Polymer Dissolution. I. On the Dissolution Behavior of Copolymers of Methyl Methacrylate and Methacrylic Acid

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SYNOPSIS

Copolymers of methyl methacrylate with methacrylic acid [P(MMA/MA)] are interesting resist materials for microlithography. At moderate baking temperatures, these copolymers undergo an intramolecular cyclization, yielding terpolymers containing anhydride moieties. This process has striking consequences for the dissolution behavior and results in higher ketone solubilities. The dissolution rates in methyl ethyl ketone (MEK) and in mixtures with ethyl glycol (EG) correlate in an Arrhenius-like manner with the reciprocal baking temperatures. Two distinct temperature ranges with different slopes between 130–180°C and 180–230°C are found. This is in good agreement with other findings, indicating a different mechanism of anhydride formation in these temperature regions. The activation energies for the dissolution of P(MMA/MA) in EG or EG/MEK mixtures are about 17 kcal/mol and those of the thermally treated material in MEK or MEK/EG or mixtures of MEK with methyl isobutyl ketone (MIBK) are in the range of 20–30 kcal/mol. For the investigation of the M_n dependence, γ-irradiated probes of the copolymer were used. We obtained the usual exponential M_n dependence with an exponent of 0.7–0.8 in MIBK and 0.3–0.4 in EG. Our findings are in agreement with a "relaxation-controlled" dissolution behavior, especially for the anhydride-containing terpolymer. No residual layers or pronounced inhibition periods indicative for gel-layer formation, however, could be found. We suggest a normal dissolution process with a very small gel layer. For the copolymer in an alcohol-containing solvent, a stress-driven dissolution behavior is more likely. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Copolymers of methyl methacrylate with methacrylic acid [P(MMA/MA)] are interesting resist materials for X-ray and electron-beam microlithography because of their irradiation sensitivity and their dissolution behavior.[1–4] At moderate baking temperatures, these polymers undergo an intramolecular cyclization, yielding anhydride moieties. This process has striking consequences for the dissolution behavior and results in higher ketone solubility.[4,5] Thereby, optimization is possible for different lithographic techniques and applications.[4,6]

To obtain more detailed information on the dissolution process, we have undertaken this laser interferometric study of dissolution kinetics in ethyl glycol (EG), methyl ethyl ketone (MEK), or methyl isobutyl ketone and their mixtures under different baking conditions.

EXPERIMENTAL

The synthesis of P(MMA/MA) in the ratio 66 : 34 mol % (M_w = 128,000, M_n = 83,000) was performed in solution by radical polymerization in the presence of AIBN. The spin coating of a 10% methyl glycol solution of the polymer at 3000 rps onto Si wafers gave layers of 1–2 μm thickness. The thermal treatment was performed either by a baking procedure of thin layers in a convection oven under air or in acetophenon solution at 200°C, yielding a product containing intramolecular anhydride moieties. The anhydride content was estimated by ^{13}C-NMR using

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an MSC 400 MHz (Bruker). Powdered probes of the copolymer in evacuated glass vials were irradiated with a ^{60}Co source in the range of 5–25 Mrad to obtain copolymers with different molecular weights. The molecular weights were determined from methylated probes in THF by GPC with a Knauer RI-Visco detector.

The dissolution process of the layers was watched by laser interferometry. The interferometer consists of a 2 mW He—Ne laser, electronic equipment, and a thermostated reaction vessel with stirrer.

RESULTS AND DISCUSSION

The Baking Temperature

In the temperature range from 130 to 230°C, the dissolution rates rise continuously in both MEK and MEK/EG 4 : 1 mixtures. The dissolution rates correlate in an Arrhenius-like manner with the reciprocal baking temperatures in accordance with higher ketone solubility at a higher anhydride content (Fig. 1).

At 230°C, a break in this linear pseudo-Arrhenius plot was observed, indicating a change in the type of process modifying the polymer layer. This is in agreement with other findings: MS investigations[7] have shown that at temperatures up to 220°C the anhydride formation is accompanied by water elimination and that at higher temperatures methanol elimination is predominant.

In the range from 160 to 220°C, the logarithms of the recently described[8] increase in methacrylic anhydride (MAN) in the solid layer also correlate linearly with $1/T$ (Fig. 2). Since both the logarithms of MAN increase c and of the dissolution rates s are linear vs. $1/T$, an logarithmic relationship exists between them:

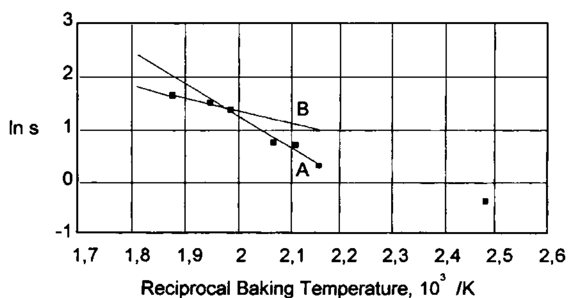

Figure 1 Natural logarithms of the dissolution rates s(nm/s) of P(MMA–MA) layers in EG/MEK 1 : 4 vs. the reciprocal baking temperatures. Regression: (A) $r^2 = 0.98$; (B) $r^2 = 0.96$.

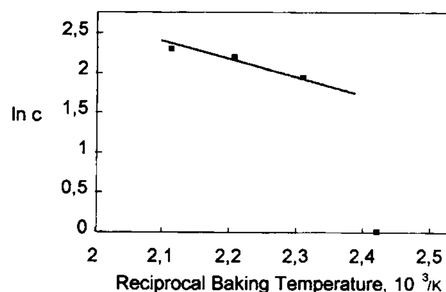

Figure 2 Pseudo-Arrhenius plot of MAN content c (mol %) in solid copolymer layers.

$$\lg s = a \lg c + b \qquad (1)$$

which reflects the connection between copolymer composition and dissolution velocity.†

The Baking Time

The dissolution rates also rise at prolonged baking times (Fig. 3), reflecting the changes in polymer composition during thermal annealing in the solid layer. The initial increases in dissolution velocity (1 h levels) are, however, much more pronounced, indicating the influence of additional factors on the dissolution velocities, especially in the very beginning of the reaction. The above-mentioned Arrhenius-like temperature dependence of the dissolution velocities holds also for the data obtained at longer baking times.

The Molecular Weight

For the dissolution rates of polymer layers, an exponential dependence on the molecular weight was found experimentally[9] and connected with the reptation process of the macromolecules in a swollen layer.[10] The molecular weight of the P(MMA/MA) was varied by γ-irradiation. The side-chain carboxyl groups preferably undergo radical decomposition and initiate main-chain scissions.[7] The dissolution velocities in MEK exhibit the expected exponential M_n dependence with an exponent value of 0.7–0.8, which was often taken as an indicator for an relaxation-controlled dissolution process involving a rubbery-like layer at the solvent–polymer interface.[11,12]

In MEK/EG, the exponent reaches about half this value (0.3–0.4); further, a break in the log–log

† The proof of the general validity of such a kind of relationship is in progress.

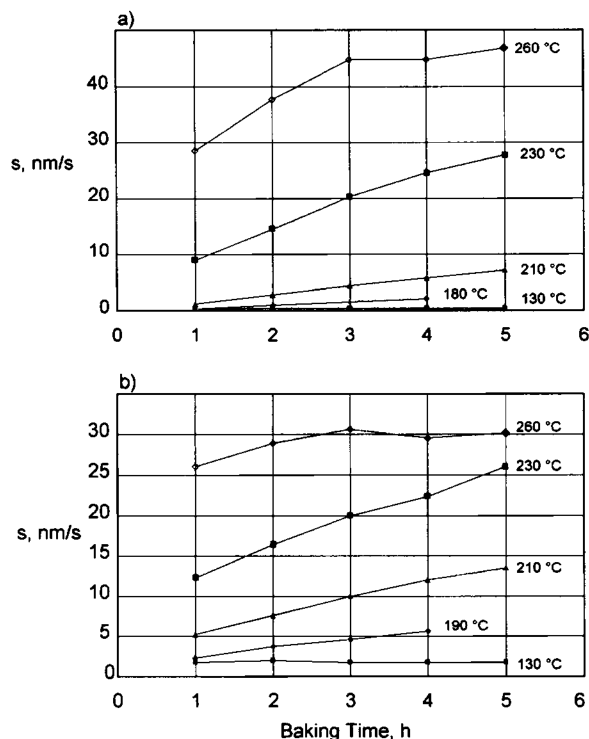

Figure 3 Time dependence of copolymer dissolution rates after thermal annealing: (a) in MEK at 25°C; (b) in EG/MEK 1 : 4 at 25°C.

correlation can be discussed (Fig. 4). This may be indicative for a stress-driven dissolution process[13] in alcohol-containing media for our systems in agreement with the somewhat lower activation energy of dissolution (see below).

Solvent Temperature

The dissolution velocities exhibit a pseudo-Arrhenius dependence from the solvent temperatures that can be used to some extent to characterize the dissolution process. Activation energies around 20–30 kcal/mol thus obtained were usually connected to a relaxation-controlled dissolution.[14-16] For PMMA in several solvents, values ranging from 17 to 30 kcal/mol were found.[14-19]

P(MMA/MA) layers annealed for 1 h at 130°C do not yet contain anhydride moieties and represent the pure MMA–MA copolymer. They very slowly dissolve in MEK and were investigated in EG and in MEK/EG mixtures 1 : 1. An activation energy for dissolution of 17 kcal/mol was estimated in both cases.

Layers of the copolymer modified by preliminary thermal treatment in solution (acetophenon, 200°C, 1 h), which guarantees the production of intramolecular anhydride moieties exclusively, and also P(MMA/MA) layers prebaked at 180°C exhibit good ketone solubility. The activation energies obtained for MEK and MIBK were 20 and 28 kcal/mol, respectively. The higher activation energy for MIBK reflects the larger size of the solvent molecule. It is well known from PMMA dissolution that in solvents of about 1 nm size the diffusion became highly hindered and the size of MIBK molecules is in this critical range.[20]

The interferometric traces and also the kinetic curves (Fig. 5) do not give evidence for a pronounced gel-layer formation during the investigated dissolution processes. In MEK, only at low temperatures and for the slow dissolution in pure MIBK were little inhibition periods seen in some cases [Fig. 5(b) and (c)]. The obtained activation energies and molecular weight dependencies for the dissolution in ketones, however, characterize the so-called normal dissolution.[9] Therefore, we conclude that a relaxation-controlled dissolution behavior with a very small gel layer determines the dissolution process

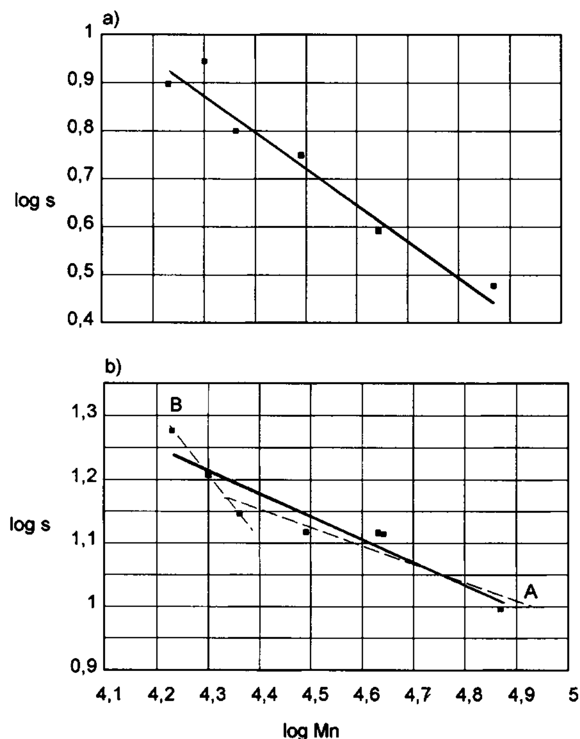

Figure 4 M_n dependence of dissolution rates for P(MAA/MA): (a) MEK at 25°C, regression: $r^2 = 0.94$, $\alpha = 0.7$–0.8; (b) MEK/EG 1 : 1 at 25°C, regression: $r^2 = 0.88$, $\alpha = 0.3$–0.4; (A) $r^2 = 0.99$, $\alpha = 0.3$; (B) $r^2 = 0.99$, $\alpha = 1$.

of thermally modified anhydride-containing terpolymers in ketones.

The lower values of activation energy and the molecular weight exponent in the case of EG-containing mixtures give some evidence that the dissolution mechanism in an alcoholic solution for the pure P(MMA/MA) should be different and tends toward a stress-driven process without a gel layer.

Solvent Composition

Both MEK and MIBK are good solvents in the thermodynamically sense for the anhydride-containing polymers under investigation. Interestingly, the experimental dissolution rate data can be described by the function

$$\lg s_{1,2} = x_1 \lg s_1 + x_2 \lg s_2 \quad (2)$$

where s_1 and s_2 means the dissolution rates in the pure solvents, and x_1 and x_2, their molar parts in the mixture (Fig. 6). If the temperature dependence of the dissolution rates is known, that relation can be rewritten:

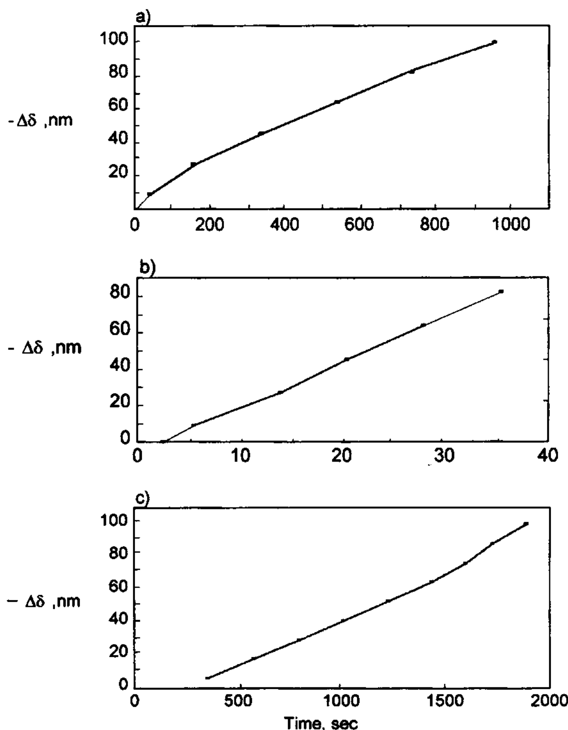

Figure 5 Thickness decrease of P(MAA/MA) Layers vs. time in EG 1 : 1 at 18°C: (a) thermally treated copolymer in MEK at 18°C; (b) and MIBK at 47°C (b).

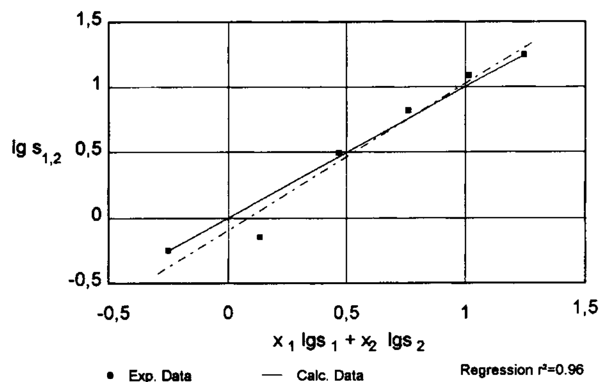

Figure 6 Correlation between dissolution rates and solvent composition according to eq. (2).

$$s_{1,2} = A_1^{x_1} \times A_2^{x_1} \exp\{-[xE_1\, x_2E_2]/RT\} \quad (3)$$

where A_1 and A_2 are the respective Arrhenius factors.†

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