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ABSTRACT

Novel vinyl monomers containing the α-CF_3 group are shown to increase the propensity toward chain scission during radiation degradation and increase the electron beam sensitivity in copolymers with methyl methacrylate and methacrylonitrile. The incorporation of 32 m/o of α-trifluoromethacrylonitrile (TFMAN) into poly(methyl methacrylate) increases sensitivity from 20×10^{-6} to 3×10^{-6} C/cm^2 (at 2 keV), increases G_s from 1.3 to 3.1, and decreases the etch rate from 100 to 79 A/min. Similar beneficial results come from incorporating TFMAN into methacrylonitrile (MCN) copolymers. Poly(trifluoroethyl methacrylate) is a highly sensitive resist ($Q = 2$ to 3×10^{-6} C/cm^2) but it exhibits a high etch rate (220 A/min). Incorporation of 31 m/o MCN into this polymer decreases the etch rate to 93 A/min while preserving a high sensitivity ($3\text{-}4 \times 10^{-6}$ C/cm^2). The G_s and G_x values of these homo- and copolymer systems as well as the copolymer of methacrylonitrile with methyl α-fluoroacrylate (MFA) were obtained. The homopolymer of MFA cross-links on irradiation but its MCN copolymers tend to be positive resists with G_r values lower than that expected if G_s were a linear function of the MFA mole fraction.

The incorporation of fluorine and chlorine into vinyl polymers for use as electron-beam (1) or x-ray (2) resists is a topic of increasing interest. Fluorine and chlorine each have high x-ray absorption coefficients. The atomic absorption coefficient at 4.15A for chlorine is 1614 (21 times that of carbon) while that for fluorine at 8.3A is 1808 (3.4 times that of carbon). Also, the incorporation of halogens might modify the radiation degradation chemistry (3) by providing favored pathways for chain scission. Indeed, we have shown that poly(methyl α-chloroacrylate) exhibits a very high chain scission propensity ($G_s > 6$) (4). Recently, we reported that fluorine incorporation at the α-position of an acrylate (*i.e.*, $[CH_2C(F)(CO_2CH_3)]_n$) dramatically reversed the degradation behavior found for other α-substituents (*e.g.*, CN, CH_3, Cl, $CH_2CO_2CH_3$), to that of a predominantly cross-linking negative resist (5, 6). In contrast, fluorine incorporation into the ester group of methacrylate polymers (*e.g.*, $[CH_2C(CH_3)(CO_2CH(CF_3)_2)]_n$) was found to enhance the chain scission susceptibility over that of the classical system, poly(methyl methacrylate) (5).

Such studies provide the fundamentally important radiation *G*-values and allow successful prediction of radiation resist behavior for integrated circuit fabrication applications. We now report further novel fluorine-containing polymers including those where the α-substituent is $-F$ or $-CF_3$, as well as copolymers of 2,2,2-trifluoroethyl methacrylate (TFEM) with methacrylonitrile (MCN). The monomer α-trifluoromethylacrylonitrile (TFMAN) was copolymerized with methacrylonitrile and methyl methacrylate (MMA), while methyl α-trifluoromethylacrylate (TFMMA) was copolymerized with methyl methacrylate. The radiation degradation susceptibilities, electron beam sensitivities, and plasma etch rates for these systems have been obtained. The structural formulas and designated abbreviations used throughout the paper are shown on the following page.

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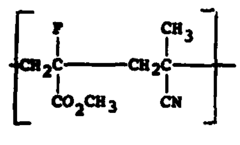
Key words: electron beam lithography, positive resists, plasma etching.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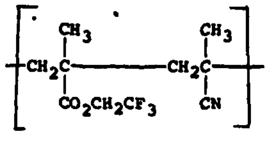
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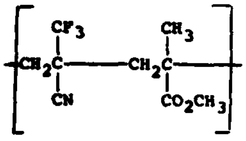
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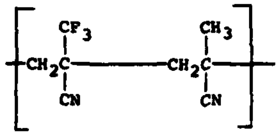
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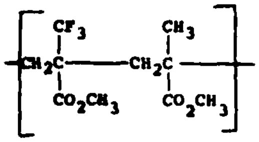
TFMMA-co-MMA

These polymer structures are of particular interest in view of Kakuchi's report (7) that the electron beam sensitivity of poly(hexafluorobutyl methacrylate) was 4×10^{-7} C/cm^2 and its x-ray sensitivity was 46 times more sensitive than poly(methyl methacrylate), *e.g.*, PMMA. They represent new structures in a larger program in our laboratories to ascertain the radiation degradation susceptibilities, electron beam behavior, and plasma etch rates of potential resist polymers as a function of polymer structure (8-16).

Experimental

Polymer molecular weights were determined by gel permeation chromatography (GPC) or membrane osmometry (MOSM). GPC was performed using a Water Associates Model 201 chromatograph equipped with four microstyragel columns (exclusion sizes: 10^6, 10^5, 10^4, and 10^3). GPC measurements were made at a flow rate of 1.0 cm^3/min of $CHCl_3$, THF, or DMF; the solvent used was dictated by the copolymer solubility. The "Universal Calibration" method was used to analyze the GPC data, and the PMMA calibration curve was used for $CHCl_3$ and THF data. A polystyrene calibration curve was used for DMF GPC data. MOSM was performed with a WESCAN Model 230 Osmometer at 30° using acetonitrile or MEK as solvent. Molecular weight data for the polymers synthesized and fractionated in this study, prior to irradiation, are found in Table I. γ-Irradiations and data analysis to obtain G (scission), G_s, and G(cross-link), G_x, were carried out as described previously (8-13).

The synthesis of methyl α-fluoroacrylate, MFA, has been described elsewhere (14) and the preparation of trifluoromethacrylonitrile and methyl α-trifluoromethylacrylate will be described subsequently (15). The MFA/MCN copolymers were prepared by emulsion polymerization at 50° using $K_2S_2O_8$ as the initiator and sodium lauryl sulfate as the surfactant. The emulsions were deoxygenated by nitrogen purging and stirred magnetically. The copolymer lattices were coagulated by pouring into stirred methanol, filtered, and dried overnight *in vacuo* at 40-50°C. MFA/MCN copolymers were fractionated by dissolving 25g of polymer into 650 ml of acetonitrile and adding methanol dropwise in the usual fashion. The copolymer compositions were determined by elemental analysis for fluorine and for carbon. The synthetic details are given in Table II.

2,2,2-Trifluoroethyl methacrylate was prepared in good yield from methacrylyl chloride and 2,2,2-trifluoroethanol in the presence of triethylamine using standard methods. It was copolymerized with MCN using the emulsion method described above for MFA/MCN copolymerizations and the conditions and results are in Table II.

Trifluoromethacrylonitrile was copolymerized with MMA or MCN by bulk polymerization using azobisisobutyronitrile (*e.g.*, AIBN) as the initiator. The monomers and AIBN were weighed into an ampul and the solution was degassed by three alternate vacuum freeze thaw cycles. The ampul was sealed, immersed in an oil bath for the reaction period, cooled, broken, and the resulting block of polymer was dissolved in acetone. The copolymers were purified by reprecipitations from acetone into methanol followed by drying *in vacuo*. Methyl α-trifluoromethylacrylate was copolymerized with MMA in the same manner. Table II lists conditions and results.

The electron beam resist sensitivities, in Table IV, were obtained at 20 keV using an ETEC LEBES E-beam microfabricator. The values are for a 6000A original resist thickness with no loss in unexposed resist thickness during development. Resist film thicknesses were measured with a Tencor Alpha-step profilometer.

Plasma etch rates were obtained with either an IPC 4005 or Tegal 421 reactor. The rf power during etching was 100 and 150W for the IPC 4005 and the Tegal 421, respectively. The pressures were 0.7 and 0.5 Torr of CF_4/4% O_2 and CF_4/8% O_2 gas mixtures, respectively. The reported values are reproducible to ±15%.

Results and Discussion

The MFA/MCN copolymers, when γ-irradiated *in vacuo*, predominantly degrade, as shown in Table III. The MCN homopolymer exhibits a large (3.3) value of

Table I. Molecular weights and compositions of fluorine-containing vinyl polymers and copolymers

Polymer or copolymer		Mole percent F-containing monomer	T_g (°C)	$\bar{M}_n \times 10^{-5}$ (MOSM)^a	$\bar{M}_n \times 10^{-5}$ (GPC)^b	$\bar{M}_w \times 10^{-5}$ (GPC)	$\bar{M}_w/\bar{M}_n$ (GPC)
PMFA		100	131^c	[illegible]	[illegible]	[illegible]	[illegible]
P(MFA-co-MCN)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
PMCN		—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
P(TFEM-co-MCN)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
PTFMAN		[illegible]	[illegible]	14.0	[illegible]	[illegible]	[illegible]
P(TFMAN-co-MCN)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
P(TFMAN-co-MMA)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
P(TFMMA-co-MMA)	[illegible]	11	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
PMMA		—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[a] MOSM is membrane osmometry.
[b] GPC is gel permeation chromatography.
[c] Measured by DSC using a du Pont Model 990 Thermal analyzer by Honeywell CRSC under contract DAAB[illegible].

Table II. Summary of the experimental conditions and results in the synthesis of MFA, TFEM, TFMAN, and TFMMA copolymers

Monomer		Initiator $K_2S_2O_8$ or AIBN[d] (g)	Surfactant SLS[c] (g)	Temp. (°C)	Time (hr)	Yield (%)	[η] (dl/g)	Polymer (m_1/m_2)
M_1 (g)	M_2 (g)							
MFA(10)	MCN(30)	0.05	0.4	50	24	[illegible]	5.0[a]	16/84
MFA(17)	MCN(23)	0.05	0.4	50	26	[illegible]	3.0[a]	20/80
MFA(27)	MCN(13)	0.05	0.4	50	26	[illegible]	6.0[a]	49/51
TFEM(1)	MCN(9)	0.04	0.3	60	48	[illegible]	—	15/85
TFEM(5)	MCN(5)	0.04	0.3	60	48	82	0.70[b]	30/70
TFEM(8)	MCN(2)	0.05	0.3	60	48	81	1.08[b]	69/31
TFMAN(1)	MMA(9)	[illegible][d]	—	60	24	[illegible]	2.01[b]	9/91
TFMAN(5)	MMA(5)	[illegible][d]	—	65	48	[illegible]	0.98[b]	32/68
TFMAN(1)	MCN(9)	[illegible][d]	—	80	504	[illegible]	2.0[a]	4/96
TFMAN(5)	MCN(5)	[illegible][d]	—	80	504	[illegible]	2.0[a]	12/88
TFMMA(0.9)	MMA(8.1)	[illegible][d]	—	65	48	[illegible]	0.26[b]	5/95
TFMMA(1.9)	MMA(6)	0.02[d]	—	—	—	[illegible]	0.90[b]	11/89

[a] Measured in acetonitrile at 30°.
[b] Measured in acetone at 30°.
[c] SLS = sodium lauryl sulfate.
[d] These reactions employed AIBN as the initiator.

Table III. Radiation degradation susceptibilities of fluorine-containing homo- and copolymers[a]

Polymer or copolymer		Mole percent F-containing monomer	$G_s - G_x$ (MOSM)	$G_s - G_x$ (GPC)	G_s (MOSM)	G_x (GPC)
PMFA[b]		100	−1.1	0.83	0-0.05	1.0
P(MFA-co-MCN)	—A	49	1.9; 1.8	1.3	1.9	0.04
	—B	20	2.0	2.3	2.0	0
	—C	16	2.1; 2.3	3.0	2.3	0
PMCN		0	3.3	3.1	3.3	0
P(TFEM-co-MCN)	—A	30	3.0	4.7	3.0	0
	—B	69	2.2	1.6; 1.5	2.2	0
PTFEM[b]		100	2.3	3.7	2.3	0
P(TFMAN-co-MCN)	—A	4	2.8	2.6; 2.5	2.8	~0
	—B	12	3.3	3.6	3.3	0
P(TFMAN-co-MMA)	—A	9	3.0	2.6; 2.3	3.0	0
	—B	32	3.1	2.3	3.1	0
P(TFMMA-co-MMA)	—A	5	1.8	1.8	1.8	~0
	—B	11	2.4	2.0	2.4	0
PMMA		0	1.3	1.4	1.3	0

[a] See Table I for compositions and initial molecular weights of these polymers.
[b] See Ref. (1).

G_s and G_x is zero, whereas the MFA homopolymer is a negative resist ($G_s - G_x = -1.1$). As one increases the MFA content of MFA/MCN copolymers from 16 to 20 to 49 mole percent (m/o), the values of G_s fall from 2.3 to 2.0 to 1.9, respectively. It is remarkable that the G_x value is zero for both the 16 and 20 MFA m/o copolymers and that of the 49% copolymer is almost zero (i.e., 0.04) when the G_x value for the MFA homopolymer is about +1. Apparently, the cross-linking is a second-order process which is largely "diluted out" in the copolymer samples. These results are graphically displayed in Fig. 1. As we recently found for other copolymers, G_s is approximately linearly related to the M_1/M_2 composition and G_x varies as a power dependence. This was previously shown for several copolymer systems including: methyl α-chloroacrylate/methacrylonitrile (4), methyl α-fluoroacrylate/methyl methacrylate (6), α-chloroacrylonitrile/methyl methacrylate (16), and vinylidene chloride/methyl methacrylate (16). The G_x experimental values all fall below those predicted by a straight line drawn between the homopolymer values.

The homopolymer of 2,2,2-trifluoroethyl methacrylate, TFEM, and its methyl methacrylate, MMA, copolymers were shown to be positive resists. The homopolymer exhibits $G_s = 2.3$ and $G_x = 0$. Similarly, TFEM/MCN copolymers degrade efficiently over the entire M_1/M_2 composition range and no evidence for cross-linking was found (e.g., $G_x = 0$, see Table III). Since $G_x = 0$ for both the homopolymers of TFEM and MCN, this was expected for the copolymers. As the MCN content increases, G_s increases.

All these copolymers have a greater propensity toward scission than MMA. The MCN component dominates because PMCN has the larger homopolymer G_s value.

The goal of examining the effect of α-trifluoromethyl substitution was achieved by (i) preparing α-trifluoromethylacrylonitrile and methyl α-trifluoromethylacrylate, (ii) copolymerizing the former with MMA and MCN, and (iii) copolymerizing the latter with MMA. Radical initiated homopolymerizations of these new monomers were sluggish and their homopolymers were not examined. Since the C-F bond is stronger than the C-H bond and F is much more electronegative than H, the effect of replacing $-CH_3$ by $-CF_3$ on chain scission was of interest. As shown in Table III, the incorporation of 9 or 32 m/o of TFMAN into TFMAN/MMA copolymers causes a large increase in G_s (e.g., to 3.1 in the latter case vs. $G_s = 1.3$ for PMMA). No tendency to cross-link was found for TFMAN/MMA, TFMAN/MCN, or TFMMA/MMA copolymers (e.g., $G_x = 0$). The TFMAN/MCN copolymers degrade with approximately the same propensity as PMCN. Furthermore, when only 11% TFMMA is incorporated into the TFMMA/MMA copolymer, G_s increases to 2.4 from its value of 1.3 for PMMA. Taken together, these results show that an α-CF_3 group at a quaternary position leads to ready radiation degradation.

These systems were next studied as electron beam resists. Lithographic images can be developed with poly(methacrylonitrile), PMCN, but toxic nitrile developers need to be used. However, PMCN does have a high glass transition temperature ($T_g = 120°$) and good plasma etch resistance. Thus, its copolymers, which are soluble in a variety of solvents, are logical resist candidates. Poly(2,2,2-trifluoroethyl methacrylate), PTFEM, exhibits an electron beam sensitivity of 2-3 × 10^{-5} C/cm^2 which is 1.6× more sensitive than PMCN, but PTFEM has a lower T_g (69°) and a poorer CF_4/O_2 etch resistance than PMCN (i.e., 230 Å/min for PTFEM vs. 36 Å/min for PMCN). The TFEM/MCN

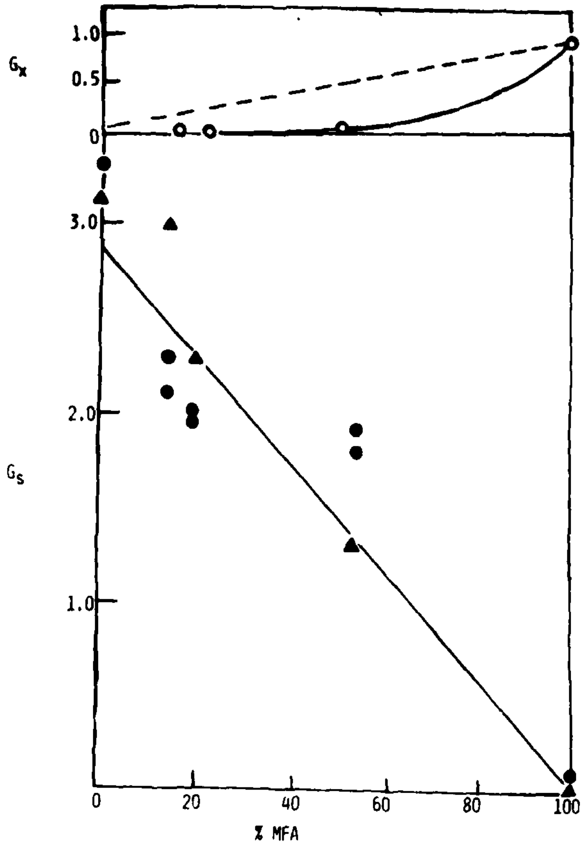

Fig. 1. G_s and G_x vs. m/o MFA for irradiated MFA/MCN copolymers. The solid line (lower) is a least squares fit of all G_s data. The triangles are GPC data, the closed circles MOSM data, and the open circles GPC data. The upper solid line is a power curve fit of the G_x data, $G_x = 9.44 \times 10^{-10}\,[\mathrm{MFA}]^{4.5}$. The dash line is a straight line connecting the homopolymer G_x values.

copolymer system should blend the better characteristics of both homopolymers. Indeed, the 69/31 TFEM/MCN copolymer ($G_s = 2.2$, $G_x = 0$) was found to have an intermediate glass transition temperature of 86° and an intermediate CF_4/O_2 etch rate of 93 Å/min while maintaining a sensitivity 5-6 times higher than that of PMMA (*i.e.*, $Q = 3\text{-}4 \times 10^{-5}$ C/cm^2 for this copolymer *vs.* $Q = 20 \times 10^{-5}$ for PMMA, $5\text{-}7 \times 10^{-5}$ C/cm^2 for PMCN, and $2\text{-}3 \times 10^{-5}$ C/cm^2 for PTFEM).

The observed E-beam resist sensitivity of the 70/30 TFEM/MMA copolymer ($2\text{-}3 \times 10^{-5}$ C/cm^2) is very close to that of the PTFEM homopolymer value. Since this copolymer, like the 69/31 TFEM/MCN copolymer, contains about 70% TFEM, these sensitivities are not surprising. Approximately half of the increase in sensitivities vs. PMMA can be accounted for on the basis of the larger copolymer G_s values. The remainder must be attributed to dissolution rate effects caused by the buildup of deesterification radiation products (*e.g.*, CO, CO_2, CH_3CF_3, etc.) in the polymer.

The MFA/MCN copolymers behave as positive resists. When the MFA concentration is ≥50%, however, the resist dose working range gets prohibitively small and swelling of the resist becomes unacceptably poor, as is observed for the negative behaving PFMA homopolymer. At 20/80 MFA/MCN, however, the copolymer performs well and swelling is minimal. The sensitivity of the 20/80 MFA/MCN copolymer is very close to that of PMCN, and its Tg is higher. The etch rates for all the MFA/MCN copolymers are low as expected, based on the low etch rates of PMFA and PMCN (see Table IV).

Table IV. Plasma etching rates and electron beam sensitivities of fluorine-containing homo- and copolymers

Polymer or copolymer	F-containing monomer (m/o)	Plasma etch rate[a] (Å/min)	Sensitivity (at 20 keV) $Q \times 10^5$ C/cm^2
PFMA	100	40	>>1[b]
P(MFA-co-MCN)—A	40	46	[c]
P(MFA-co-MCN)—B	20	30	6
P(MFA-co-MCN)—C	16	38	—
PMCN	0	36	5-7
P(TFEM-co-MCN)—B	69	93	3-4
PTFEM	100	230	2-3
P(TFEM-co-MMA)	70	—	2-3
P(TFMAN-co-MCN)—B	12	33	5
P(TFMAN-co-MMA)—B	32	79	3
P(TFMMA-co-MMA)—B	11	100	15
PMMA	0	100	20
P(TFEM-co-MMA)[d]			

[a] Using CF_4/O_2 plasmas (see Experimental section).
[b] A negative resist at 10 keV.
[c] Resist swells badly (see text).
[d] This polymer exhibits a T_g of 75° which is between that of PMMA (105°) and PTFEM (69°).

The effect on lithographic properties of incorporating an α-trifluoromethyl group can be illustrated by the 32/68 TFMAN/MMA copolymer (Table IV). Its electron beam sensitivity was 3×10^{-5} C/cm^2 which is about the same as that exhibited by P(TFEM) and 6-7 times that of PMMA. This is consistent with its high observed G_s value of 3.1 and undetectable (*i.e.*, $G_x = 0$) cross-linking propensity. Another benefit is this copolymer's relatively high T_g value (98°C). Finally, the incorporation of 32 m/o TFMAN reduced the CF_4/O_2 plasma etch rate from 100 Å/min for PMMA to 79 Å/min. Clearly, the incorporation of $-CF_3$ at the alpha position leads to improved resists.

The same beneficial properties were observed for the 12/88 TFMAN/MCN copolymer. Its etch rate (33 Å/min) was slightly lower than that of PMCN (36 Å/min) and its sensitivity (5×10^5 C/cm^2) was slightly better than that of PMCN (see Table IV). Even the incorporation of only 11 m/o of TFMMA into an MMA copolymer increased the electron beam sensitivity from 20×10^{-5} to 15×10^{-5} C/cm^2. This correlates with this copolymer's high G_s value of 2.4 and $G_x = 0$. Thus, the α-CF_3 group appears to be a very promising structural feature to incorporate into electron beam lithographic resists. Synthetic work to prepare copolymers with higher TFMAN and TFMMA contents are now underway.

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