh(8)]	–	
3445[w]	–	3445[w]	Overtone and combination band of C═O

[(1)–(5), (7)–(13)] = sp; [(6) = b and sp].

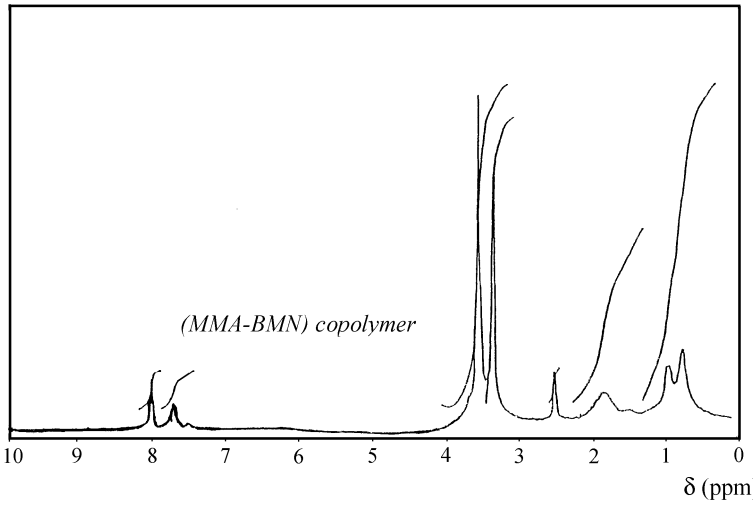


FIGURE 5 ^{1}H-NMR spectrum of the prepared MMA-BMN copolymer sample.

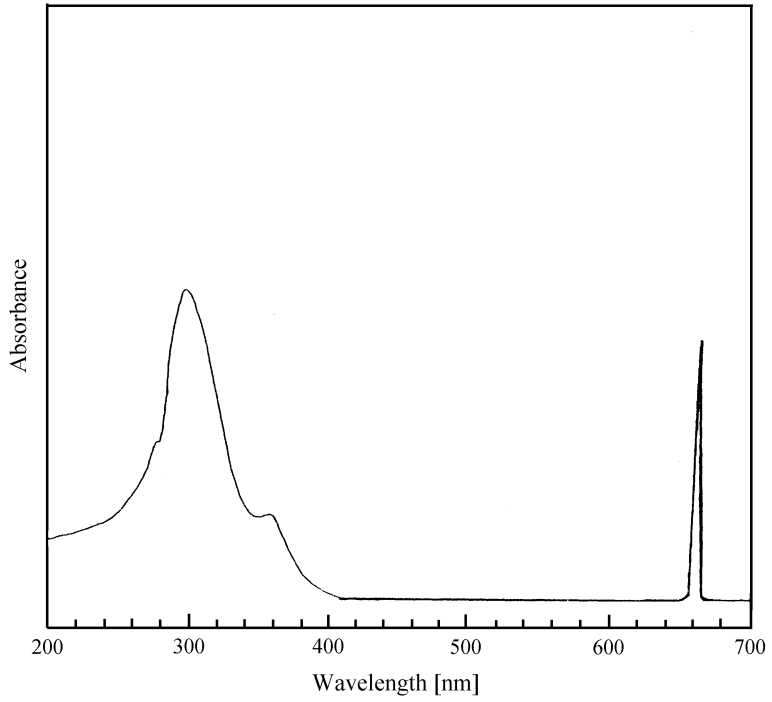


FIGURE 6 Ultraviolet-visible spectrum of the prepared MMA-BMN copolymer sample.

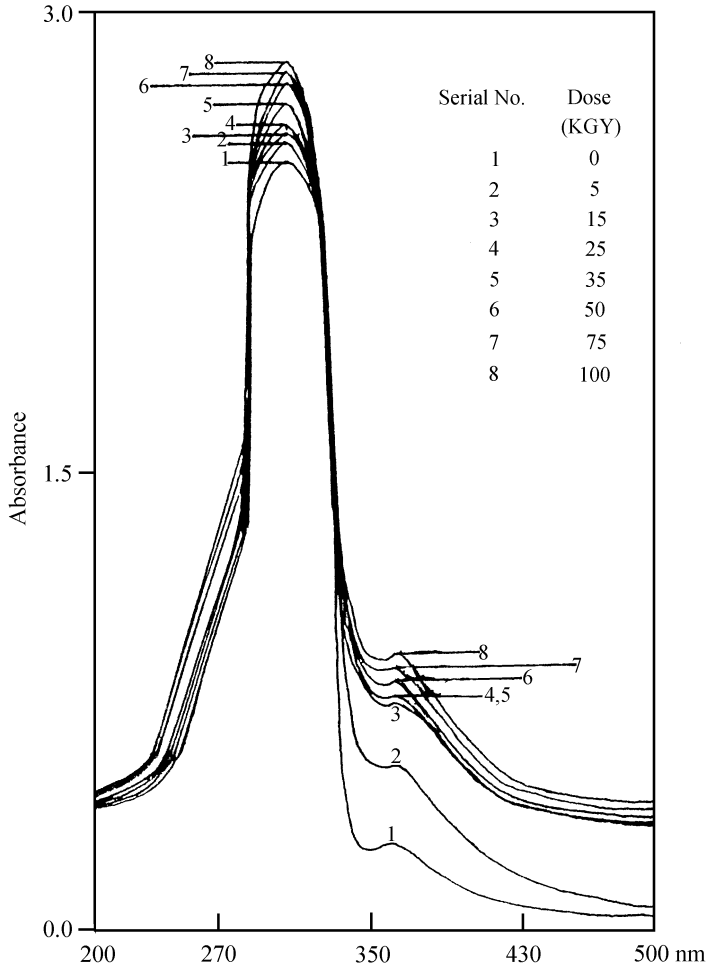


FIGURE 7 Ultraviolet spectra of PMMA blended film with MMA-BMN copolymer (1%) with the increasing of the γ-irradiation doses.

(ii) The singlet signal appears at $\delta = 1.0$ ppm, may be due to the methylene protons in MMA unit.
(iii) The singlet signal appears at $\delta = 1.8$ ppm, is due to aliphatic methine group proton in MMA unit.
(iv) The singlet signal appears at $\delta = 3.3$ ppm, is due to the OCH_3 protons in MMA unit.
(v) One multiplet signal appears at $\delta = 7.6$ ppm and singlet signal appears at $\delta = 8.0$ ppm are due to the phenyl ring protons.

3.4. Ultraviolet-Visible Studies of MMA-BMN Copolymer

The ultraviolet-visible spectrum of the prepared copolymer using dimethyl formamide (DMF) as solvent for the copolymer sample and reference is represented in Figure 6. There are four maximum absorption bands (λ max) at 279, 307, 361 and 664 nm. These bands are due to $\pi-\pi^*$-transition E_2-band in benzene ring, $\pi-\pi^*$-transition B-band ($A_{1g} - B_{2u}$), $\pi-\pi^*$-transition of substituted benzene ring and the visible absorption band due to the colour and conjugation of the phenyl ring with the substituted aliphatic side chain respectively.

3.5. Ultraviolet Spectra of PMMA Film Blended with MMA-BMN Copolymer (1%) during Radiolysis

The ultraviolet spectra of PMMA film blended with MMA-BMN copolymer (1%) before and after irradiation with different exposure doses (5, 15, 25, 35, 50, 75 and 100 KGy) are summarized in Figure 7. From which it is clear that there are three maximum absorption bands at 275 nm, 295 nm and 366 nm. The absorbance values of these bands increase with the increasing of the γ-exposure doses. For the different wavelengths (λ_{max}). The relationship between the absorbance values and the exposure γ-doses are represented in Figure 8. At the two maximum absorption bands appear at 275 nm and 295 nm, a linear relationship is found between (0 – 100) KGy for

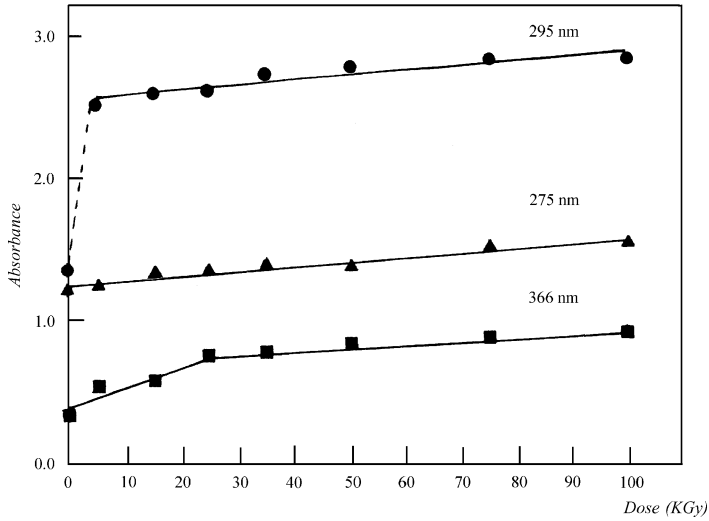


FIGURE 8 Relation between exposure doses and absorbance at different wavelengths for PMMA blended film with MMA-BMN copolymer (1%).

the first and between (5 – 100) KGy for the second. But for the third band appears at 366 nm, two linear parts are found in the range from (0 – 25) KGy and from (25 – 100) KGy. The behavior of the three bands with the increasing of the irradiation doses indicates that this type of PMMA films can be used as a dosimeter at the two λ_{max} (275 nm and 295 nm) in the ranges between (0 – 100) KGy and (5 – 100) KGy, respectively.

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