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NEGATIVE-WORKING ELECTRON BEAM RESIST BASED ON POLY(METHYL METHACRYLATE)

by

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Increasing the molecular weight of the PMMA component to 450,000 (M_w) increases the sensitivity to 1 $\mu C/cm^2$, but results in poorer resolution. Use of nearly monodisperse PMMA ($M_n \cong M_w$ = 29,000) improves the contrast to a γ value of 2.3 without affecting resolution or sensitivity relative to the blends with low molecular weight PMMA.

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Negative-Working Electron Beam Resist Based on Poly(methylmethacrylate)

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ABSTRACT

Blends of polymethylmethacrylate (PMMA) and dipentaerythritol pentaacrylate (DPEPA) respond to electron beam exposure as negative resists, with sensitivity that increases with increasing DPEPA concentration. Blends of 80 wt. % PMMA (M_n = 22,500) and 20 wt. % DPEPA exhibit an electron sensitivity of 4 $\mu C/cm^2$ (based on 50% of exposed film remaining) and a contrast (γ) of 1.2. Resolution of 0.25 μm has been demonstrated with this blend without the use of non-solvent rinses or plasma de-scumming. This superior resolution for a negative electron resist is attributed to the small degree of swelling of the PMMA host polymer.

Increasing the molecular weight of the PMMA component to 450,000 (M_w) increases the sensitivity to 1 $\mu C/cm^2$, but results in poorer resolution. Use of nearly monodisperse PMMA ($M_n \cong M_w$ = 29,000) improves the contrast to a γ value of 2.3 without affecting resolution or sensitivity relative to the blends with low molecular weight PMMA.

Image formation in these blends is largely controlled by differential dissolution rates, with reactive plasticizer (DPEPA) enhancing dissolution in unexposed regions and inhibiting dissolution after exposure. The degree of polymerization and crosslinking of the plasticizer necessary for inhibiting dissolution rates is less than that required for complete insolubilization of the resist film. Thus, exposure at moderate doses results not only in a non-swelling image, but also one that is easily stripped with developing solvent after processing. This mechanism differs greatly from that of conventional crosslinking negative electron beam resists for which exposure renders the exposed regions insoluble in any developing solvent.

INTRODUCTION

Developing high resolution negative electron resists that do not swell during solvent developing has been a serious challenge in the microelectronics field. Conventional negative electron resists, such as poly(chloromethylstyrene) (PCMS), suffer from severe swelling problems such as "bridging" and "snaking".[1,2] Even with elaborate rinsing schemes and plasma descumming, the resolution of these resists usually is limited to about half a micron.[3] We have investigated blends containing a host polymer and a reactive monomer to provide resist materials with improved sensitivity and resolution. It was hoped that the interpenetrating network formed during exposure of such blends would not be as susceptible to swelling as a crosslinked single component negative resist. We recently reported some success combining a vinyl chloride terpolymer with reactive plasticizers for enhanced sensitivity and resolution.[4] These blends resulted in excellent sensitivity of less than 1 $\mu C/cm^2$, but swelling continued to limit resolution.

In the present work, we seek to minimize resist swelling by blending reactive plasticizer with poly(methylmethacrylate) (PMMA). PMMA is well known for its excellent film properties and particularly for its lack of swelling which has enabled its use for very high resolution imaging.[5] PMMA is also expected to be

desirable for use in these blends because it does not crosslink by itself during electron exposure, and thus should not lead to a highly crosslinked system which would contribute to swelling. Scissioning of the PMMA is not expected to interfere with the functioning of the blended resists, since exposures of these blended resists are generally carried out with lower electron doses than those at which PMMA undergoes appreciable chain-scissioning. The question of how simultaneous scissioning of the base polymer and polymerization of reactive monomer would affect resist contrast warranted investigation of these systems.

In the present paper, we present the lithographic evaluation of blends of PMMA with dipentaerythritol pentaacrylate (DPEPA), a penta-functional acrylate monomer that is compatible with PMMA. The effect of the concentration DPEPA on the lithographic response of these blends is evaluated using electron beam flood exposures. The effects of molecular weight and molecular weight distribution on the sensitivity, contrast, and resolution of the blends is evaluated. The lithographic mechanism of these blends is investigated using a chromatographic technique to analyze the compositions of the exposed and unexposed blends and by measuring dissolution rates.

EXPERIMENTAL

The reactive monomer, dipentaerythritol pentaacrylate (DPEPA), was obtained from Polymer, Monomer and Dajac Laboratories, Inc. Three different forms of polymethylmethacrylate (PMMA) were used in formulating the PMMA/DPEPA blends, each with differing molecular weights and molecular weight distributions. A low molecular weight PMMA was obtained from duPont (Elvacite 2008) with measured molecular weights of M_n = 22,500 and M_w = 38,000. High molecular weight PMMA was obtained from KTI Chemicals (resist grade, 496K, 6% in chlorobenzene), with measured molecular weights of M_n = 205,000 and M_w = 450,000. The monodisperse PMMA is a GPC standard, obtained from Polymer Laboratories, Ltd., with $M_n \simeq M_w$ = 29,000.

Molecular size determinations were made using a Waters gel permeation chromatograph (GPC) equipped with μStyragel columns, also from Waters. Tetrahydrofuran (THF) was used as the eluting solvent in all cases. PMMA calibration standards were used for molecular weight correlations.

Electron flood exposures were used for preliminary sensitometry and for preparation of exposed resist films for dissolution rate measurements and for GPC/LC analysis. Coated silicon wafers were placed in the film cassette of a modified RCA EMV-3 transmission electron microscope (TEM) and exposed to a broad beam of electrons using an accelerating voltage of 50 kV. Films were exposed to the beam for specified time periods. Incident electron doses were determined from the exposure time and the electron charge density which was measured with a Faraday Cup.

Films for lithographic evaluation were spin-cast from solutions in chlorobenzene. Spin speeds varied from 3000 to 5000 rpm, and the solids concentration in the casting solutions varied from 7 to 12 wt. %. Typical film thicknesses were 0.5 to 1 μm, as measured with a Lietz Film Thickness Interferometer and/or a Tencor Instruments Profilometer. Test patterns for sensitometry and evaluation of contrast and resolution were exposed using a Cambridge EBMF 10.5 at the National Nanofabrication Facility (NNF) at Cornell University. All patterns were exposed using an accelerating voltage of 20 kV. Patterns were dip-developed in methyl isobutyl ketone (MIBK) at 23°C, followed by blowing dry with nitrogen gas. Solvent

rinses were not used after development. The developed patterns were post-baked for 15 min. at 80°C. No descum procedures were used. Resolution of the patterns was evaluated using a Cambridge S200 SEM.

Dissolution rates were determined by measuring film thicknesses of exposed (Cambridge, 20 kV) patterns after developing for various lengths of time. Dissolution rates were also measured using a laser interferometer film thickness monitor.[6]

The polymer and monomer fractions of the blended films were analyzed using a gel permeation chromatography (GPC)/liquid chromatography (LC) technique.[7] Films were flood exposed with the RCA TEM, and the exposed films were dissolved in THF. The resulting solutions were injected onto a series of three μBondagel columns (Waters, E1000, E500 and E125) followed by a 100 Å μStyragel column (also from Waters). The solvent delivery system for these analyses was an HP 1090 HPLC. Peaks were detected with a UV detector at 220 nm. This series of columns resulted in distinguishable peaks for both the PMMA base polymer and the DPEPA plasticizer.

RESULTS

Lithographic Response:

Resist films of blends of PMMA and DPEPA decrease in solubility upon exposure to electrons, and thus function as negative electron resists. The sensitivity of these resist blends improves with increasing concentration of DPEPA, as observed by electron flood exposures at 50 kV. Blends with 10% or less DPEPA exhibit limited sensitivity, while those with 20% or more DPEPA exhibit sensitivities in the 1 to 5 $\mu C/cm^2$ range, based on 50% thinning (Figure 1). This lithographic response occurs at doses below those at which PMMA is expected to scission appreciably, and thus such scissioning does not interfere with the reduction in solubility caused by DPEPA. At very high doses (100-1000 $\mu C/cm^2$ at 20 kV), some scissioning probably occurs, leading to a reduction in resist film thickness with extreme overexposure (Figure 2).

Blends containing 20% DPEPA were selected for further investigation because of their superior contrast and film properties. Blends containing 80 wt.% PMMA (M_n = 22,500) and 20 wt.% DPEPA exhibit an electron sensitivity of 4 $\mu C/cm^2$ at 20 kV (based on 50% thinning, which corresponds to $D_{g,0.5}$, the 50% gel dose). The contrast attained with this blend when developing with MIBK is about 1 (γ). Very little swelling is observed during developing of patterns in this resist blend. Because of this lack of swelling, it is not necessary to use a non-solvent rinse, and development can be carried out in a single step, using a single developing solvent (MIBK in most cases). We have demonstrated resolution of 0.25 μm using this blend (Figure 3). Scumming is not observed, and there is no need for a plasma de-scum after development.

Prebaking at temperatures of 150°C and above results in thermally induced crosslinking which prevents unexposed resist from being completely dissolved during developing. Fortunately, insoluble residues in unexposed resist do not occur after prebaking for one hour at temperatures of 120°C or less. The lithographic responses of the blends are the same after a one hour prebake at 80°C as after no prebake at all, except that developing times are increased by prebaking.

Molecular Weight Effects:
The initial molecular weight and molecular weight distribution of the base polymer have significant effects on the lithographic response of these blends. Increasing the molecular weight of the PMMA host polymers to 450,000 (M_w) improves the sensitivity ($D_{g,0.5}$) of the 20% DPEPA blend to 1 $\mu C/cm^2$ (Figure 4). However, the resolution is diminished due to some swelling observed during development of this high molecular weight blend. Use of nearly monodisperse PMMA ($M_w \simeq M_n$ - 29,000) in blends with 20% DPEPA increases the contrast to 2.3, without affecting sensitivity or resolution relative to the polydisperse host with M_n - 22,500 (Figure 4). Interestingly, these molecular weight effects are very similar to those reported for conventional negative electron resists like poly(chloromethylstyrene) (PCMS).[8]

Lithographic Mechanism:
Image formation in these blends is largely controlled by differential dissolution rates, with DPEPA enhancing dissolution in unexposed regions and inhibiting dissolution after exposure (Figure 5). This mechanism is very distinct from that of conventional negative electron beam resists such as PCMS. PCMS is rapidly developed (10-20 sec.) to a point where the remaining exposed and crosslinked resist is completely insoluble in the developing solvent (Figure 6). Development of PCMS probably involves extraction of low molecular weight, uncrosslinked polymer from the exposed regions. Such a development process involves swelling which limits the resolution of such resists and necessitates the use of carefully selected non-solvent rinses[3] and plasma de-scumming. In comparison, the PMMA/DPEPA blends, under the proper conditions, can be developed in a manner similar to that of pure PMMA, with layers of resist being removed sequentially during development. It is this developing process that allows for greater resolution without the use of non-solvent rinses or de-scumming.

Another advantage of the exposure and developing mechanism of the PMMA/DPEPA blends is that exposed resist can be easily stripped after processing with developing solvent. This avoids the plasma stripping required for removal of conventional negative electron resists after processing.

It is believed that the formation of radicals by the PMMA host polymer contributes to the exposure mechanism of the PMMA/DPEPA blends. PMMA is known to produce radicals at electron doses well below the doses used for imaging of these blends.[9,10] The role of these radicals is believed to be important because blending DPEPA with a more inert base polymer such as a novolac does not result in any lithographic response below an electron dose of 100 $\mu C/cm^2$.

In order to gain more understanding of the exposure mechanism, we evaluated the PMMA/DPEPA blends using a GPC/LC technique to analyze both the polymer and monomer in the blend.[7] This technique was used to evaluate and compare the effects of baking and electron exposure. Baking films of the blend at 150°C for one hour causes thermally induced crosslinking, resulting in insoluble gel formation. GPC/LC analysis of the soluble portion of the baked films shows that predominantly the DPEPA component of the blend is crosslinking and becoming incorporated into the insoluble portion of the gel. This is evidenced by the ratio of the area of the PMMA peak to the area of the DPEPA peak. This ratio (PMMA/DPEPA) increased from 0.9 for unbaked films to 6.1 for films baked at 150°C (Figure 7). When the blended films are flood exposed to 50 KeV electrons, some interesting observations are made

with the GPC/LC chromatographs of the soluble portion of the films (Figure 8). With doses of 5 and 10 $\mu C/cm^2$, some scissioning of PMMA is observed by an increase in the elution time for this component. With an electron dose of 5 $\mu C/cm^2$, the DPEPA component forms a large peak probably associated with dimer (Figure 8). Then at 10 $\mu C/cm^2$ a number of peaks appear which are associated with fragmentation or scissioning of DPEPA (these peaks are not observed after electron irradiation of pure PMMA at this dose[11]). The chromatographs do not show an increase in the PMMA:DPEPA peak area ratio as was observed with the baked films. This indicates that PMMA is being incorporated into the gel along with DPEPA, probably by reaction of the PMMA radicals formed duirng exposure.

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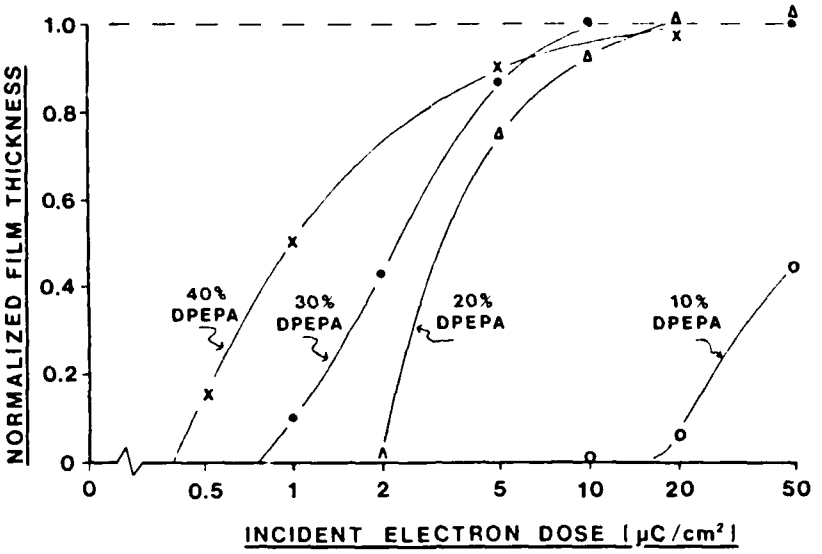

Figure 1. Effect of DPEPA concentration on the lithographic response of PMMA/DPEPA blends, using flood electron exposures at 50 kV.

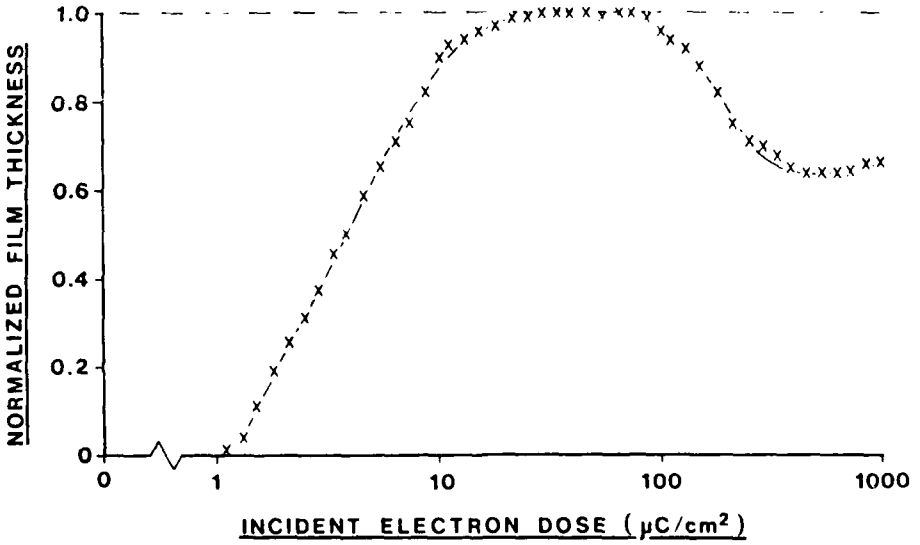

Figure 2. Lithographic response of PMMA (Mn = 22,500) with 20 wt. % DPEPA exposed from 1 to 1000 $\mu C/cm^2$, (Acc. Volt. = 20 kV).

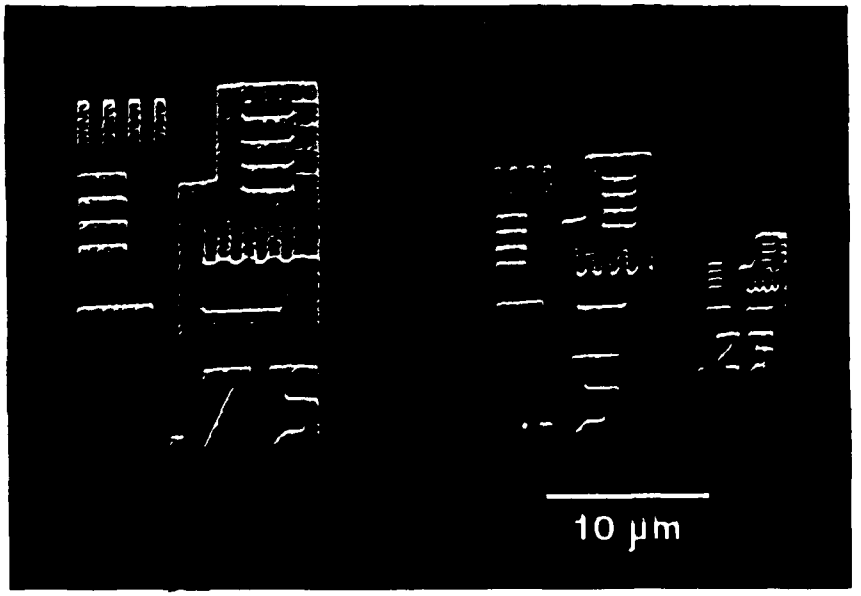

Figure 3. SEM photomicrograph of 0.5 and 0.25 µm features in PMMA/20% DPEPA, exposed at 5 µC/cm^2 (20 kV), and developed with MIBK. No solvent rinses or plasma descum were used.

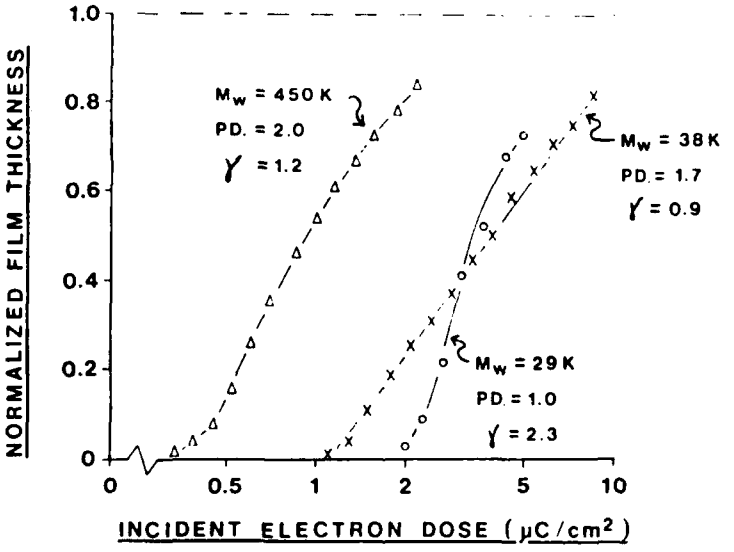

Figure 4. Effect of molecular weight and molecular weight distribution of PMMA on the lithographic response of PMMA/20% DPEPA blends. All films were exposed with an accelerating voltage of 20 kV and were developed with MIBK.

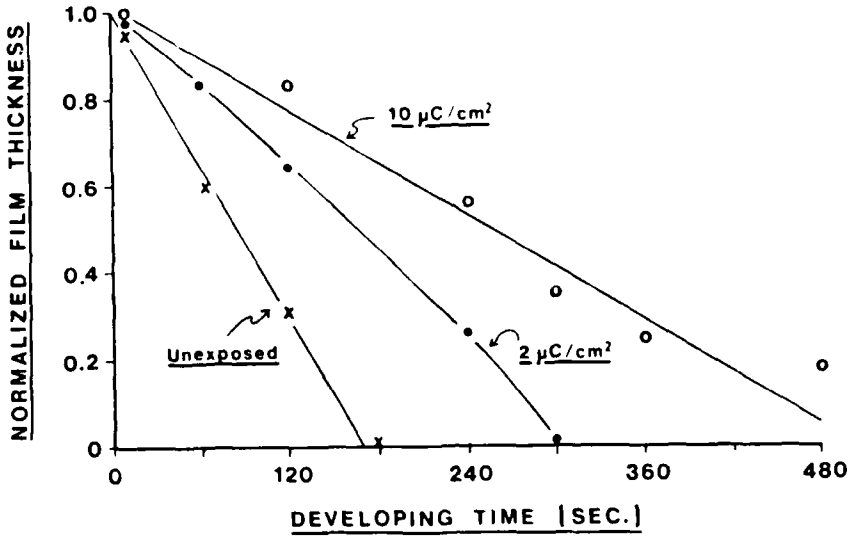

Figure 5. Dissolution kinetics of PMMA/20% DPEPA in MIBK at 23°C (exposures at 20 kV).

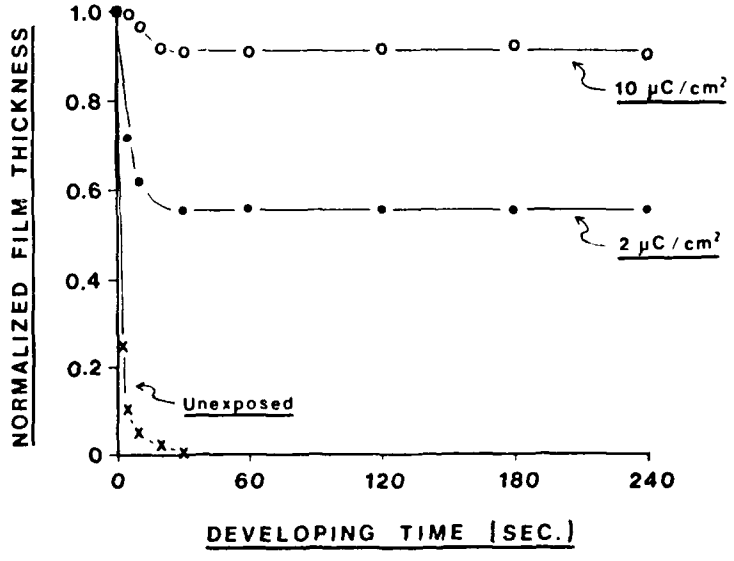

Figure 6. Dissolution kinetics of polychloromethylstyrene (PCMS).

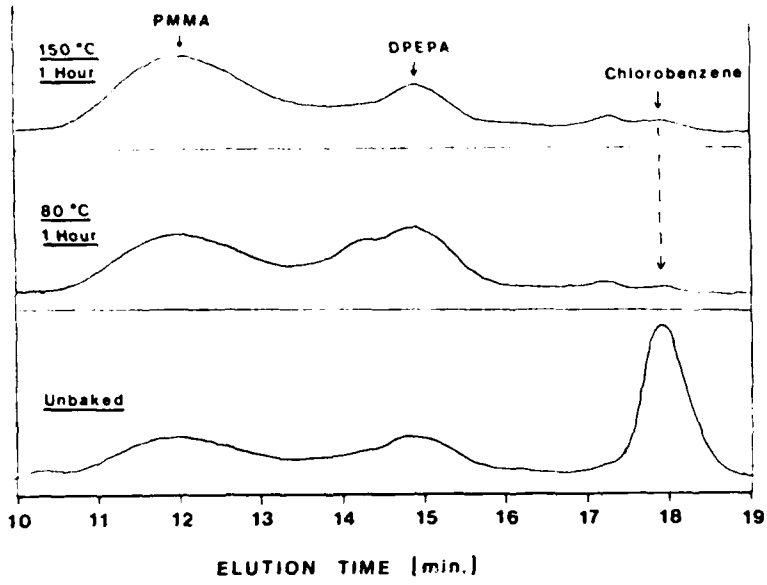

Figure 7. GPC/LC analysis of baked and unbaked films of PMMA/20% DPEPA.

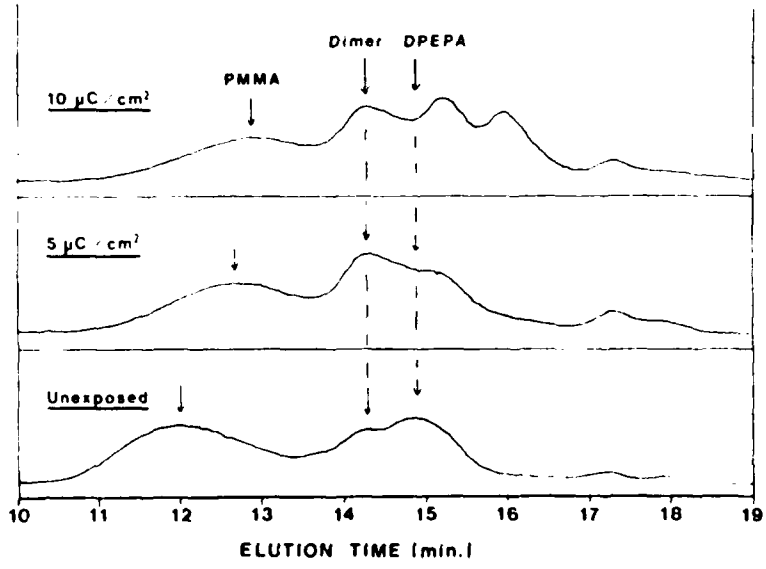

Figure 8. GPC/LC analysis of exposed and unexposed films of PMMA/20% DPEPA. (Electron exposures at 50 kV).

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