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DISSOLUTION RATES OF POLYMERS AND COPOLYMERS BASED ON METHYL,
ETHYL, AND BUTYL METHACRYLATE

by

R. J. Groele and F. Rodriguez

Prepared for presentation before the
Division of Polymeric Materials: Science and Engineering,
American Chemical Society
Los Angeles, CA, Sept. 25-30, 1988

Olin Hall, Cornell University
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Ithaca, NY 14853

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19 ABSTRACT (Continue on reverse if necessary and identify by block number) ✓ The rate of dissolution (DR) of thin (1 μm) films of various methacrylate polymers was measured using laser interferometry. The polymers were all of high ($M_n > 500 \times 10^3$) molecular weight and included homopolymers of methyl methacrylate, MMA, ethyl methacrylate, EMA, and n-butyl methacrylate, BMA, as well as copolymers of MMA with EMA and with BMA. Glass transition temperatures estimated by DSC ranged from 36°C (PBMA) to 115°C (PMMA). Films were applied to silicon wafers by conventional spinning and baking. The DRs in methyl isobutyl ketone at 30°C ranged from 0.042 μm/min (PMMA) to c. 150 μm/min (PBMA). Activation energy, E_a, in the limited span of 20 to 400 decreased as T_g decreased. In agreement with other workers, E_a for PMMA was 25 kcal/mol. However, the E_a dropped almost to half that value for PEMA and for BMA-rich copolymers.					
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DISSOLUTION RATES OF POLYMERS AND COPOLYMERS BASED ON METHYL, ETHYL, AND BUTYL METHACRYLATE.

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Introduction

The dissolution rate, DR, of thin films of organic polymers is a critical parameter in microlithography. The difference in DR between irradiated and unexposed film (the resist) permits the production of a polymer mask or stencil through which the various operations of doping, insulating, and metallizing can be carried out on the surface of a silicon wafer. The stencil acts in an analogous fashion to the stencil in another, more familiar, form of lithography, silk screening. For some years, poly(methyl methacrylate), PMMA, has been regarded as a standard material for thin films in which sub-micrometer patterns are drawn by scanning electron beams. PMMA is a positive-working resist material in that it becomes more soluble on irradiation through the process of random chain scissioning.

Because of PMMA's importance, it is instructive to measure the effects of variations in structure on DR. Many a commercial "PMMA" is, in fact, a copolymer. It was the extreme variability of DRs found when PMMAs from several industrial sources were compared that led to the present study. Polymers and copolymers of methyl, ethyl, and n-butyl methacrylate were examined. The abbreviations MMA, EMA, and BMA are used for the three monomers.

Experimental details

Polymers were prepared by bulk polymerization using 0.05 g of 2,4-dichlorobenzoyl peroxide in 20 ml of monomer or monomer mixture.

After 24 h at 60°C, the glassy polymer (high conversion) was recovered, dissolved in acetone, precipitated by addition of water, and dried. All molecular weight measurements were made by size exclusion chromatography ("gel permeation chromatography", GPC). A Waters Model 201 HPLC was used with four μ -Styragel columns having nominal pore diameters of 500, 10^3 , 10^4 , and 10^5 Å. The eluting solvent was tetrahydrofuran (THF) pumped at 2 ml/min. PMMA standards (Polymer Laboratories Ltd) were used for calibration so the molecular weights are PMMA equivalents (Table 1). Polydispersity of the recovered polymers varied only over a narrow range (Table 1).

Glass transition temperatures were estimated from DSC traces. The solvent used in the dissolution measurements was methyl isobutyl ketone, MIBK.

The laser interferometer used for dissolution rate measurement has been described previously [1,2]. In essence, the reflected laser light intensity is monitored while the polymer dissolves. The sinusoidal oscillations give a direct measure of the index of refraction of the film and its rate of dissolution. For the present study, a 2 mW unpolarized HeNe laser (Spectra Physics Model 102-4) with wavelength of 632.8 nm was directed horizontally towards a vertically mounted wafer with an incident angle of 10°. The reflected light was collected by a silicon photodiode with a relatively large active area in order to minimize sensitivity to movements of apparatus. A transimpedance amplifier with variable gain converted the photocurrent to a voltage signal proportional to the light intensity. For some of the work a chart recorder with adjustable chart speed was convenient. For the rapidly-dissolving systems, it was more satisfactory to use an IBM PC/XT computer equipped with a Data Translation DT-2801 12 bit A/D converter. A commercial software package, ASYSTANT+® [Macmillan Co.], was found to facilitate acquisition, storage, manipulation and plotting of the data. An example of the computer-recorded signal is given later (Fig. 2). The thickness period d is given by [2]:

$$2d = \lambda / (n_2^2 - n_1^2 \sin^2 \Theta_1)^{1/2} \quad (1)$$

where λ is the wave length of the laser light, n_2 is the index of refraction of the polymer film, n_1 is the index of refraction of the solvent, and Θ_1 is the incident angle of the beam. The DR is simply the ratio of d to the time per cycle in the reflected light trace.

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Polymer films were coated from 4% solutions in chlorobenzene onto 3-inch diameter silicon wafers using a Headway Research Model EC-101D spinner. A spinning speed of 1,600 rpm was used to get approximately one μm -thick films. After spin coating, the polymer films were baked. Baking is usually done to above the glass transition temperature of the polymer and serves to remove residual solvent and to anneal stresses in the film caused by the spin coating step. The standard cycle used for all the materials was (a) 1 h at 150°C in an air-circulating oven followed by (b) a slow cooling to about 70°C over a period of 30 min, also in the oven.

Results and discussion

The thermograms of the various copolymers (Fig. 1) were interpreted to give values of the glass transition temperatures for the materials (Table 1). The results for the homopolymers are in reasonable agreement with literature reports. As usual, transition temperatures from DSC tests are 5 to 10° above those obtained by dilatometry. The copolymer results are internally consistent. All the copolymers form clear films indicating no obvious inhomogeneity. Indeed, none is to be expected since the relative reactivity ratios are very near to unity for these randomly polymerized systems.

All the polymers (except PBMA) exhibited the well-behaved dissolution pattern of PMMA. The reflected light traces were almost perfectly sinusoidal and the wafers retained no residue of polymer after dissolution. As an example, the dissolution trace for a 1:1 MMA:BMA copolymer as acquired directly and stored in an IBM-PC can be seen to be quite regular (Fig. 2). PBMA itself was rather difficult to characterize since it dissolved so rapidly. Because the polymers differed slightly in molecular weight, the DR for each was adjusted to a reference value of $M_n = 700,000$. In the high molecular weight region, Cooper [3] had found that the DR varied with the M_n to the -0.23 power for PMMA.

$$(\text{DR})/(\text{DR}^*) = \{(M_n^*)/(M_n)\}^{0.23} \quad (2)$$

where a reference dissolution rate and molecular weight are denoted by asterisks. For an M_n of 842,000 the adjustment amounts only to about 4%. For an M_n of 642,000, it is about 2%. These are minor factors compared to the differences found with composition. The polydispersity was almost the same for all so no adjustment was made for it.

DR results for all the polymers in methyl isobutyl ketone, MIBK, at 20°C are summarized in Fig. 3. The transition with composition is smooth, but not linear. The actual rate for PBMA is less certain than for the others since it dissolved so rapidly. The variability in DR of commercial (nominally) methyl methacrylate polymers can be interpreted in terms of the copolymer results. Addition of only 5% BMA or 10% EMA to an MMA polymer can almost double the DR. With 25% BMA, a copolymer dissolves about 25 times faster than the PMMA of the same molecular weight.

Using published values of intrinsic viscosity parameters, one can estimate a kind of thermodynamic goodness criterion for the ketone solvent and the various polymers. Data are available for the Mark-Houwink parameters K and a for the intrinsic viscosity $[\eta]$ of PMMA, PBMA, and PEMA in 2-butanone at 25°C [4].

$$[\eta] = K(M_n)^a \quad (3)$$

It is to be expected that dissolution in MIBK would parallel that in butanone at least to some extent. The K values are 7.1, 2.83, and 9.7 (all times 10^{-5} dL/g) for the three homopolymers, respectively. In the same order, the exponents on the molecular weight are 0.72, 0.79, and 0.68. Using these numbers, intrinsic viscosities for a molecular weight of 700,000 are, again in the same order, 1.15, 1.17, and 0.92 dL/g. These numbers are close enough to each other to make it seem unlikely that the faster dissolution of PBMA could be attributed to MIBK being a superior solvent in the thermodynamic sense.

An explanation which might be offered lies in the lower T_g of the copolymers of MMA. This cannot be the whole answer as we can see by considering other experiments in which T_g was varied. In this test, a 1:4 mixture of poly(epichlorohydrin):PMMA was found to dissolve in methyl ethyl ketone at 30°C about 9 times as fast as PMMA. For this blend, the T_g of the mixture is about 40°C measured by DSC [5]. This result can be

compared with, say, 75% BMA copolymer with a similar T_g but which dissolves about 2,000 times faster than PMMA. Poly(epichlorohydrin) is a high molecular weight "plasticizer" with $M_n = 300,000$. The same effect is noted if a low molecular weight plasticizer is used. When poly(ethylene oxide), PEO, with a M_n of 3,900 is blended with PMMA, the T_g is depressed to 65°C by 20% PEO [5]. Cooper found that the 20% PEO blend dissolved about 2.5 times as fast as PMMA [3]. This is, once again, a far cry from the increase in rate observed for the BMA and EMA copolymers with similar T_g s. It is rather obvious that alteration of T_g is not by any means the only factor in changing DR.

Another way of considering the differences with T_g is to compare DRs at several temperatures. Dissolution rates were measured at three temperatures (Table 2). The effect of changing the dissolution temperature and T_g can be seen by plotting DR versus the difference between dissolution temperature $T(DR)$ and T_g (Fig. 4). PMMA actually dissolves faster than the copolymers when the basis of comparison is $[T_g - T(DR)]$.

If the rate is assumed to have an Arrhenius temperature dependence, an activation energy for DR can be calculated (Fig. 5, Table 2). The Arrhenius dependence will generally hold over a narrow temperature range as in this case. The activation energy measured for PMMA matches values previously reported (Table 3). Cooper had reported that solvent systems with widely different DRs all had the same activation energy [6]. However, Ueberreiter had observed a decrease in activation energy near the glass transition temperature for PMMA in dimethyl phthalate [10]. He attributed this to separate mechanisms of the dissolution process for the rubbery, glassy, and transition states. Above 80°C, the activation energy he reported was only about 5 kcal/mole.

It is conceivable that the experimental technique could enter into the picture. Upon immersion of the coated wafer in the solvent, thermal equilibrium is not immediately obtained. Rough calculations of unsteady state heat transfer with reasonable liquid film heat transfer coefficients indicate that the wafer should be within 1°C of the solvent temperature within a few seconds of immersion. If we assume that the liquid film coefficient h is controlling, a simple energy balance relates the temperature of the wafer, $T(w)$ to its original temperature $T(o)$ and that of the solvent $T(s)$ at any time t by the density ρ , specific heat c , and thickness z of the wafer [11]:

$$2.303 \log \{ [T(s) - T(o)] / [T(s) - T(w)] \} = ht / (z\rho c) \quad (4)$$

For the silicon wafers employed, $z = 0.36$ mm and $\rho c = 1.65$ J/cm³K.

A "worst-case" calculation assuming a liquid film heat transfer coefficient of 570 W/m²°K (100 Btu/h.ft.²°F in engineering units) gives a time of 2.2 seconds for 90% attainment of equilibrium. Experimental evidence of changing temperature would be a change in DR as

the film dissolves. In fact, there is no discernible change in the periodicity of the sinusoidal traces even when films dissolve completely in less than a minute.

Conclusions

Copolymers of MMA with EMA and BMA dissolve more rapidly than PMMA more or less in proportion to the monomer content. Neither the thermodynamic "goodness" of the solvent nor the decreased interval in temperature between T_g and dissolution temperature seem sufficient to explain the differences. The decrease in activation energy for dissolution as MMA content decreases deserves further attention.

Acknowledgments

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Table 1 Characterization of Methacrylate Homopolymers and Copolymers
Polymer Composition(Wt.%)

Polymer Composition(Wt.%)			Molecular Weight			T _g (DSC)
MMA	EMA	BMA	M _n	M _w	M _w /M _n	°C
100	0	0	690	1,470	2.13	115
75	25	0	642	1,360	2.12	98
50	50	0	778	1,600	2.06	80
25	75	0	842	1,790	2.13	78
0	100	0	793	1,660	2.09	73
75	0	25	1,020	1,760	1.73	86
50	0	50	681	1,570	2.31	72
25	0	75	800	1,570	1.96	56
0	0	100	621	1,490	2.40	36

Table 2 Dissolution Rates and Activation Energies (PMMA in MIBK)

Polymer Composition(Wt.%)			Dissolution Rate, $\mu\text{m}/\text{min}$			Activation Energy
MMA	EMA	BMA	20°C	30°C	40°C	kcal/mol
100	0	0	0.0091	0.042	0.147	25.4
75	25	0	0.041	0.19	0.48	22.5
50	50	0	0.22	0.76	1.79	19.2
25	75	0	0.81	2.4	6.3	18.6
0	100	0	2.8	7.3	16.4	16.2
75	0	25	0.19	0.74	1.55	19.0
50	0	50	3.2	8.6	18.4	16.0
25	0	75	26	61	115	13.5
0	0	100	>70	>150	>230	c. 11

Table 3 Activation Energies for Dissolution

Polymer	Solvent	Activation Energy kcal/mol	Reference
PMMA	Methyl ethyl ketone	26	6
PMMA	Methyl isobutyl ketone	24	7
PMMA	Methyl isobutyl ketone	25	8
Polystyrene	Iodohehexane	25	9

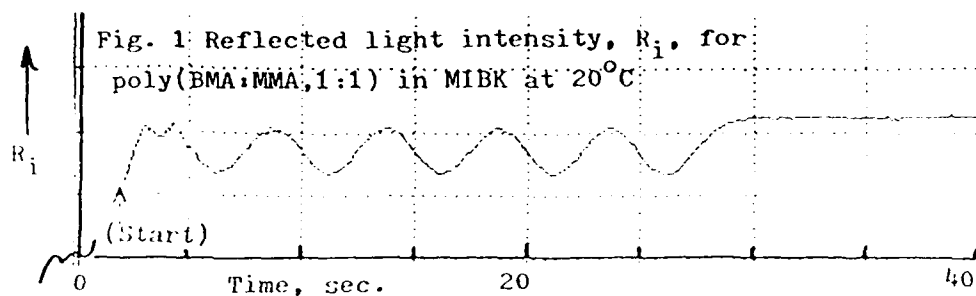


Fig. 3 Dissolution rate as a function of difference between glass trans. and dissolution temperatures

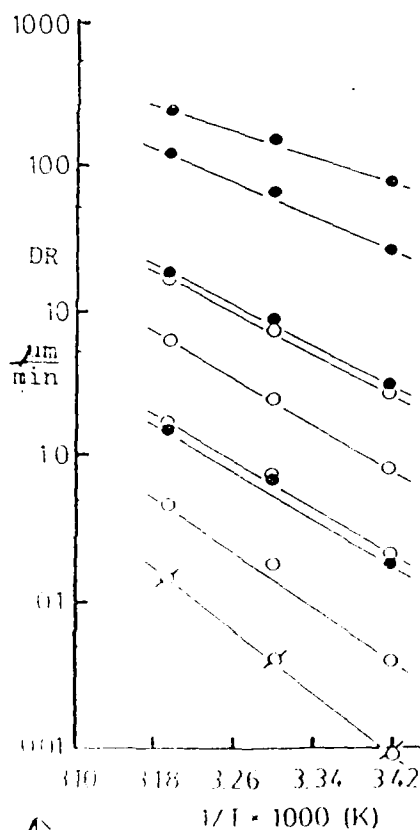
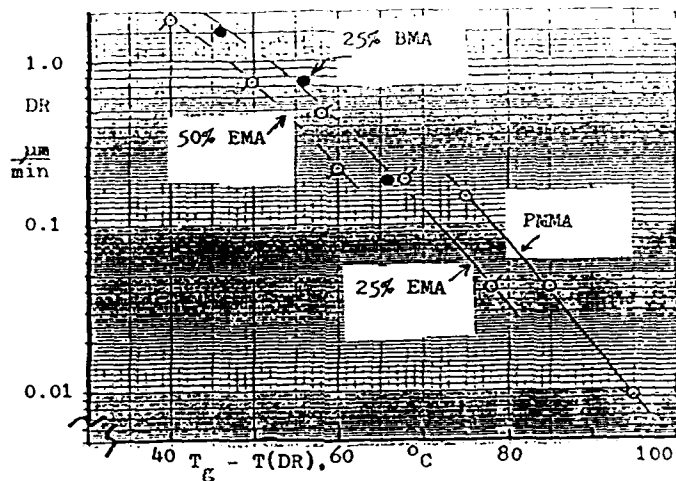
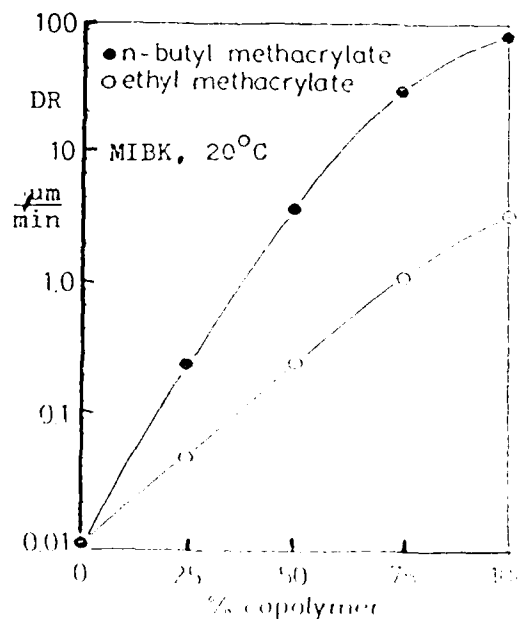


Fig. 4 Arrhenius plots for 20, 30, and 40°C. Hollow circles, EMA & copolymers, solid circles, BMA & copolymers. (See also Table 2)

Fig. 2 Dissolution rate for copolymers of MMA (adjusted to $M_n = 700,000$)



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