

Synthesis and Evaluation of Methyl Methacrylate Copolymers and Terpolymers as Electron Beam Resists. II. Methyl Methacrylate Copolymers and Terpolymers Containing Aromatic Rings

IVAN GITSOV* and OLGA G. TODOROVA

R&D Institute for Special Chemicals, 1741 Sofia-Vladaya, Bulgaria; and Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria

SYNOPSIS

Terpolymers of methyl methacrylate and methacrylic acid with vinyl monomers, styrene, 4-(α,α -dimethylbenzyl) phenyl methacrylate and 2-naphthyl methacrylate, were synthesized by radical terpolymerization. The molecular weights of the polymers obtained cover the range of 40,000 to 120,000. It was established that the molecular weight characteristics of the terpolymers are influenced by the content of methacrylic acid in the initial polymerization mixtures, by the chemical nature of the aromatic vinyl comonomer, and by the nature of the solvent and the concentration of the initiator. The sensitivity of the polymers towards radiation was estimated by the G -values obtained after the products were subjected to γ -ray treatment. The influence of the chemical composition of the terpolymers on their sensitivity is discussed in detail. © John Wiley & Sons, Inc.

INTRODUCTION

Homopolymers, which meet the contradictory requirements of the modern microlithographic process, hardly exist. Thus, copolymerization represents a convenient way for obtaining polymers with desired properties by incorporation of units with different chemical natures in the polymer chain. Many attempts have been made to improve the quality of poly(methyl methacrylate)—a widely used positive electron resist, by copolymerization of methyl methacrylate (MMA) with different comonomers.^{1,2} Often, the achieved results have been unsatisfactory, since the incorporation of comonomers in the polymer chain deteriorates either the sensitivity or the dry-etching stability of the materials obtained.¹⁻³ On the other hand, terpolymers are rarely investigated as suitable materials in electron-beam lithography.^{4,5} Their synthesis is not difficult, and the products

formed might offer an acceptable superposition of monomer units with chemical properties, enabling formation of resists with useful properties.

The aim of this work is to investigate the radical terpolymerization of MMA and methacrylic acid (MAA) with styrene (St), 4-(α,α -dimethylbenzyl)phenyl methacrylate—cumylphenyl methacrylate (CPMA) and 2-naphthyl methacrylate (2-NMA).

It is known that the polymers of MMA and MAA have valuable properties as electron-beam resists (EBRs)—good sensitivity, excellent contrast, and adhesion to wafers—but they are thermally unstable. It is established⁶ that the dry etching durability of the materials used as EBRs could be predicted by the following empirical correlation:

$$A = N / (N_C - N_O)$$

where N is the total number of atoms in the constitutional repeating unit of the polymer chain, N_C and N_O are, respectively, the numbers of carbon and oxygen atoms therein. The smaller the value of A , the greater the dry etching stability of the material

* To whom correspondence should be addressed at his present address: Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853-1301.

(Table I). It is obvious that the thermally unstable poly-MMA, poly-MAA and their copolymers have *A* with the highest values (*A* = 6, 5, and 5.5, respectively), while the polymers containing aromatic rings, which manifest good plasma etching durability, have the lowest *A*-values. It has to be expected that the polymers of CPMA and 2-NMA, which have low values of *A* (2.41 and 2.5, respectively), would exhibit good thermostability in the conditions of plasma etching. Their incorporation as components in the copolymers of MMA and MAA would improve their thermostability without sensitivity deterioration. Indeed, the investigations of Hatada et al.⁸ have shown that the polymers of α -substituted benzyl methacrylates possess a commensurable sensitivity to poly-MMA. It could be assumed that the combination of the characteristic features of the individual homopolymers: high contrast (poly-MMA), excellent sensitivity and adhesion (poly-MAA), and good thermostability (poly-St, CPMA, and 2-NMA) in the corresponding terpolymers will enable the obtaining of products suitable for use as positive tone EBRs. The synthesis of these terpolymers has not been investigated, nor has their behavior during interaction with irradiation been examined. This fact determined the choice of the terpolymers poly(MMA-MAA-St), poly(MMA-MAA-CPMA), and poly(MMA-MAA-2-NMA) for synthesis and evaluation as positive EBRs. The preliminary estimation of the sensitivity of the polymer products obtained towards irradiation was made on the basis of *G*-values obtained after irradiation with γ -rays. The effect of the chemical composition of the terpolymers on their sensitivity is discussed as well.

EXPERIMENTAL

Reagents

The initiator 2,2'-azoisobutyronitrile (AIBN, Fluka AG) was recrystallized from ethanol, m.p. 102–103°C.

Table I Dry Etching Durabilities of Some Polymers

Polymer	<i>A</i>	Relative Dry-Etch Rate ⁷
poly-MMA	5.00	1.0
poly-BzMA ^a	2.78	0.4–0.7
poly-PhMA ^b	2.75	0.3–0.7
poly- α -MSt ^c	2.10	0.2–0.5

^a (BzMA) Benzyl methacrylate.

^b (PhMA) Phenyl methacrylate.

^c (α -MSt) α -methyl styrene.

MMA, MAA, and St (Fluka AG) were purified by known methods⁹; CPMA was obtained and purified according to Ref. 10; 2-NMA was synthesized and purified using the method described in Ref. 11.

Chloroform (CHL, Factory for pure reagents, Sofia-Vladaya) was dried by CaCl₂, distilled, and stored over molecular sieve 4 Å; methyl isobutyl ketone (MIBK, Merck) was distilled twice prior to use.

Copolymerization

A definite quantity of AIBN was added to a 2 mol/L comonomers's solution in glass ampoules. After twofold freezing in liquid nitrogen, and thawing, the ampoules were sealed under vacuum and were heated in a thermostat at 60°C for a definite period of time. In all cases investigated, the polymerizations proceeded in a homogeneous phase. The polymers formed were precipitated in methanol, purified from homopolymers by reprecipitation from tetrahydrofuran (THF) in methanol, and dried under reduced pressure at room temperature.

Analyses

The molecular weight characteristics and the chemical composition of the terpolymers were investigated by gel permeation chromatography with photo-diode array detection (GPC-PDA). The system used was "Waters" GPC III, equipped with an automatic injector WISP 712, two ultraStyragel columns (Linear and 100 Å), and PDA detector M990+. THF was used as mobile phase, the nominal flow rate being 1.0 cm³/min at 45°C. The molecular weights were calculated towards poly-St standards on the "Waters" M840 Chromatography control and data station. The contents of the aromatic units in the terpolymers were determined from the area of the chromatographic peaks, recorded by the PDA detector, at the following wave lengths: 261.6 nm (for poly-St), 271.4 nm (for poly-CPMA), and 286 nm (for poly-2-NMA). The calibrations curves for the dependence of peak area vs. polymer quantity were constructed by injection of well defined amounts of poly-St, poly-CPMA, and poly-2-NMA, having as broad molecular weight distributions as the terpolymers studied.

The content of MAA was determined as follows: the terpolymers were dissolved in THF and were titrated with 0.1 N solution of KOH in the presence of bromthymol blue as indicator.

The chemical composition of the terpolymers was also investigated by ¹H-NMR, using data and methods described in Refs. 12–14. The analyses were

carried out on a "Bruker" WM apparatus at 250 MHz in CDCl_3 and TMS as an internal standard. A typical spectrum of poly(MMA-MAA-St) is shown in Figure 1.

Irradiation

The terpolymers were subjected to irradiation with γ -rays from a ^{60}Co source in air, at room temperature and different duration, until doses between 20 and 100 kGy were achieved. The changes in the molecular weight characteristics of the treated polymers were measured by GPC, using the above described method and conditions. G -values were determined using the equation¹⁶:

$$1/\bar{M}_n = 1/\bar{M}_n^0 + 1.04 \times 10^{-7} G_s D$$

where \bar{M}_n^0 and \bar{M}_n are, respectively, the number average molecular weights of the polymers before and after irradiation, G_s is the scission constant, and D is the irradiation dose in kGy. Each point on the curves is the average value of three consecutive measurements with margin of error $\pm 3.5\%$.

Dry Etching

The etching rates were estimated using plasma etching in the system $\text{CF}_4 + 5\% \text{O}_2$ ($100 \text{ cm}^3/\text{min}$) in a tunnel reactor equipped with glass sample carrier.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Terpolymers

An advantage of the comonomers chosen is their mutual solubility in one another, as well as their solubility in the solvents used. This ensures homogeneity of the polymerization systems.

The results of the polymerization are presented in Tables II–IV. Regardless of the solvent used, and of the initial molar ratios of the comonomers, polymerizations proceeded with high yields (97–99%). In some cases, this result might lead to substantial drifts in the composition of the terpolymers formed. Investigations of similar systems have shown, however, that only a slight increase of inhomogeneity in the chemical composition occurs with an increase in molecular weight.^{17,18} Our investigations using GPC/PDA show that the terpolymers studied are slightly enriched with the aromatic comonomer in the higher molecular weights region.

With the increase of the MAA-content in the initial polymerization mixtures, the molecular weights of the terpolymers formed also increase, and their polydispersity decreases (Table II, Fig. 2). A similar dependence has been observed in the copolymerization of MAA with St,⁹ where copolymers with the highest molecular weights were obtained in CHCl_3 . In such nonpolar solvents, MAA forms associates with the carboxyl groups in the monomer or in the

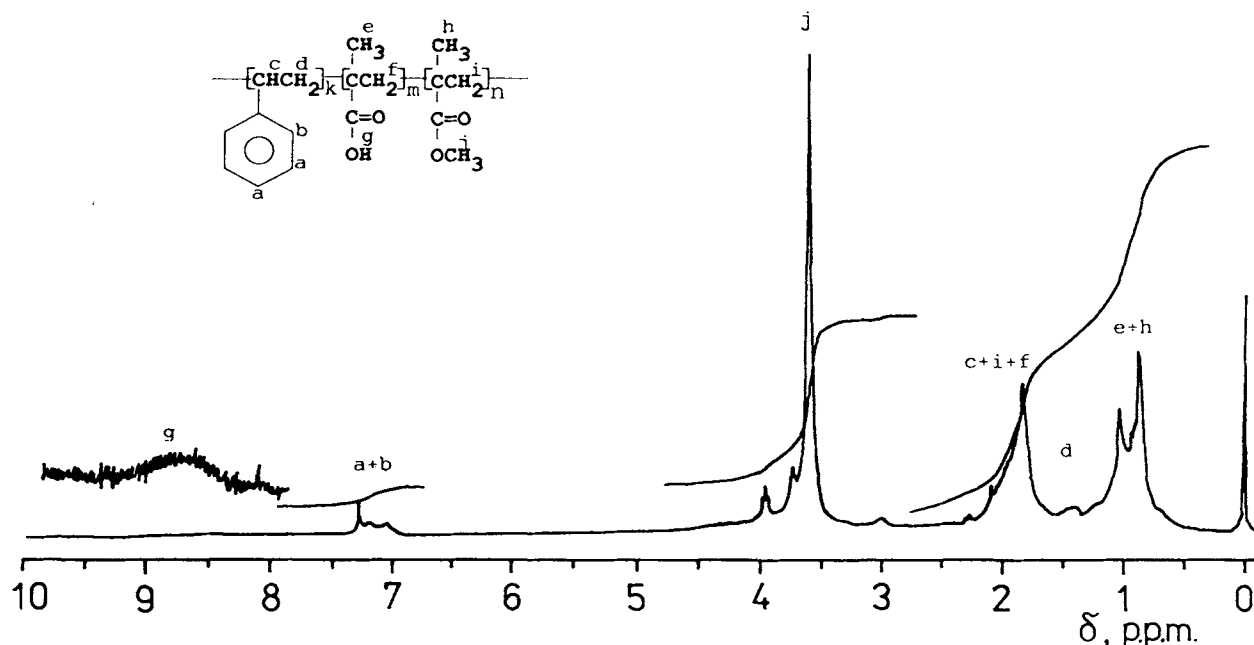


Figure 1 ^1H -NMR spectrum of terpolymer obtained by polymerization of MMA and MAA with styrene. CDCl_3 , Bruker WM 250 MHz, room temperature.

Table II Terpolymerization of MMA and MAA with X (X = Styrene, Cumylphenyl Methacrylate and 2-Naphthyl Methacrylate)

Molar Ratio (MMA : MAA : X)	Polymerization Time (h)	Yield (wt %)	\bar{M}_w (GPC)	\bar{M}_w/\bar{M}_n (GPC)
X = Styrene				
7.0 : 1.0 : 1.0	70	98	91,000	2.05
7.0 : 0.8 : 1.0	70	97	81,000	2.19
7.0 : 0.5 : 1.0	70	99	39,000	2.75
X = Cumylphenyl methacrylate				
7.0 : 1.0 : 1.0	86	98	121,000	2.98
7.0 : 0.8 : 1.0	86	98	113,000	2.97
7.0 : 0.5 : 1.0	86	97	46,000	3.30
X = 2-Naphthyl methacrylate				
7.0 : 1.0 : 1.0	90	96	84,000	2.05
7.0 : 0.8 : 1.0	90	99	82,000	2.25
7.0 : 0.5 : 1.0	90	99	66,000	3.47

[AIBN] = 0.5 mol% ; CHCl₃, 60°C.

growing polymeric radical. These associates exhibit higher activity, not only above that of unassociated molecules, but also above that of the molecules connected by hydrogen bonds with the solvent. It is evident that with the increase of MAA-concentration, the formation of more reactive associated forms

Table III Influence of the Solvent on the Molecular Weight Characteristics of Terpolymers Obtained during Polymerization of MMA and MAA with X (X = Styrene, Cumylphenyl Methacrylate and 2-Naphthyl Methacrylate)

Solvent	Polymerization Time (h)	Yield (wt %)	\bar{M}_w (GPC)	\bar{M}_w/\bar{M}_n (GPC)
X = Styrene				
CHCl ₃	70	99	44,000	2.19
MIBK	70	99	40,000	2.51
X = Cumylphenyl methacrylate				
CHCl ₃	86	98	62,000	3.95
MIBK	86	98	53,000	1.76
X = 2-Naphthyl methacrylate				
CHCl ₃	90	99	73,000	2.16
MIBK	90	99	56,000	2.36

[AIBN] = 1 mol %; [MMA] : [MAA] : [X] = 8.0 : 1.0 : 0.5; 60°C.

will be favored. This is probably the reason for the higher molecular weights attained with these terpolymers.

If CHCl₃ is substituted by a solvent, which forms hydrogen bonds with MAA, for example, MIBK, the formation of associates is hampered, MAA reactivity decreases, and the polymer products obtained are of lower molecular weight (Table III). These results are in accord with the data obtained with acetone and dioxane as polymerization media for similar systems.^{9,15}

The concentration of the initiator also influences the molecular weight characteristics of the terpolymers (Table IV).

The chemical nature of the comonomer, which carries the aromatic function, influences greatly the molecular weights of the polymers obtained (Table V). Regardless of the type of the solvent used, and of the initial molecular ratios of the comonomers, molecular weights of the terpolymers predominantly increase in the order St < CPMA < 2-NMA.

Evaluation of the Sensitivity of the Terpolymers

The sensitivity of polymers towards electron-beam irradiation is commonly determined by measuring the dependence of the residual thickness of a polymer film coated on a wafer after development as a function of the irradiation dose. The principal drawback of this method is the dependence of the

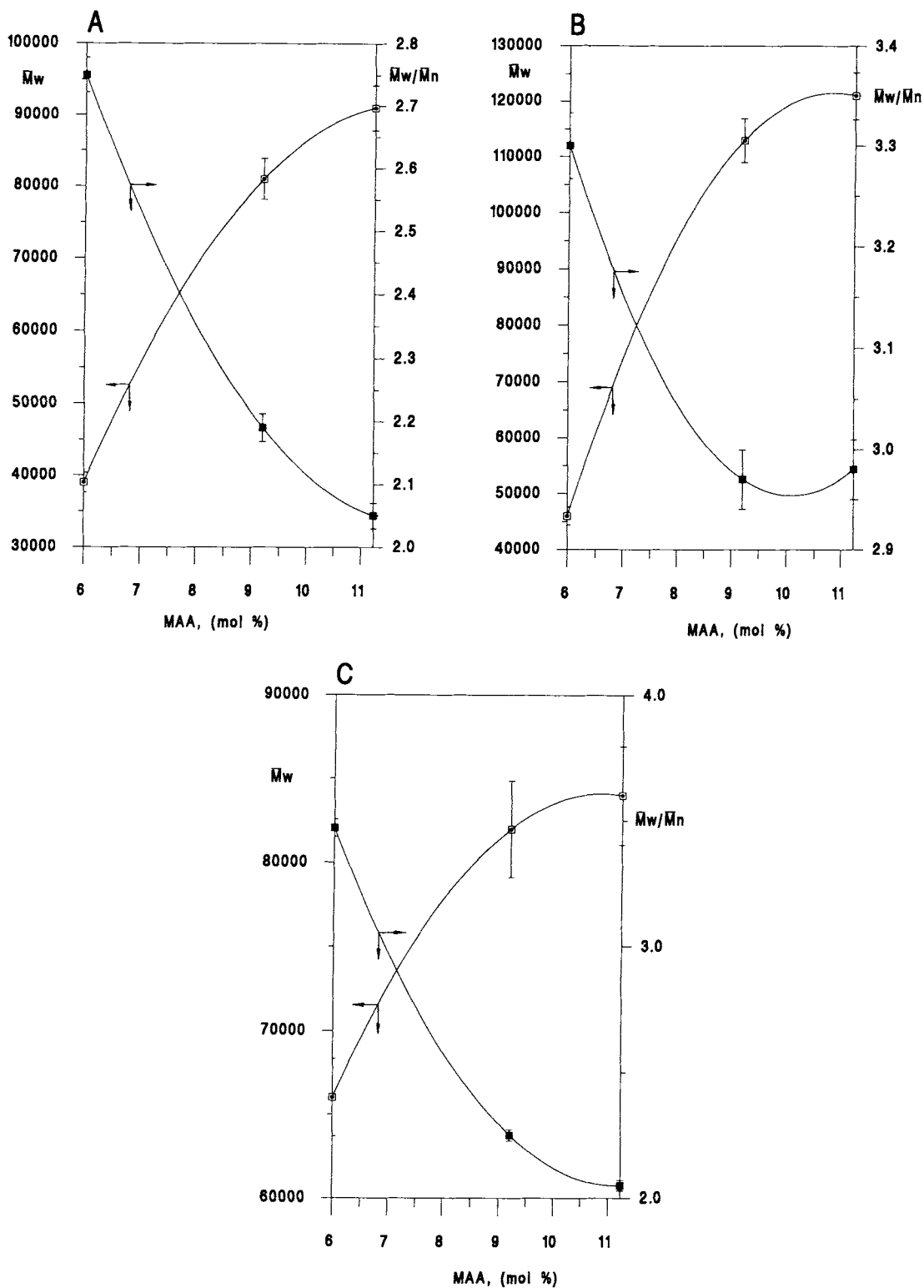


Figure 2 Influence of the initial concentration of MAA on the mol wts and mol wt distributions of terpolymers formed by polymerization of MMA and MAA with styrene (A), cumylphenyl methacrylate (B), and 2-naphthyl methacrylate (C), initiated by AIBN in CHCl_3 at 60°C .

Table IV Influence of the Initiator's Concentration on the Molecular Weight Characteristics of Terpolymers Obtained during the Polymerization of MMA and MAA with X (X = Styrene and 2-Naphthyl Methacrylate)

[AIBN] (mol %)	Polymerization Time (h)	Yield (wt %)	\bar{M}_w (GPC)	\bar{M}_w/\bar{M}_n (GPC)
X = Styrene				
1.0	70	97	40,000	2.51
0.5	70	97	56,000	1.98
X = 2-Naphthyl methacrylate				
1.0	90	99	56,000	2.36
0.5	90	99	88,000	2.66

[MMA] : [MAA] : [X] = 8.0 : 1.0 : 0.5; MIBK; 60°C.

sensitivity values on the molecular weight of the polymer, the chemical composition of the developer, and the conditions of the development. The equipment required for the investigation is expensive and is not readily available.

The preliminary evaluation of the sensitivity of polymers could also be made on the basis of the radiation chemical yield of destruction when samples are subjected to irradiation by γ -rays. The advan-

Table V Dependence of the Molecular Weight Characteristics of Terpolymers Obtained During Polymerization of MMA and MAA with X (X = Styrene-St, Cumylphenyl Methacrylate-CPMA and 2-Naphthyl Methacrylate-2-NMA) on the Nature of X

Molar Ratio [MMA] : [MAA] : [X]	X	\bar{M}_w (GPC)	\bar{M}_w/\bar{M}_n (GPC)
7.0 : 0.5 : 1.0	St	35,000	2.5
	CPMA	44,000	3.0
	2-NMA	61,000	3.2
8.0 : 1.0 : 0.5	St	44,000	2.2
	CPMA	62,000	3.9
	2-NMA	72,000	2.2
8.0 : 1.0 : 0.5 ^a	St	40,000	2.5
	CPMA	53,000	1.8
	2-NMA	56,000	2.4
8.0 : 0.5 : 1.0	St	42,000	2.8
	CPMA	70,000	2.2
	2-NMA	81,000	2.2

^a [AIBN] = 1 mol %; 24 h; 60°C; yield = 10% (weight). The polymerization is carried out in MIBK.

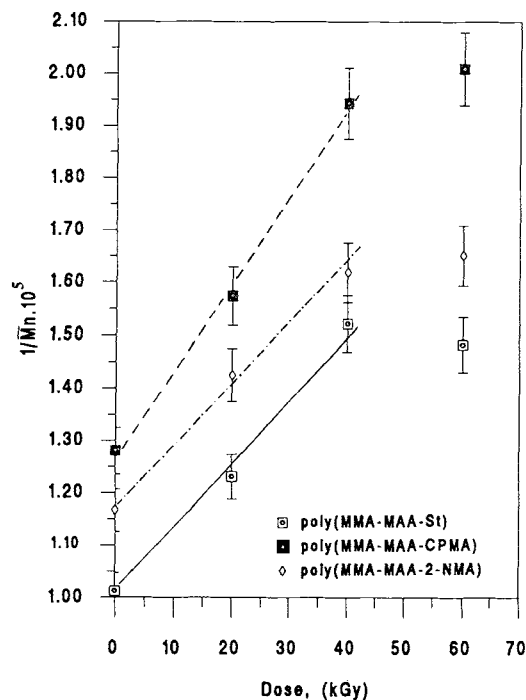


Figure 3 Influence of the irradiation dose on the changes in \bar{M}_n of poly(MMA-MAA-St) (—), poly(MMA-MAA-CPMA) (---), and poly(MMA-MAA-2-NMA) (-·-).

tages of this approach are several: the polymer could be irradiated in the form of granules or powder, the changes in the molecular weight, indicating the degree of destruction, are easily measured, etc. Using this approach, the influence of the residual thinner in the polymer film, the developer, and the conditions of development are avoided; the values of the constant of scission (G_s) depend slightly on the molecular weight characteristics of the polymers studied. This fact makes G_s an absolute constant for characterization of polymer's sensitivity, which depends only on the chemical structure of the irradiated materials.

While investigating these dependencies, terpolymers with close molecular weights and polydispersities, and the same content of the three comonomers, are selected. The influence of the chemical nature of the comonomer bearing the aromatic function on the sensitivity of the whole terpolymer could be traced in this way. The results obtained are shown in Figure 3. It should be noted that with the three polymer products, the dependence of $1/\bar{M}_n$ on the dose of irradiation deviates greatly from the linear one after doses exceeding 60 kGy are attained. The comparative studies showed that when poly-2-NMA and poly(MMA/2-NMA) are irradi-

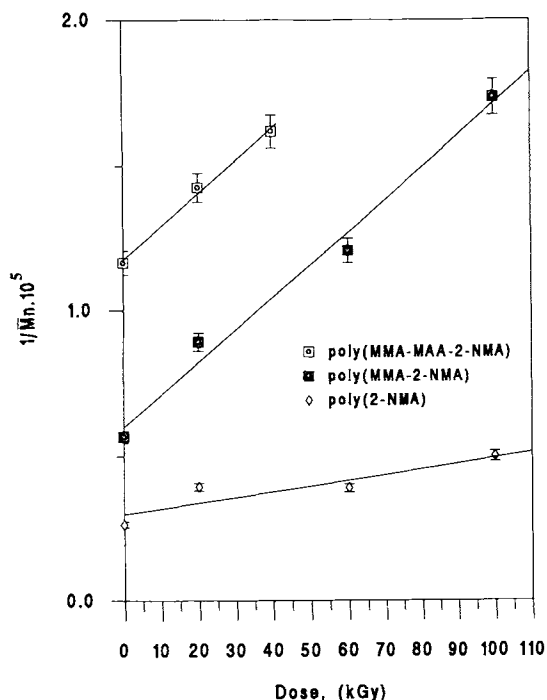


Figure 4 Influence of the irradiation dose on the changes in \bar{M}_n of poly (MMA-MAA-2-NMA), poly(MMA-2-NMA), and poly(2-NMA).

ated, $1/\bar{M}_n$ changes linearly with doses up to 100 kGy (Fig. 4). Most probably, the observed differences in the behavior of the polymers investigated towards γ -rays after incorporation of MAA units in the polymer chain indicate that, at doses above 60 kGy, the scission and crosslinking are already dependent on dose.¹⁹ The reactions of systems containing units able to undergo competitive scission and crosslinking simultaneously are extremely dif-

Table VI Influence of the Chemical Composition of Methacrylate Homo-, Bi-, and Terpolymers on their Constants of Scission (G_s)

Polymer	G_s
poly(MMA-MAA-St)	1.22 ± 0.008
poly(MMA-MAA-CPMA)	1.60 ± 0.007
poly(MMA-MAA-2-NMA)	1.09 ± 0.007
poly(MMA-2-NMA)	1.06 ± 0.014
poly(2-NMA)	0.19 ± 0.035
poly(MMA-MAA) ³	2.00
poly(MMA) ²¹	0.77
poly(BzMA) ^{a,22}	0.14
poly(1-NMA) ²³	0.14 (benzene solution)
poly(PhMA) ^{b,22}	0.44

^a (BzMA) Benzyl methacrylate.

^b (PhMA) Phenyl methacrylate.

ficult to predict and analyze.²⁰ Each of the methacrylate constituents can degrade via main chain- and/or side chain scission; the aromatic groups can crosslink at several sites as well. That is why the different mechanisms of polymers' response towards irradiation could not be traced in detail.

The values of G_s are calculated from the linear part of the curves (Table VI). The polymer products containing CPMA are the most sensitive towards irradiation. The sensitivities of the terpolymers and copolymers investigated in the present study are considerably higher than the sensitivities of pure poly-MMA and other substituted polymethacrylates containing aromatic rings, but lower than those of poly(MMA-MAA).

Evaluation of Dry Etch Stability of the Terpolymers

The small values of A (Table I) and G_s (Table VI), for the polymers investigated, suppose a greater stability towards dry etching. Indeed, the rate of RIE is comparatively lower than that of poly-MMA and lower or approximately the same as that of its aromatic derivatives (Table VII). The results obtained confirm the established connection between the empirical constant A and the stability of a given polymer towards dry etching.

CONCLUSIONS

The studies on the chosen terpolymers containing MMA, MAA, and monomers bearing aromatic rings show that if suitable chemical composition and molecular weight characteristics are chosen, these

Table VII Influence of the Chemical Nature of Polymeric Materials on their Dry-Etch Durability

Polymer	Etch Rate ($\text{\AA}/\text{min}$)
poly(MMA-MAA-St)	24
poly(MMA-MAA-CPMA)	25
poly(MMA-MAA-2-NMA)	27
poly(MMA-2-NMA)	25
poly(2-NMA)	14
poly(MMA) ⁷	52
poly(BzMA) ⁷	20
poly(PhMA) ⁷	16
poly(α MSt) ⁷	9

^a (BzMA) Benzyl methacrylate.

^b (PhMA) Phenyl methacrylate.

^c (α MSt) α -Methyl styrene.

products might be used as positive EBRs with increased stability to dry etching. However, the results obtained should be regarded only as a preliminary evaluation, which can serve for experiments at real technological conditions.

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