

DTIC FILE COPY

OFFICE OF NAVAL RESEARCH

Contract N00014-85-K-0474

Technical Report No. 13

MOLECULAR WEIGHT DEPENDENCE OF E-BEAM RESIST SENSITIVITY

by

F. Rodriguez, B. C. Dems, A. A. Krasnopoler, Y. M. N. Namaste, and
S. K. Obendorf

Prepared for presentation before the
ACS Division of Polymeric Materials: Science and Engineering
International Symposium on Radiation Curing of Polymeric Material
Dallas, TX, April 9-14, 1989

Olin Hall, Cornell University
School of Chemical Engineering
Ithaca, NY 14853

MAY 12, 1989

DTIC
ELECTE
MAY 15 1989
S E D

Reproduction in whole or in part is permitted for
any purpose of the United States Government

*This document has been approved for public release
and sale; its distribution is unlimited

89 3 13 076

AD-A207 835

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release.		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			Distribution is unlimited.		
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 13			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Cornell University		6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research		
6c. ADDRESS (City, State, and ZIP Code) Olin Hall, Cornell University Ithaca, NY 14853			7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N 00014-85-K-0474		
8c. ADDRESS (City, State, and ZIP Code)			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
			WORK UNIT ACCESSION NO.		
11. TITLE (Include Security Classification) Molecular Weight Dependence of E-Beam Resist Sensitivity					
12. PERSONAL AUTHOR(S) F. Rodriguez, Y. M. N. Namaste, B. C. Dems, A.A. Krasnopoler, & S. K. Obendorf					
13a. TYPE OF REPORT Technical Report		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) 89 May 12	
				15. PAGE COUNT 31	
16. SUPPLEMENTARY NOTATION Prepared for presentation before the ACS Div. of Polymeric Materials: Science & Engineering, Symp. on Radiation Curing, Dallas, TX April 9-14, 1989					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
			Micro lithography, Resist, Crosslinking, Scissioning Poly (methyl methacrylate), Electron Beam Resist (AU)		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
Any measure of lithographic sensitivity must take into account both the events during exposure (latent image formation) and their subsequent conversion into an etch-resistant stencil (real image formation) by selective dissolution. Poly(methyl methacrylate), a popular <u>positive</u> chain-scissioning resist, is developed by dissolving exposed areas. Poly(chloromethyl styrene), a <u>negative</u> resist, crosslinks on exposure and is developed by dissolving the unexposed polymer. In each case the equations relating primary exposure events to parameters such as molecular weight need to be coupled with the dissolution characteristics to define sensitivity. The reconciliation of lithographic sensitivity (and resolution) with conventional radiation measurements also requires an understanding of important secondary phenomena. Some, like microporosity and gel-swelling, may also depend on the initial molecular weight and molecular weight distribution of the polymer. Key Words:					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. J. Milliken			22b. TELEPHONE (Include Area Code) (202) 696-4410		22c. OFFICE SYMBOL

MOLECULAR WEIGHT DEPENDENCE OF E-BEAM RESIST SENSITIVITY

F. Rodriguez, , B. C. Dems, A. A. Krasnopoler, School of Chemical Engineering,
Olin Hall, and Y. M. N. Namaste and S. K. Obendorf, Fiber Science Program, MVR Hall,
Cornell University, Ithaca, NY 14853.

Microolithography is the process of producing microscopic patterns on a surface. The most prominent commercial application of the process is in the electronics industry. Patterns forming transistors, capacitors, wires, and other features are produced on silicon single-crystal substrates. Gallium-arsenide is another semiconductor surface used. The same features may be required on a quartz, glass or other substrate for use as a mask in replicating patterns. The feature dimensions shrink as more devices are crowded onto a central processing unit (CPU) chip or random-access memory (RAM) chip for computers. Photolithography with UV light has been used commercially for features down to about $0.8 \mu\text{m}$. Both the masks used to produce these patterns and the patterns themselves when dimensions below about $1 \mu\text{m}$ are needed, often make use of computer-controlled, focussed electron beams.

In practice, a thin film of polymer (the "resist") is coated on the surface, typically in a thickness of 0.5 to $2 \mu\text{m}$. Selected areas are altered by exposure to the electron beam. The most common reactions induced by the beam (Fig. 1) are chain scission, crosslinking, and polymerization. Chain scissioning increases the solubility of the exposed resist which can then be washed away leaving behind the unexposed polymer to act as a mask during etching, doping, metallizing, etc. A polymer that responds to radiation by increased solubility is termed a "positive" resist. Crosslinking and polymerization of polyfunctional monomers both insolubilize the exposed area. In this case, a solvent is used to wash away the unexposed material. Such a polymer system (a "negative" resist) leaves behind a mask made of insolubilized polymer.

tion For	
GRA&I	☒
TAB	☐
ounced	☐
location	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

The sensitivity of a polymer for lithographic purposes differs somewhat from the classical criteria of radiolytic yield. The usual measure of sensitivity is expressed in terms of chain scissions resulting from 100 electron volts of absorbed energy, $G(s)$, or crosslinks resulting from the same amount of absorbed energy, $G(x)$. The absorbed energy can also be expressed as rads or Grays (1 Gray = 100 rad). Other yields (H_2 , monomer, other fragments) can be measured, but $G(s)$ and $G(x)$ often suffice to characterize the response of a polymer to radiation.

From the lithographic viewpoint, scissioning and crosslinking are only important insofar as they permit the production of a mask or stencil - a cohesive, adherent, dimensionally stable polymer film with open areas. This means that the latent image produced by radiation has to be converted to a 3-dimensional image by dissolution.

For a positive resist, there is seldom a perfect developer which will dissolve exposed polymer and not affect the unexposed material. The approach most often used to express lithographic response combines the effects of exposure and development in a "contrast curve" (Fig. 2). Experimentally, contrast curves are made using exposures at various dose levels. For a given developing time, the film thickness remaining, d , may be measured for each dose and normalized in terms of the original thickness, d_0 . Occasionally one sees curves in which the thickness is normalized by dividing by the thickness of unexposed polymer remaining, d_u , after development of the exposed areas. This latter method can be deceptive since it will not reveal even drastic thinning of the original polymer mask. Also, this can result in a different apparent contrast. Good resolution of fine lines in the polymer film requires a high contrast (a steep slope). The time of development can be varied to produce a series of contrast curves, and, with forced developing, any exposure can be developed.

The contrast, γ , is defined as $(-1/\text{slope})$ of a plot of normalized thickness remaining versus $\log D$, where D is the incident dose of electrons. The same slope should be obtained when the abscissa is any quantity proportional to the absorbed dose. In practice, thickness

does not decrease linearly with dose but shows some curvature. In this case, contrast is calculated from the slope of the portion of the curve near zero thickness. Lithographic sensitivity can be defined in several ways. Since any dose can be developed, a different criterion is needed. One rather subjective definition of sensitivity is the minimum dose which will give a "satisfactory" pattern. Somewhat more objective is to select the minimum dose which will give vertical wall patterns under specified conditions. An easier and more commonly used technique is to determine the minimum dose required for complete development of an exposed area while removing no more than 10% of the unexposed film. To determine this dose, a "thinning" curve (Fig. 3) can be constructed from a family of contrast curves.

For a negative resist, a contrast curve also can be constructed (Fig. 2). In a crosslinked system, the time of development should not alter the curve since extraction of sol from the thin film network is very rapid. Contrast is defined now as $(1/\text{slope})$. A problem with all polymer resists, but especially acute with negative ones, is that of distortion of the remaining pattern by solvent swelling during development.

NEGATIVE (CROSSLINKING) RESISTS

Theoretical Models for Insolubilization

The equations relating gel formation to crosslinking have been presented by Flory¹ and Charlesby². At the point of gelation, the crosslink density, $\nu/2$, (mols/g) for any distribution of molecular weights with weight-average molecular weight M_w is¹

$$\nu/2 = 1/2M_w \quad (1)$$

where each crosslink connects (on the average) two molecules of molecular weight M_w . Since the crosslink yield, $G(x)$ is in crosslinks per 100 e.v. absorbed energy per gram, the dose to gel, $D(g)$, is related to M_w by

$$G(x)D(g)/(100N) = 1/2M_w \quad (2)$$

where N is Avogadro's number, 6.023×10^{23} molecules/mol and D(g) is in e.v./g.

For a monodisperse polymer, the soluble fraction s (sol) is given by¹

$$-\ln(s) = \delta (1 - s) \quad (3)$$

where d is the ratio of crosslinks at any point to the crosslinks needed to cause incipient gelation. Assuming that intermolecular crosslinks are introduced in proportion to radiation dose, d is also D/D(g).

The expressions for a polymer with the "most probable" distribution*

*Footnote to be inserted:

In the most probable distribution, the weight fraction of x-mer, w(x) is given by

$$w(x) = x(1-p)^2 p^{x-1}$$

where x is the degree of polymerization (number of repeat units of molecular weight M_m), the number average degree of polymerization is

$$x_n = 1/(1-p),$$

and the weight average degree of polymerization is

$$x_w = (1+p)/(1-p).$$

Neglecting end groups in polymer chains, molecular weight $M = xM_m$.

undergoing both scissioning and crosslinking were presented by Charlesy and Pinner². The expression for dose to gel, D(g), is modified to be

$$G(x)D(g)/(100N) = (1/2M_w)/\{1 - (G(s)/4G(x))\} \quad (4)$$

When G(s) equals or exceeds 4G(x), no gel forms. The expression for the sol fraction s when gel does form is²:

$$s + s^{1/2} = [G(s)/2G(x)] + 100N/[M_w D G(x)] \quad (5)$$

Equation 5 should be used with some caution, since it has been successfully applied

usually only when s is less than 0.5 which is, of course, no longer a situation of great lithographic interest. Examples of radiation plots of $(s + s^{1/2})$ versus $(1/D)$ for high-molecular weight polyethylene² or poly(ethylene terephthalate)⁴ show distinct concave downward curvature.

To be useful in lithography, a polymer should be capable of being almost completely insolubilized by radiation. That is, s should approach something less than 0.05 as D becomes large. In terms of equation 5, this is a condition of

$$s + s^{1/2} = G(s)/2(Gx) < 0.2736 \quad (6)$$

Simulation of Contrast Curves

To convert the various predictions of these theoretical equations to contrast curves, it is convenient to use as a reference condition the point at which a dose of D^* yields a gel fraction = "sol" fraction, s , of 0.5.

Then, if $a = G(s)/2G(x)$:

$$s + s^{1/2} - a = 100N/[M_w DG(x)] \quad (7)$$

and

$$D/D^* = (1.2071 - a)/(s + s^{1/2} - a) \quad (8)$$

The contrast, γ , can be obtained by differentiating Eq. 7 and combining it with Eq. 8 to give:

$$ds/dD + (0.5s^{-1/2})ds/dD = (1.2071 - a)D^*/(-D^2) \quad (9)$$

$$ds/d\ln D = Dds/dD = -(1.2071 - a)(D^*/D)/(1 + 0.5s^{-1/2}) \quad (10)$$

$$\text{and } \gamma = -ds/d\log D = -2.303ds/d\ln D \quad (11)$$

Combining these with equation 8 gives a general equation for contrast as a function of s :

$$\gamma = 4.606 s^{1/2}(s + s^{1/2} - a)/(1 + 2 s^{1/2}) \quad (12)$$

At D^* , $s = 1/2$, the contrast is

$$\gamma^* = 1.349(1.2071 - a) \quad (13)$$

At $s = 1$, it is

$$\gamma = 1.535(2 - a) \quad (14)$$

In similar fashion, contrast can be derived from equation 3 for the monodisperse polymer (only crosslinking, no chain scission).

$$(\ln s)/(1-s) = -D/D(g) = -1.3863 (D/D^*) \quad (15)$$

$$\{(1-s)^{-1}s^{-1} - (1-s)^{-2}\ln s\} ds/dD = -1.3863/D^* \quad (16)$$

Multiplying by D and substituting back for D/D* from equation 15 gives:

$$\{s^{-1} + (1-s)^{-1}\ln s\} ds/d\ln D = \ln s \quad (17)$$

and the contrast as a function of s becomes:

$$\gamma = -2.303s(1-s)\ln s/(1-s + s\ln s) \quad (18)$$

At $s = 1/2$, $\gamma^* = 2.601$, and as s goes to 1, $\gamma = 2(2.303) = 4.606$.

Simulated contrast curves (Fig. 4) for equation 8 with $a = 0, 0.25$ and 0.5 and for equation 15 illustrate several effects. Polydispersity decreases contrast as does chain scissioning. Unlike the idealized contrast curve of Fig. 2, the slopes of these plots are not constant. That is to say, the contrast varies with the thickness remaining. What is important to the lithographer is that attempts to overcome, say 5% thinning, are likely to run into trouble because the doses needed become disproportionately large, even in a well-ordered system where little scissioning occurs. Actually, most lithographers are more concerned with the contrast and dose to achieve an s of 0.5. It has to be emphasized that equation 8 is not very reliable for s greater than 0.5. In some cases, plots of $(s + s^{1/2})$ seem to consist of two branches with a lower value of a at higher doses.

Comparison with Experimental Data

Contrast curves for two samples of poly(chloromethylstyrene) (Fig. 5) confirm the prediction of equation 1. The dose at $s = 0.5$, D^* , is inversely proportional to M_w . The same can be said for the data of other workers who examined three molecular weights of the same polymer⁵. Moreover, the contrast curve predicted by equation 15 (monodisperse) gives a very good fit to the lower molecular weight sample. The higher molecular weight sample has a

slope which does not correspond to the ideal. On the other hand, this behavior could be expected from the non-linear plots of $(s + s^{1/2})$ versus $1/D$ that have been reported on gamma radiation of several polymers. In fact, the data can be fitted approximately with a lower half of $a = 0.5$ and an upper half of $a = 0.25$. This should not be taken as a suggestion that chain scissioning is occurring. It does confirm a correlation between the two types of experiments. Some of the same reasons advanced by Charlesby and others to explain the non-linearity of gamma radiation results can be invoked here. Extraction of non-network, highly-branched polymer chains may be inefficient. Impurities may play a larger role with higher molecular weight polymers because the doses involved are lower and competitive reactions more important.

A further example (Fig. 6) illustrates the importance of molecular weight distribution. An unfractionated vinyl chloride terpolymer exhibits very low contrast. However, a low molecular weight fraction of that terpolymer yields a curve which approximates equation 15 for the monodisperse polymer. Unfortunately, a curve for fractionated polymer of the same weight-average molecular weight as the unfractionated polymer is not available.

POSITIVE (SCISSIONING) RESISTS

Theoretical Models for Scission

Random chain scission characterized by a yield of $G(s)$ increases the number of polymer chains in a system while crosslinking decreases the number. A plot² of the number of molecules per unit mass, $1/M_n$, should be linear with dose, D :

$$1/M_n - 1/M_{n0} = [G(s) - G(x)]D/(100N) \quad (19)$$

where M_{n0} is the number-average molecular weight at $D = 0$. Any initial molecular weight distribution will tend to approach the "most probable" as scissioning proceeds in the absence of crosslinking. If the initial distribution is the "most probable", the weight average molecular weight, M_w , will follow a similar pattern:

$$1/M_w - 1/M_{w0} = [G(s) - 4G(x)]D/(200N) \quad (20)$$

As noted earlier in equation 4, no gel should form when $G(s) > 4 G(x)$. Since both equations are linear in D , the ratio of the slope for equation 19 to that for equation 20, defined as $K(r)$, will give the value of $G(x)/G(s)$, that is:

$$[G(s) - G(x)]/[G(s)/2 - 2G(x)] = K(r) \quad (21)$$

And thus:

$$G(s)/G(x) = [4K(r) - 2]/[K(r) - 2] \quad (22)$$

In the case where $G(x)$ is nil, $K(r)$ is 2, and so on.

Models for Dissolution Rate

Unlike the sensitivity of typical negative resists, lithographic sensitivity for a positive resist depends on the relative dissolution rates of exposed and unexposed areas. A number of studies have been reported on the effect of molecular weight, M , on rate of dissolution, R .

A 3-parameter model was proposed by Greeneich⁶:

$$R = R^0 + \beta/M^a \quad (23)$$

where R^0 , β , and a are fitted constants with no particular physical significance. Others⁷⁻⁹ have used log-log plots of R versus M with an assumption that the slope will be relatively constant over a restricted range. This agrees with equation (23) when $R \gg R^0$.

A further complication arises from the observation that R for an exposed polymer may be greater than that for an unexposed polymer of the same molecular weight. That is, the process of irradiation induces a change in addition to lowering molecular weight which increases dissolution rate by a factor of up to two. "Microporosity", probably caused by gas evolution during exposure, has been invoked for PMMA⁷ and for a copolymer of alpha-methylstyrene and maleic anhydride¹⁰. Stillwagon⁸ showed that for the case of a polysulfone, the change could be erased by annealing an exposed polymer without changing its molecular weight.

Cooper¹¹ measured the dissolution rates of unexposed PMMA films with a variety of molecular weights, $R(\text{unexp})$. These were compared with films from a high molecular weight PMMA which had been reduced in molecular weight by electron beam radiation, $R(\text{exp})$. She

found that the ratio of $R(\text{exp})$ to $R(\text{unexp})$ for a given molecular weight was relatively constant (Fig. 7). The Cooper data for unexposed PMMA can be replotted (Fig. 8) to be consistent with

$$\log (8.00 R) = 1.09 \times 10^5 / M_n \quad (24)$$

If the rate is referred to a condition of R^* corresponding to a molecular weight of M^* , we can write:

$$\log(R/R^*) = (1/M_n - 1/M_n^*) 1.09 \times 10^5 \quad (25)$$

Since most positive resists will approach the most probable distribution on scissioning, it may seem immaterial whether M_n or M_w is used to correlate R . However, a simple test can be made by combining two molecular weights of the same polymer in various proportions to give a range of values of M_n and M_w . When this is done (Fig. 9) it becomes obvious that M_n is the proper parameter. This result is not intuitively evident. One might expect R to scale with other transport-related properties such as melt viscosity (which correlates well with M_w) or the radius-of-gyration (which correlates well with M_v). One can conclude that the dissolution process is more sensitive to the low molecular-weight end of a distribution than it is to the high end.

Simulation of Contrast Curves

In order to simulate contrast curves, two models for dissolution rate dependence on molecular weight can be used. The Gamma model is based on equation 25 and the Exponential model is based on a modification of equation 23 with two parameters.

A. The Gamma Model

Equation (19) with $G(x) = 0$ and equation (25) can be combined to give a contrast curve by eliminating M_n . The reference condition of D^* (related to resist sensitivity) where the dissolution rate is R^* is used. R^* is selected to be the rate corresponding to dissolution of half the original film thickness, d^0 , in an arbitrary development time t_d . We assume that R is uniform so that it is simply related to the thickness removed ($d^0 - d$):

$$R = (d^0 - d)/t_d = (d^0/t_d)(1 - d/d^0) \quad (26)$$

If we let $y = R/R^*$, then:

$$y = 2(1 - d/d^0) \quad (27)$$

We can rewrite equations 19 and 25 as

$$1/M_n - 1/M_n^* = G(s)(D - D^*)/(100N) \quad (28)$$

$$1/M_n - 1/M_n^* = (1/K)\log y \quad (29)$$

where K is the proportionality constant for rate of dissolution (eg., 1.09×10^5 in equation 25).

Then, letting $x = D/D^*$ and $K_L = \{KG(s)D^*/100N\}$,

$$\log y = \{KG(s)D^*/100N\}(D/D^* - 1) = K_L(x - 1) \quad (30)$$

The contrast curve is a function of only one lumped parameter, K_L . The contrast γ is $(-1/\text{slope})$ of the contrast plot or

$$-\gamma = d(d/d^0)d\log D = -(dy/d\log D)/2 \quad (31)$$

Differentiation of equation 30 gives

$$(1/y)(dy/dD) = 2.303 K_L/D^* \quad (32)$$

Rearrangement results in

$$Ddy/dD = 2.303 yK_L(D/D^*) \quad (33)$$

And, using equation 31,

$$dy/d\log D = (2.303)^2 yK_L x = 2\gamma \quad (34)$$

Equation 30 gives

$$x = (\log y)/K_L + 1 \quad (35)$$

and

$$\gamma = (2.303)^2 yK_L \{(\log y)/K_L + 1\}/2 \quad (36)$$

so that

$$\gamma = (2.303)^2 y \{(\log y) + K_L\}/2 \quad (37)$$

At D^* , $y = 1$, and the contrast reduces to

$$\gamma^* = (2.303)^2 K_L/2 \quad (38)$$

Thus the lumped parameter K_L essentially determines the contrast at D^* . which is given by

$$\gamma^* = 2.652KD^*G(s)/100N \quad (39)$$

This predicts that the contrast will be highest for resists of low sensitivity (high D^*), high chain scissioning yields (high $G(s)$) and high molecular weight dissolution sensitivity (high K). All of these predictions have been observed with experimental data.

Eliminating K_L between equations 30 and 38 gives

$$\log y = 0.3772\gamma^* (x - 1) \quad (40)$$

This expression can be used to plot theoretical contrast curves for various values of γ^* (Figure 10). These plots indicate that considerable thinning of unexposed film is predicted when contrast is less than 4. This is not always observed in experimental results.

B. The Exponential Model

A contrast curve can be constructed from a two-parameter modification of equation 23:

$$R/R^o = (M^o/M)^a \quad (41)$$

Equation 19 with $G(x) = 0$ gives

$$M^o/M = M^oG(s)D + 1 \quad (42)$$

Combining the two and using the reference condition of R^* again:

$$R^*/R^o = b = (1 + M^oG(s)D^*)^a \quad (43)$$

where $(1/2b)$ is the fractional thinning of unexposed polymer when polymer exposed to dose D^* has been developed to half its original thickness. For example, when $b = 10$, then $d/d^o = 0.95$ for the unexposed (but developed) polymer and $d/d^o = 0.5$ at a dose of D^* .

Now with $y = R/R^*$ and $x = D/D^*$ again, dividing equation 41 by equation 43,

$$y = (1 + M^oG(s)D)^{a/b} = (1 + M^oG(s)D^*x)^{a/b} \quad (44)$$

But, also using equations 41 and 43,

$$M^oG(s)D^* = (M^o/M^*) - 1 = (b^{1/a} - 1) \quad (45)$$

Thus we can have an equation for the contrast curve in terms of two parameters corresponding to the slope of the dissolution rate-molecular weight plot and the thinning of unexposed polymer.

$$y = \{1 + (b^{1/a} - 1)x\}^{a/b} \quad (46)$$

An expression now can be derived for contrast based on equation 31.

$$dy/dx = (a/b)\{1 + (b^{1/a} - 1)x\}^{a-1}(b^{1/a} - 1) \quad (47)$$

And $\gamma = (2.303/2)xdy/dx \quad (48)$

At $x = 1$, $\gamma = \gamma^*$,

$$\gamma^* = (2.303/2)a\{1 - b^{-1/a}\} \quad (49)$$

Representative plots for equation 46 are included in Figure 10. Curves D and E with $a = 4$ and 1, respectively, are not very different in the region where d/d_0 is less than 0.5.

Comparison with Experimental Data

For PMMA in MIBK, contrast data can be fitted, as one might expect, by the Gamma model (Fig. 11). Workers usually select the slope at zero thickness to define the contrast. In this case, the contrast would range from 4.4 to 5.8 going from left to right.

Sensitivity does not vary greatly with molecular weight. Indeed, there is little difference observable for three molecular weights all developed with the same solvent (Fig. 12). It should be noted that the test on the highest molecular weight was run several years before the other two. The reason for the insensitivity lies in the fact that dissolution rate is not a linear function of molecular weight. The same dose (same number of chain scissions) that changes a molecular weight from 1,000,000 to 100,000 will change a molecular weight of 100,000 only to 50,000. However, the ratio of dissolution rates (R/R^*) is the same in either case according to equation 25. For a given polymer, according to equation 32, the contrast should decrease and the thinning of unexposed areas should increase as development is pushed to obtain lower values of D^* .

As mentioned earlier, an objective way of defining sensitivity is to plot the thinning of unexposed film when a film exposed to dose D is developed completely. The "sensitivity" can be defined as the dose at which thinning is 10%. This treatment ignores the differences in

contrast which may result. With that caveat in mind, curves for PMMA and a copolymer of methyl methacrylate with monomethyl itaconate illustrate the point (Fig. 13)¹².

Sensitivity Relationships for Positive Resists - Nomograph

Specialists in radiation degradation sometimes have trouble communicating with specialists in microlithography. When dealing with a chain-scissioning polymer, the first group prefers $G(s)$ as a measure of sensitivity, while the second group prefers the incident dose of electrons D_i needed to achieve a given difference in dissolution rate, contrast, or actual pattern transfer. D_i is a function of polymer thickness, polymer density, and the accelerating voltage (see below, equation 54).

A nomographic solution to the various equations involved is useful for several reasons:

1. It permits rapid comparison between the sensitivity criteria used by the two groups of workers,
2. It gives a picture of the relative importance of each parameter in arriving at the measure of sensitivity,
3. It allows rapid estimation of the effect of changing one variable on the consequent value of some other variable.

The complicating feature in joining the two measures of sensitivity is the variable dissipation of energy depending on the thickness penetrated by an electron beam. Gamma rays are scarcely attenuated at all when traversing as much as a few cm of an organic material. Thus, a polymer film only several μm thick receives the same gamma radiation dose throughout its cross section. In contrast, electrons in the range of 10 to 50 kV are much more limited in penetrating effectiveness. As the electrons slow down, they are capable of depositing more energy per unit thickness. For example, virtually all the energy of 5 kV electrons is deposited in the first μm of an organic resist that is encountered. For a polymer film of density ρ and thickness z irradiated with electrons of energy V_a , the ratio of energy absorbed, D_a , to incident dose, D_i , is given by¹³

$$D_a/D_i = (k_1 V_a/\rho z) \int \Lambda(f) df \quad (50)$$

where $f = z/R_g$ (51)

$$R_g = (0.046/\rho)(V_a)^{1.75} \quad (\text{The Grun range}) \quad (52)$$

$$\Lambda(f) = 0.74 + 4.7f - 8.9f^2 + 3.5f^3 \quad (\text{The depth-dose function}) \quad (53)$$

This set of equations is further complicated by the units employed in common practice.

Conversion factors used in arriving at a value of the constant $k_1 = 1.00$ are:

$$1 \text{ electron} = 1.602 \times 10^{-19} \text{ C} \quad (\text{C} = \text{coulomb})$$

$$1 \text{ rad} = 100 \text{ erg/g}$$

$$1 \text{ erg} = 6.242 \times 10^{11} \text{ electron volt}$$

The equations as written are consistent with the following units:

$$D_a, \text{ Mrad}; \quad D_i, \mu\text{C/cm}^2; \quad \rho, \text{ g/cm}^3; \quad z, \mu\text{m}; \quad \text{and } V_a, \text{ kV}$$

The scissioning yield is given by equation 19 rewritten as

$$G(s) = k_2 \{ 1/M_n - 1/M_{no} \} / D_a \quad (54)$$

where $k_2 = 0.965 \times 10^6$ when the units used are:

$$G(s), \text{ scissions/100 electron volt}; \quad M_n, \text{ g/mol}, \quad \text{and } D_a, \text{ Mrad}.$$

The present nomograph (Figure 14) has been constructed by conventional methods¹⁴ and is relatively compact. Compromises have been made in the choice of ranges for each variable and in the accuracy with which the depth dose function can be represented. All of the equations are used with the following assumptions:

1. There is no cross-linking by radiation.
2. There is no accounting for electrons scattered from the substrate and re-entering the film.

General description:

There are four sets of axes labelled I, II, III, and IV. A straight line connecting any two axes (with the same roman numeral) will intersect the third axis of the set to solve a single equation. The systems are:

- I. Multiplication of D_a times $G(s)$.

II. Division of D_a by D_i .

III. Equation 54, the product of $G(s)$ and D_a given as a function of initial and final molecular weights.

IV. Equation 50, D_a/D_i given as a function of V_a and the product of ρ and z .

Example

Under conditions where an absorbed dose of 15 Mrad changes the molecular weight from an original value of 300,000 to a final value of 40,000,

a) What is $G(s)$?

b) What equivalent D_i is required at a V_a of 20 kV?

Additional data: $z = 1.10 \mu\text{m}$, $\rho = 1.20 \text{ g/cm}^3$.

Nomographic solutions are:

Use System III to get the product of $G(s) \times D_a = 20.7$ from the initial and final molecular weights.

Use System I to get $G(s) = 1.39$ from $D_a = 15$ and $G(s) \times D_a = 20.7$

Use System IV to get $D_a/D_i = 2.37$ from ρz and V_a .

Use System II to get $D_i = 6.33$ from D_a and D_a/D_i .

The nomograph, of course, can only be read to two significant figures rather than the three indicated above.

CONCLUSIONS

The theoretical equations for scissioning and crosslinking can be used to correlate the results of lithographic behavior of thin films on irradiation. The same deviations can be expected that are found when the equations are used for bulk samples exposed to gamma radiation. Positive resists of the type considered here depend on a change in dissolution rate, R , with polymer molecular weight, M . The form of the relationship between R and M is still a matter of some controversy.

The idealized contrast curve consisting of a linear thickness dependency on logarithm of dose is not likely to be realized in practice. Indeed, such a curve would contradict the clear predictions of theory for both positive and negative resists.

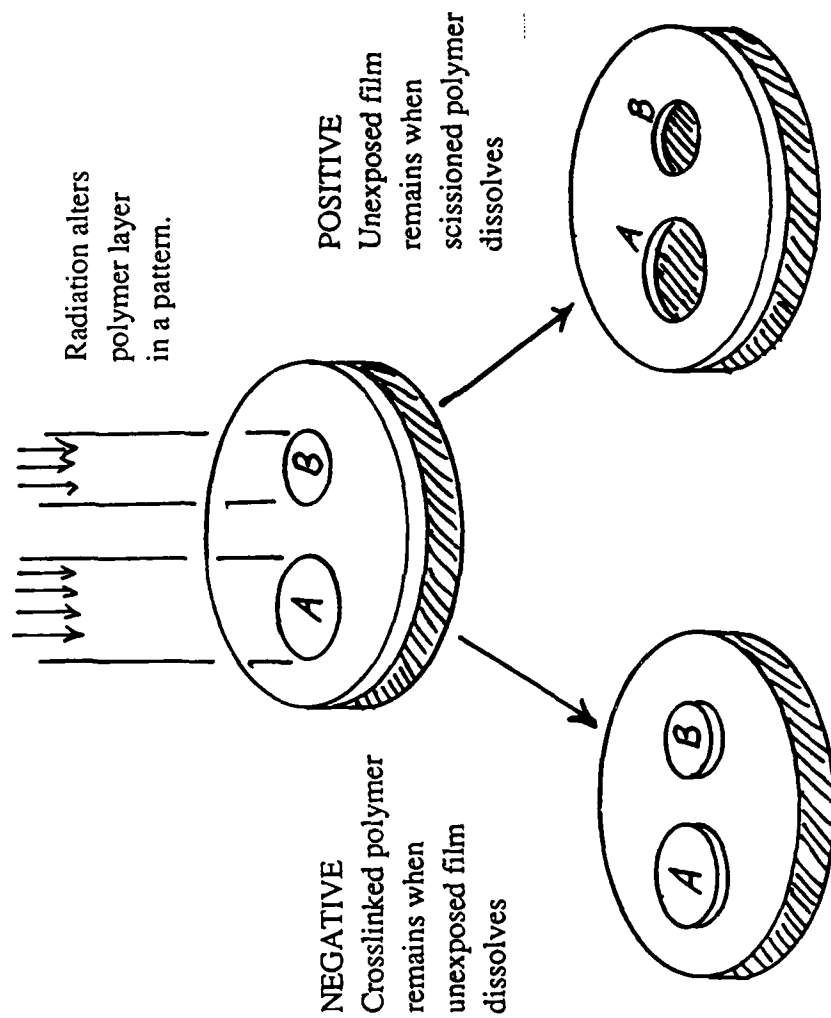
ACKNOWLEDGMENTS

This work is supported in part by the Office of Naval Research. The cooperation of the National Nanofabrication Facility at Cornell is gratefully acknowledged.

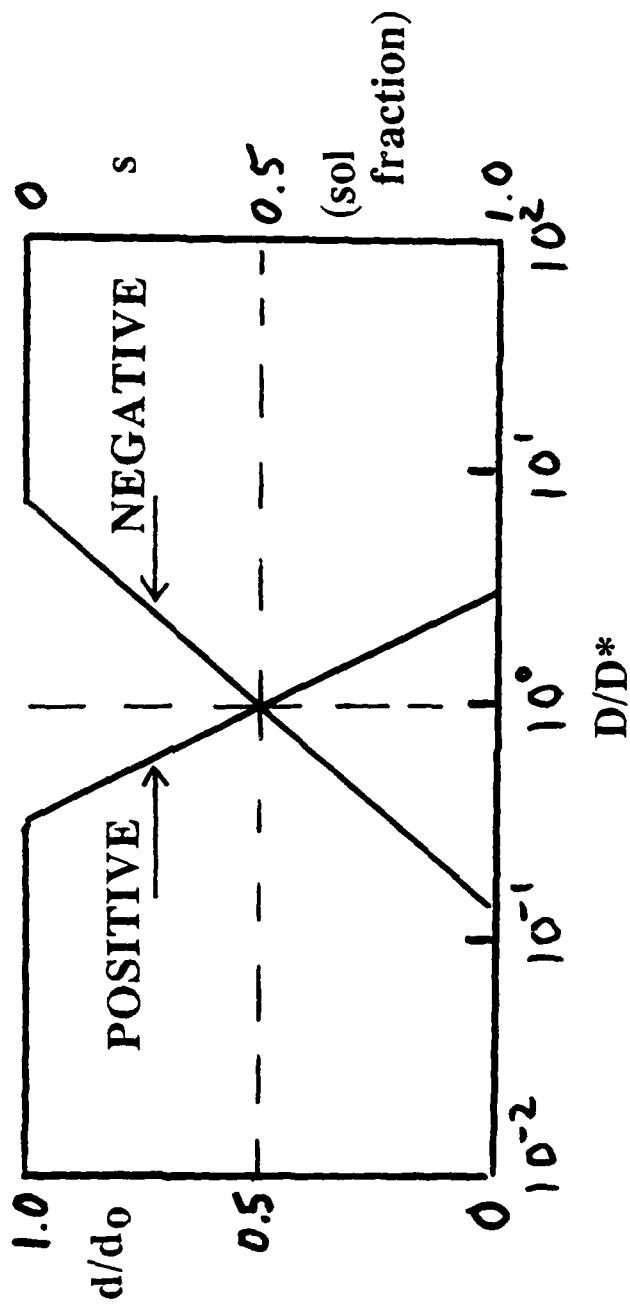
REFERENCES

1. Flory, P. J., "Principles of Polymer Chemistry," Cornell Press, Ithaca, NY, 1953, Chapter 9.
2. Charlesby, A., and S. H. Pinner, Proc. Roy. Soc., Ser. A 249, 367 (1959).
3. Flory, P. J., op. cit., Chapter 8.
4. Turner, D. T., in "The Radiation Chemistry of Macromolecules," Vol. 2, M. Dole (ed), Academic Press, New York, 1973, Chap. 8.
5. H. S. Choong and F. J. Kahn, J. Vac. Sci. Tech., 19 (4), 1121 (1981).
6. Greeneich, J. S., J. Electrochem. Soc., 121, 1669 (1974).
7. Ouano, A. C., Polym. Eng. Sci., 18, 306 (1978); 20, 160 (1980).
8. Stillwagon, L., in "Polymer Materials for Electronic Applications," E. D. Feit and C. Williams, Jr. (eds), ACS, Washington, DC, 1982, p. 19.
9. Manjkow, J., J. S. Papanu, D. S. Soong, D. S. Hess, and A. T. Bell, J. Appl. Phys., 62, 2 (1987).
10. Rodriguez, F., R. J. Groele, and P. D. Krasicky, SPIE Vol. 539 Advances in Resist Technology and Processing (1985), p. 14.
11. Cooper, W. J., P. D. Krasicky, and F. Rodriguez, Polymer, 26, 1069 (1985).
12. Anderson, C.C., PhD Thesis, Cornell University, 1985.

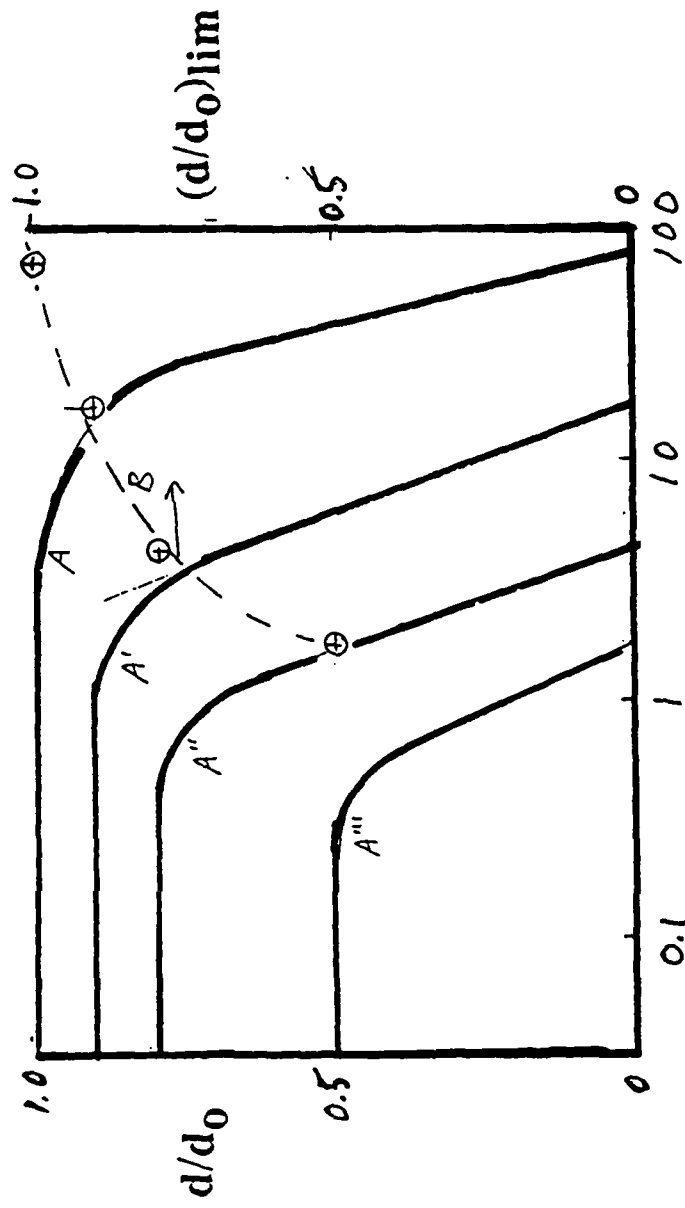
13. Thompson, L. F., C. G. Willson, and M. J. Bowden, "Introduction to Microlithography, ACS, Washington, DC, 1983, Chapter 2
14. Levens, A. S., "Nomography," 2nd ed., Wiley, New York, 1959.



1. Pattern transfer by irradiation of positive or negative polymer resist.

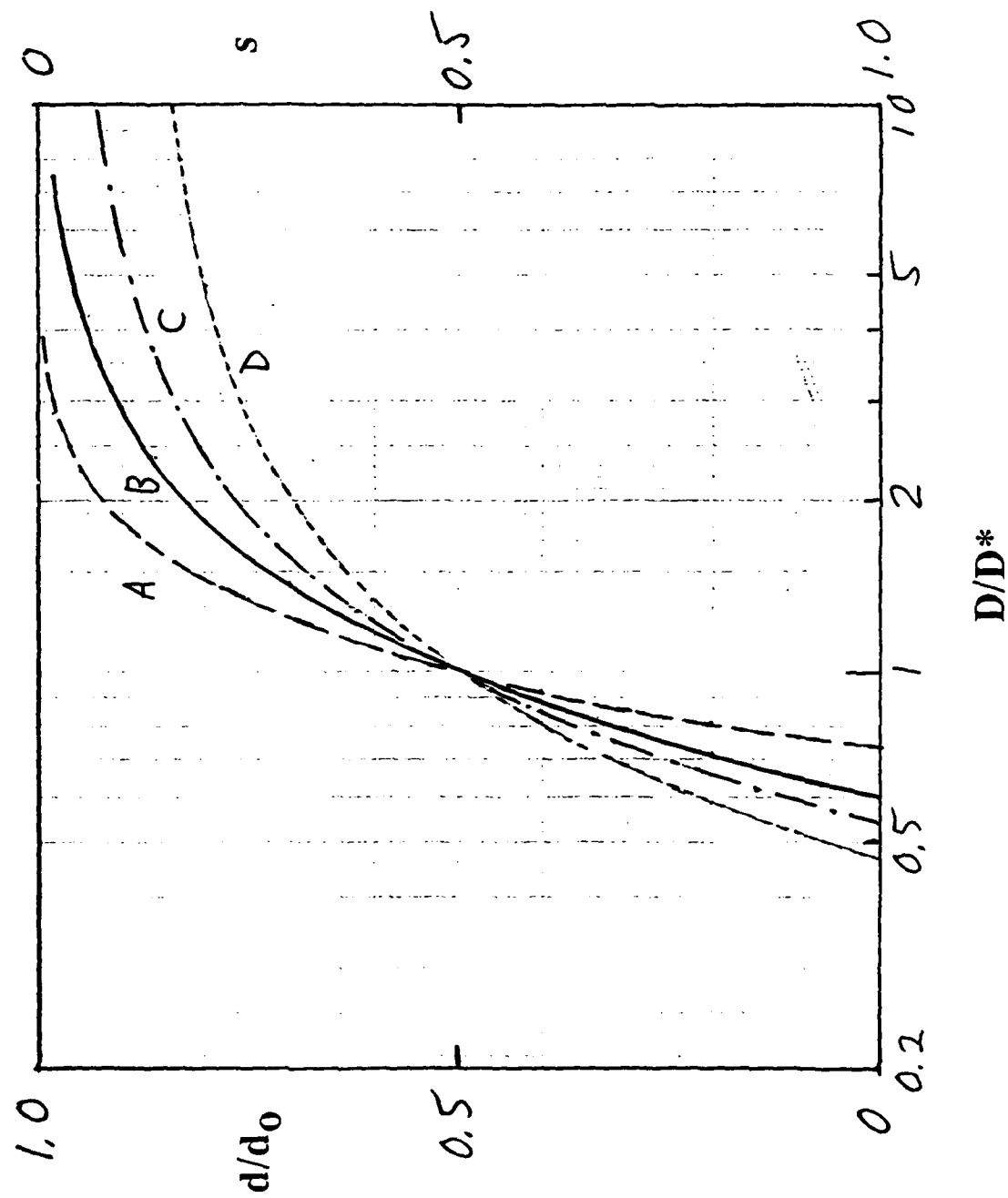


2. Idealized contrast curves. D^* is the dose that allows 1/2 of the original film to remain after development.

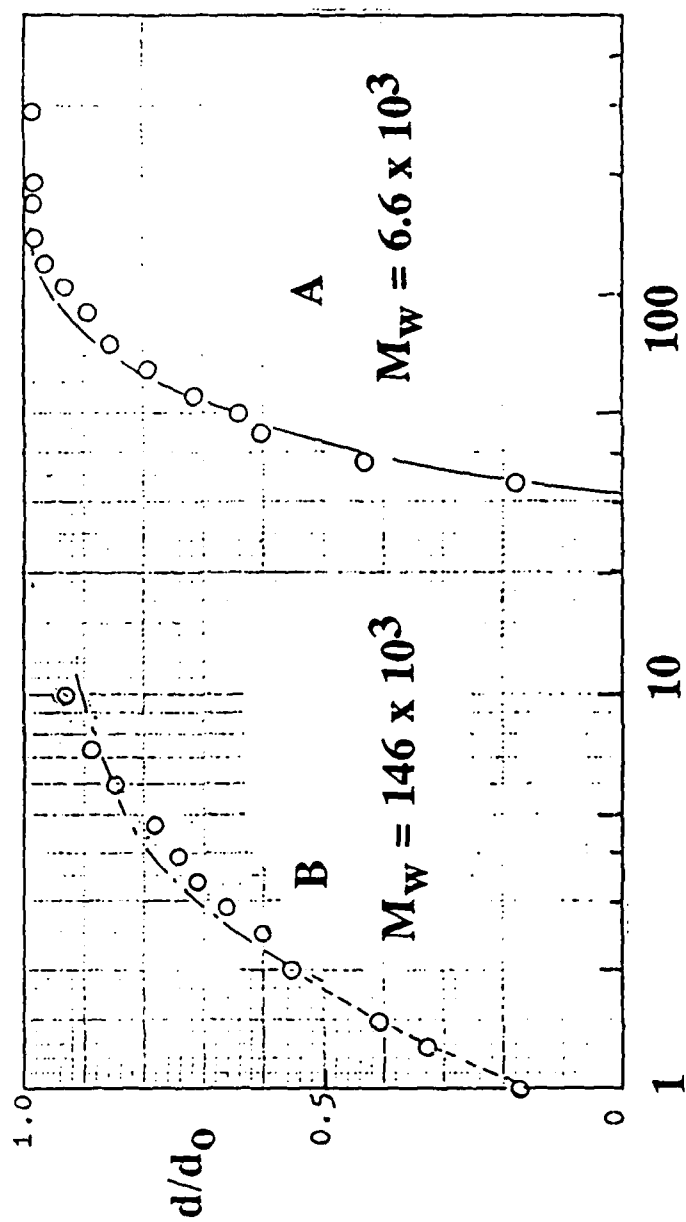


$\log D, \mu\text{C}/\text{cm}^2$

3. The thinning curve, B, is obtained from a series of contrast curves (development time increasing from A to A'''). The limiting value of normalized thickness is plotted versus the corresponding dose needed to remove polymer completely.

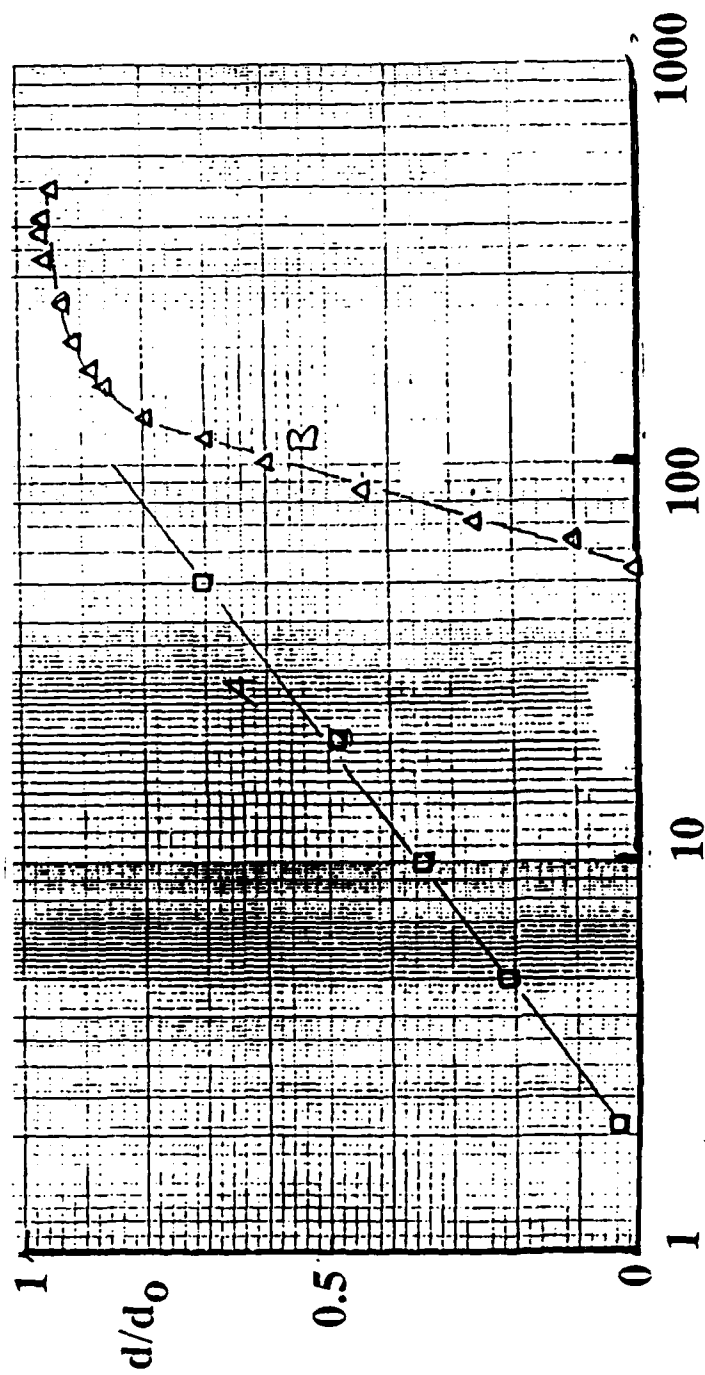


4. Plots of equation 15, (A); and equation 8 with $a = 0$, (B); $a = 0.25$, (C); and $a = 0.5$, (D).



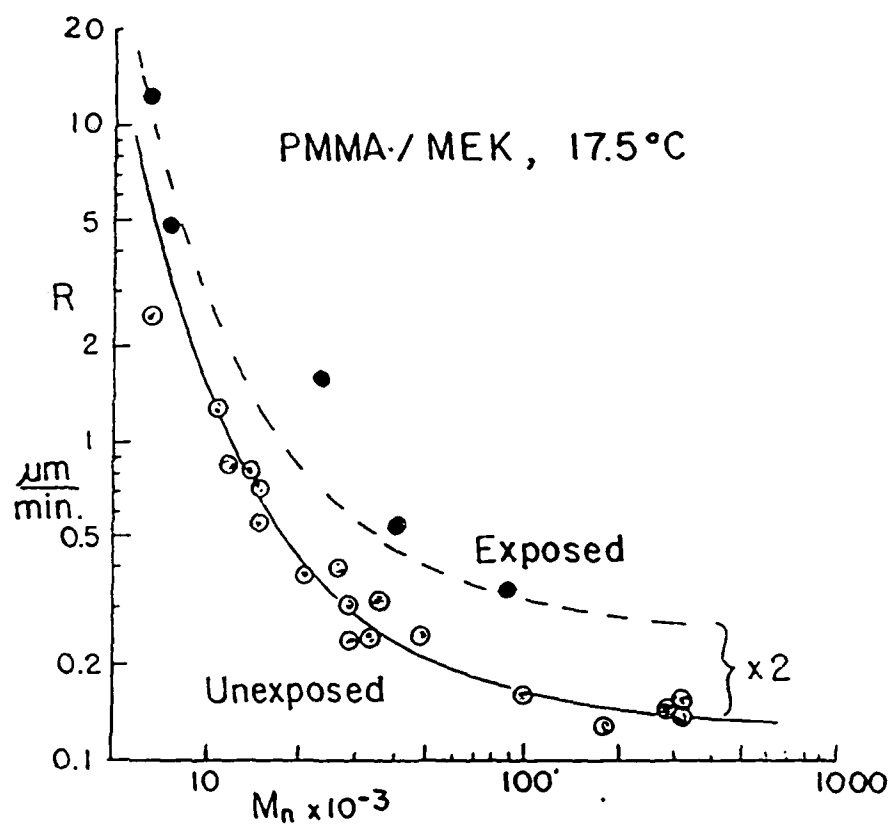
INCIDENT DOSE, D , $\mu\text{C}/\text{cm}^2$

5. Experimental contrast curves (symbols) for poly(chloromethylstyrene) fitted (lines) with equation 15, (A); and equation 8, (B) in which the lower half uses a value of $a = 0.5$ and the upper half uses $a = 0.25$.

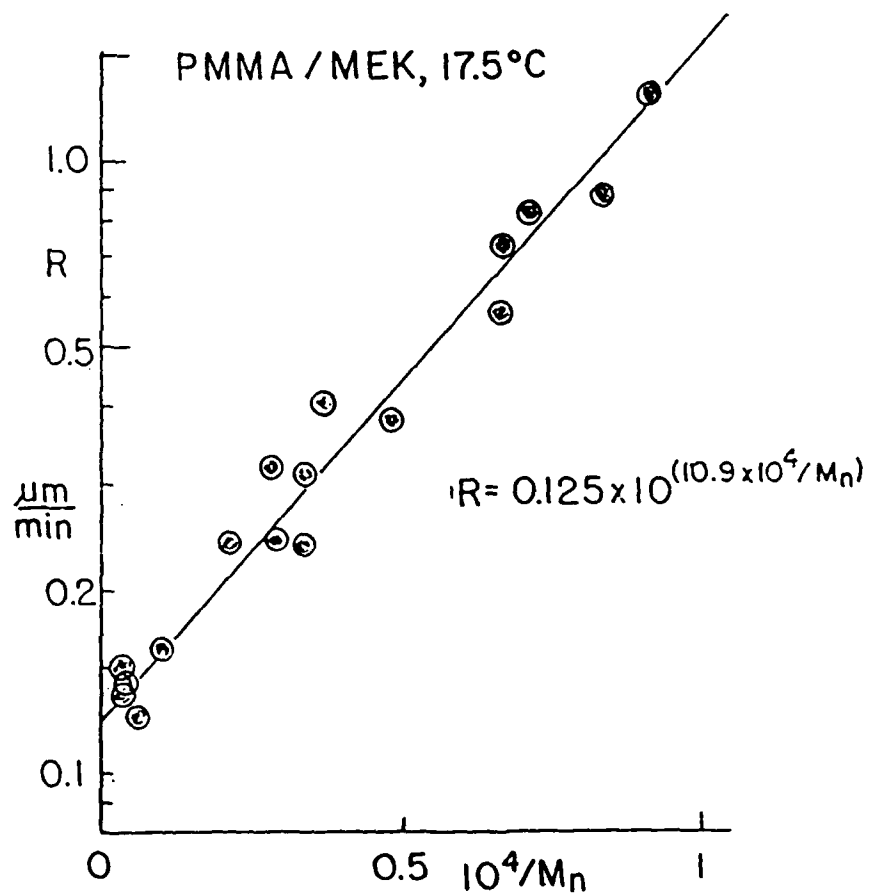


INCIDENT DOSE, D , $\mu\text{C}/\text{cm}^2$

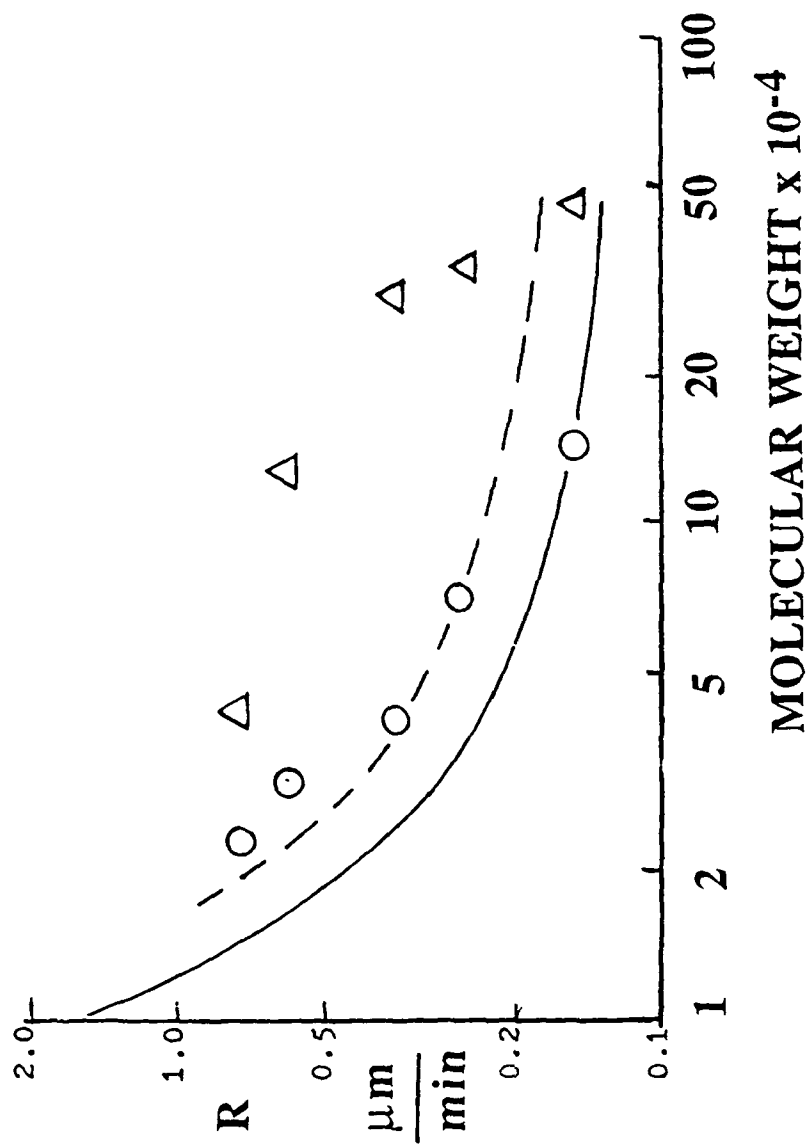
6. Experimental contrast curves for A, and unfractionated vinyl chloride terpolymer, $M_n = 48 \times 10^3$, $M_w = 85 \times 10^3$, and B, a fraction isolated from the same polymer with $M_n = 30 \times 10^3$ and $M_w = 42 \times 10^3$.



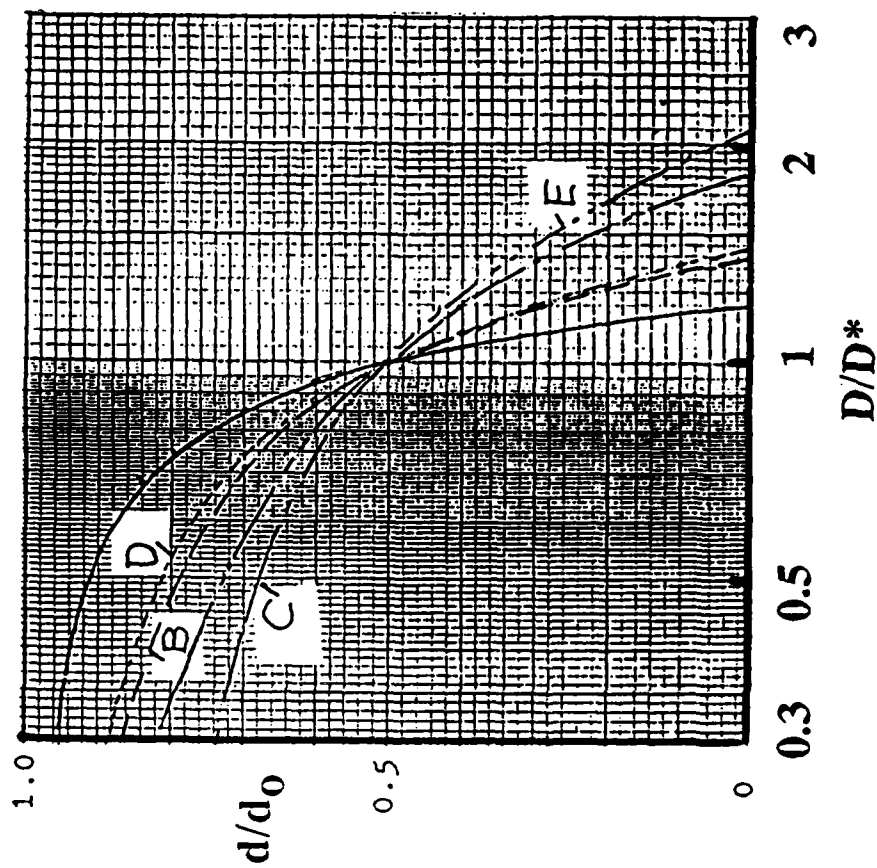
7. Dissolution rates for PMMA in methyl ethyl ketone¹¹.



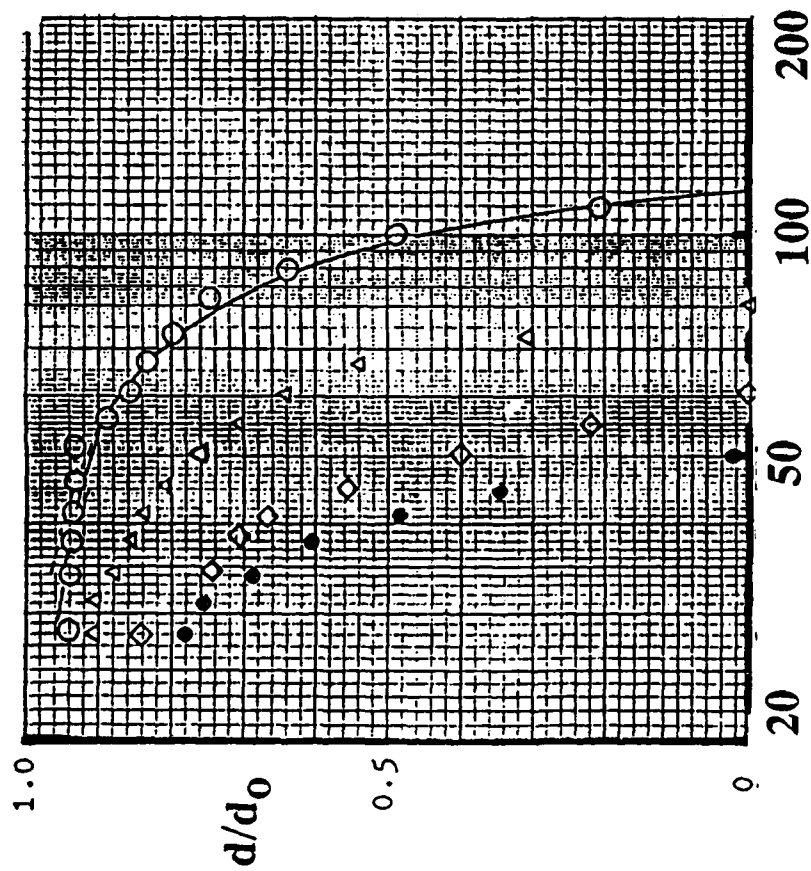
8. Data of Figure 7 replotted.



9. Dissolution rates for mixtures of PMMA with molecular weights calculated as weight-average (Δ) or number-average (o). Solvent was methyl ethyl ketone at 23°C. Cooper's data¹¹ at 17.5°C (solid line) for unexposed polymer is adjusted to 23°C (dashed line) for comparison.

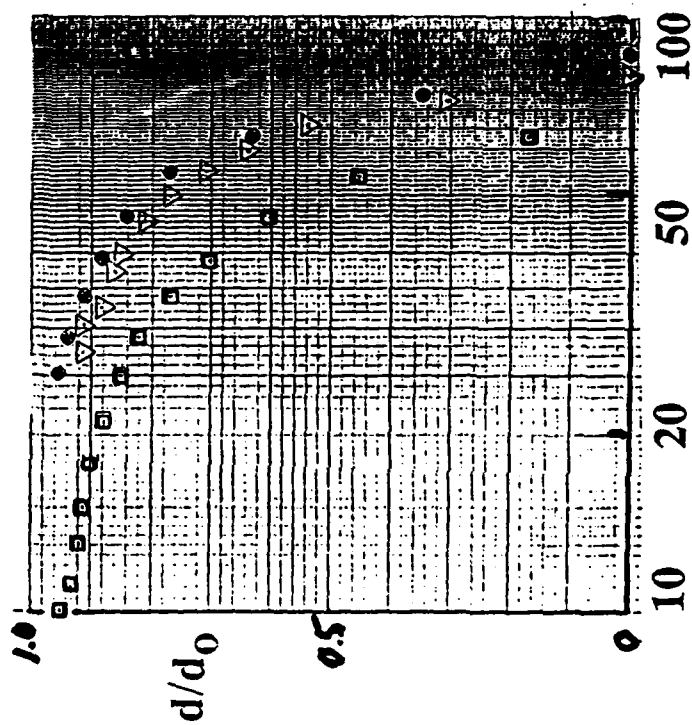


10. Contrast curves drawn according to equation 40 with $\gamma^* = 4$, (A); 2, (B); and 1, (C); and according to equation 46 with $b = 10$ and $a = 4$, (D); and $a = 1$, (E).



INCIDENT DOSE, D , $\mu\text{C}/\text{cm}^2$

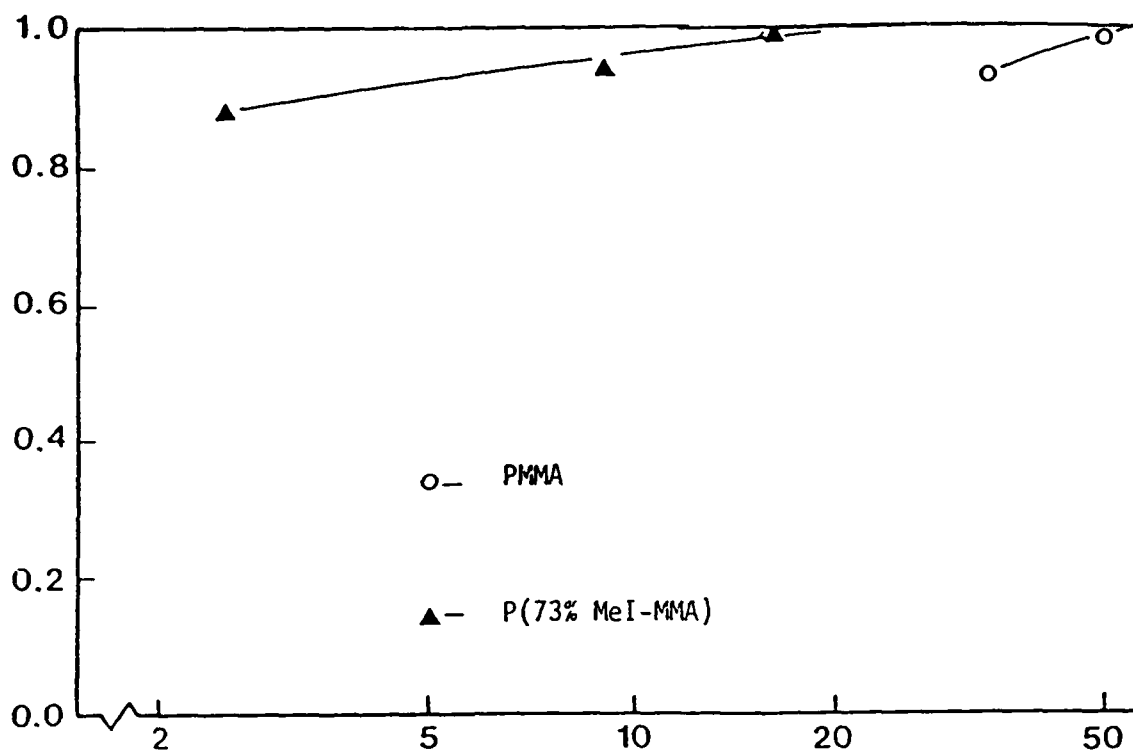
11. Contrast curves for PMMA developed in methyl isobutyl ketone for 1, 3, 5, and 10 minutes (right to left). Solid line is equation 30 with $\gamma^* = 4$. Dotted line (almost superimposed except at low doses) is equation 46 with $a = 8$ and $b = 80$.



INCIDENT DOSE, D , $\mu\text{C}/\text{cm}^2$

12. Contrast curves for PMMA developed in methyl isobutyl ketone. $M_w = 38 \times 10^3$, developed 0.5 min., ($\square$); $M_w = 496 \times 10^3$, developed 1 min. ($\circ$); and $M_w = 950 \times 10^3$, developed 3 min. (∇).

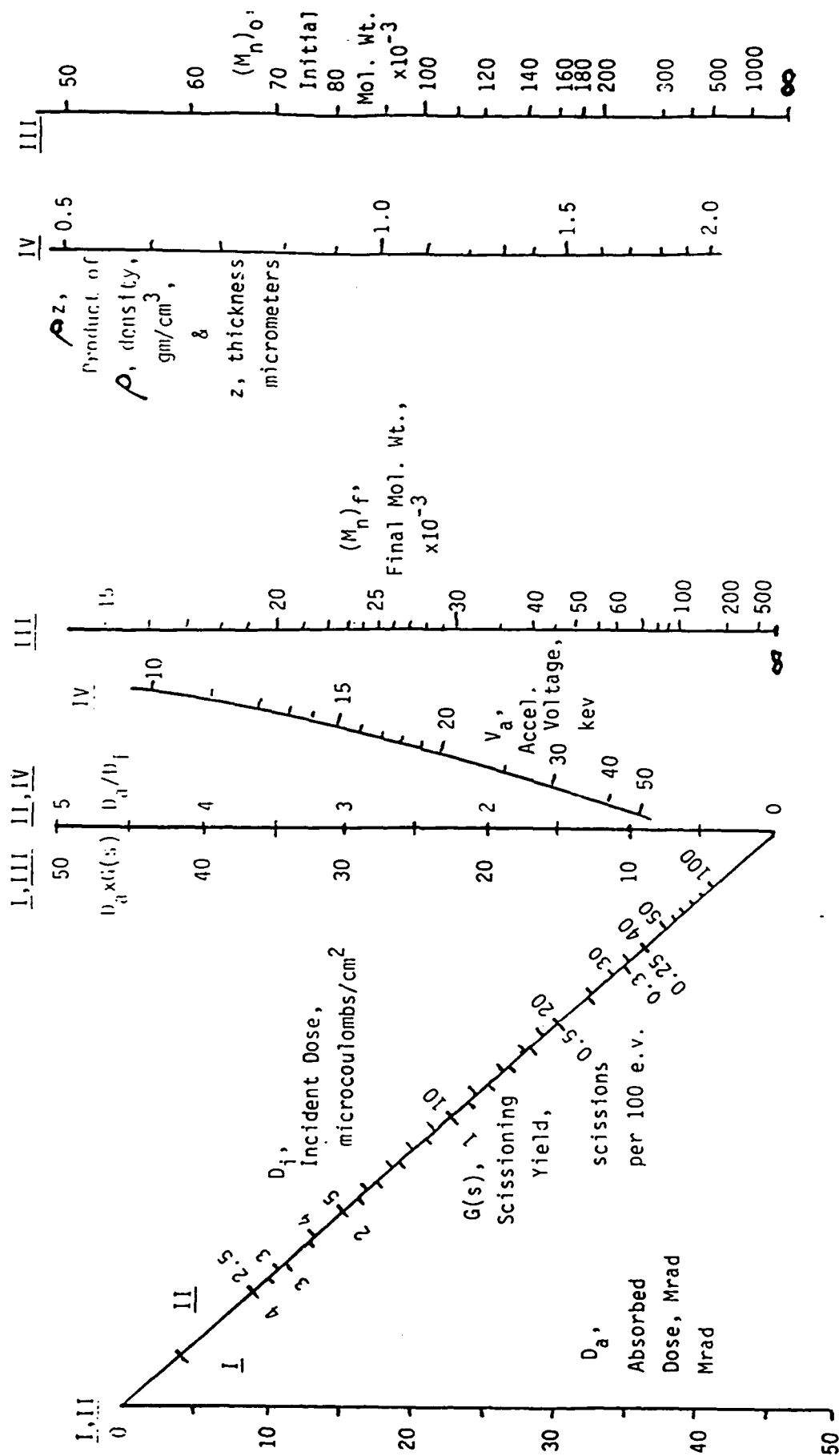
d/d_0 , Unexposed thickness remaining



INCIDENT DOSE, D , $\mu\text{C}/\text{cm}^2$

13. Comparison of thinning behavior¹² for a copolymer of monomethyl itaconate (73 wt.%) with methyl methacrylate ($\blacktriangle$) and PMMA ($\circ$).

14. Sensitivity nomograph.



TECHNICAL REPORT DISTRIBUTION LIST, GENERAL

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Chemistry Division, Code 1113 800 North Quincy Street Arlington, VA 22217-5000	3	Dr. Ronald L. Atkins Chemistry Division (Code 385) Naval Weapons Center China Lake, CA 93555-6001	1
Commanding Officer Naval Weapons Support Center Attn: Dr. Bernard E. Douda Crane, IN 47522-5050	1	Chief of Naval Research Special Assistant for Marine Corps Matters Code OOMC 800 North Quincy Street Arlington, VA 22217-5000	1
Dr. Richard W. Drisko Naval Civil Engineering Laboratory Code L52 Port Hueneme, California 93043	1	Dr. Bernadette Eichinger Naval Ship Systems Engineering Station Code 053 Philadelphia Naval Base Philadelphia, PA 19112	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	2 <u>high</u> <u>quality</u>	Dr. Sachio Yamamoto Naval Ocean Systems Center Code 52 San Diego, CA 92152-5000	1
David Taylor Research Center Dr. Eugene C. Fischer Annapolis, MD 21402-5067	1	David Taylor Research Center Dr. Harold H. Singerman Annapolis, MD 21402-5067 ATTN: Code 283	1
Dr. James S. Murday Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1		