

# Poly(methyl methacrylate): influence of tacticity on its use as an electron resist

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The effects of tacticity on the molecular weight distribution, the sensitivity and nature of products after exposure to electron beams are reported. Significant differences in the sensitivity are observed, the isotactic polymer being more sensitive than either the syndiotactic or atactic polymers. The differences in the degradation product can be explained in terms of two competing processes; the first associated with chain scission leading to the expected reduction in molecular weight, and secondly chain extension with a consequent increase in molecular weight. Measurements of the contact angle also indicate changes with the tacticity, indicating differences in the surface energy; however, these data are the opposite of the adhesion strength determined by tape tests. The implications of these observations on the performance of poly(methyl methacrylate) as an electron resist are discussed.

**Keywords** Tacticity; poly(methyl methacrylate); adhesion; electron resist; contact angle measurements; development characteristics

## INTRODUCTION

Poly(methyl methacrylate) (PMMA) is extensively used as a positive electron resist and as such has been investigated extensively<sup>1-6</sup>. The effect of radiation on PMMA has been studied by Charlesby<sup>7</sup> and the effects of electron irradiation by Schultz *et al.*<sup>8</sup> The effects of tacticity have received only limited attention and the object of this paper is to supplement and extend these earlier studies.

For a good electron resist, it is desirable that the polymer should have good adhesion to the substrate during development, degrade easily to a material which has approximately the same molecular weight distribution as the original material but one-fifth of its weight average molecular weight and exhibit solvent selectivity.

PMMA can exhibit stereoisomerism tacticity. Changes in reaction conditions used in synthesis of the resist can lead to differences in the proportions of each type of sequence structure. Problems associated with batch-to-batch variation may in part be ascribed to consequences in the tacticity of the polymer in the resist. The effects of molecular weight distribution before and after the electron irradiation have been explored in a number of publications<sup>1-6</sup>. Investigations of solutions of stereospecific PMMA<sup>9-13</sup> have indicated the formation of complexes between iso- and syndiotactic sequences as well as strong self-association of syndiotactic polymer. As a consequence of these intermolecular interactions, a fringe micelle structure may be formed in the solid with dimensions several times larger than the region of specific polymer chain interaction and this may influence the degradation behaviour of the polymer. Such inhomogeneities may be expected to influence the resolution of the material and ultimate limits possible in terms of edge definition. It is therefore crucial that the effects of tacticity on electron resist behaviour are properly defined.

## EXPERIMENTAL

### Materials

The sample of atactic PMMA was obtained from BDH, and the stereospecific polymers were obtained from Polymer Laboratories (UK). The isotactic material was 98% stereospecific and the syndiotactic material was 87%. The latter polymer was supplied as nominally 100% by the manufacturers. However, examination of the <sup>1</sup>H n.m.r. spectra obtained at 90 MHz in deuterated chloroform using tetramethyl silane (TMS) as reference indicated that the syndiotactic polymer was of lower purity than indicated by the suppliers.

### Molecular weight distribution data

The  $M_w$  and  $M_n$  values before and after irradiation were obtained using gel permeation chromatography (g.p.c.) using tetrahydrofuran (THF) as solvent. The apparatus used was a conventional Walters analytical instrument equipped with both refractive index and u.v. detectors and the data were computed in the usual way.

### Preparation of films for electron beam exposure and contact angle measurements

The films studied were prepared by spinning chromium-covered glass substrates on a Dage-Precima spinner at 1200 rpm using a 10% solution in chlorobenzene as solvent. The thickness of the films was measured using a Rank Talystep. The films are typically of 4  $\mu$ m thickness and were built up by spinning resist over the previously baked spun coating. The films were baked for 1 h at 433 K, which is well above the boiling point of the solvent. All the films were irradiated at 20 kV at the Electron Beam Lithography Unit of the SERC, Rutherford Laboratory, Chilton. At this electron beam acceleration potential, the electron penetration is approx-

**Table 1** Contact angle and work of adhesion for various PMMA polymers for two contacting fluids: water and glycerol

Polymer	Contact angle (deg)		Work of adhesion (erg cm <sup>-2</sup> )	
	H <sub>2</sub> O	Glycerol	H <sub>2</sub> O	Glycerol
Atactic PMMA	61	59.5	108	97
Syndiotactic PMMA	64	62	104	95
Isotactic PMMA	70.5	66	96	91

approximately 10  $\mu\text{m}$ . The films used in this study are rather thicker than would be typically used for mask construction as it was necessary to obtain sufficient material for g.p.c. analysis.

Contact angle measurements were performed by photographically measuring the bubble formed using droplets approximately 10  $\mu\text{l}$  in size obtained from an Agla microsyringe. Care was taken to check the uniformity of the polymer films and data were collected from a number of different points. The contact angle was estimated by construction of the tangent to the drop profile both on the advancing and receding edges. The experiments were repeated at least three times on different days and the angles determined to the nearest degree. The precision of the measurements was better than  $\pm 2^\circ$ . In order to obtain reproducibility of data it was essential that the substrate surface be kept in an extremely clean condition. Only freshly prepared polymer solutions were used in film preparation in order to avoid possible photochemical crosslinking influencing the results. It was found in all cases that the receding and advancing angles were identical.

#### Refractive index measurements

The refractive indices of the stereospecific polymers were measured using ellipsometry operating at 6328  $\text{\AA}$ .

#### Development curves

The coated wafers (of thickness 1600  $\text{\AA}$ ) were exposed using a Philips PSEM 500 scanning electron microscope attached to a microprocessor-driven digital scanning system controlling the beam position. The acceleration voltage used was 25 kV with beam sizes of 640  $\text{\AA}$  and 0.125  $\mu\text{m}$  and a current of  $1.9 \times 10^{-10}$  and  $6 \times 10^{-10}$  A respectively. The incident dose was changed by varying the exposure time and the areas irradiated were  $2.7 \times 10^{-4}$   $\text{cm}^2$ . The current and voltages were measured to a precision of 2%.

Following exposure the films were developed for 60 s in a 2:3 solution of methyl isobutyl ketone (MIBK) in isopropyl alcohol (IPA) at 295 K with gentle agitation to enhance the dissolution of soluble material.

The thickness of the resist remaining in the exposed areas after development was measured on a surface profile Talystep.

## RESULTS AND DISCUSSION

The performance of an electron resist is influenced by a number of factors. Exposure to the electron beam leads to degradation, the efficiency of this process defining the sensitivity. The ability of the polymer to adhere to the surface is crucial for the efficient development of the

exposed film. In this paper we will attempt to evaluate the effects of tacticity on both of these aspects.

#### Surface tension measurements

In the absence of specific chemical interactions between the polymer and the substrate, the strength of adhesion should be directly proportional to the intermolecular van der Waals type interactions. These latter interactions can be estimated by contact angle measurements and allow estimation of the work of adhesion using the Young–du Pre equation

$$W_A = f_{SV} + v_{LV}(1 + \cos \theta) \quad (1)$$

where  $W_A$  is the work of adhesion,  $f_{SV}$  is the free energy of the immersion of the solid in the vapour,  $v_{LV}$  is the surface tension of the liquid and  $\theta$  is the contact angle. Values of the work of adhesion are presented in Table 1. The data indicate that the contact angle changes with tacticity. The tendency for water to spread over isotactic PMMA is less than with other PMMAs, reflecting changes in the surface energy.

Studies by Bergen<sup>14,15</sup> have indicated that contact angle measurements do not necessarily reflect the strength of adhesion of a polymer to a substrate. It has been proposed that apparent anomalies observed in certain systems can be explained in terms of the influence of the substrate structure. Tape test measurements on the films studied have indicated that syndiotactic and atactic PMMA are relatively easily detached as compared with isotactic films which could only be removed by solvent treatment. This implies that the isotactic films are more strongly adhering to the substrate than in the case of either the atactic or syndiotactic polymer. This trend is the reverse of that which would have been predicted on the basis of the work of adhesion (Table 1).

#### Calculation of Hamaker constants

In view of the above anomaly, it appeared desirable to calculate the intramolecular interaction energy between the polymer and the substrate. The Hamaker constants are derived from the theory of Lifshitz<sup>16</sup> and the procedure used for their estimation has been outlined by Hough and White<sup>17</sup>. The Hamaker constants are defined for a silica(s)–polymer(p)–air(a) configuration by:

$$A_{s-p-a} = (3kT/2)\Delta_{sp}\Delta_{sp} \quad (2)$$

where  $k$  is the Boltzmann constant,  $T$  is the temperature and  $\Delta_{12}$  is defined by

$$\Delta_{12} = \frac{\epsilon_1(i\epsilon_n) - \epsilon_2(i\epsilon_n)}{\epsilon_1(i\epsilon_n) + \epsilon_2(i\epsilon_n)} \quad (3)$$

where

$$\epsilon_n = n(2\pi kT/h)$$

The function  $\epsilon(i\epsilon_n)$  can be written as

$$\epsilon(i\epsilon_n) = 1 + \frac{C_{uv}}{1 + (\epsilon_n/\omega_{uv})^2} \quad (4)$$

where  $C_{uv}$  is the oscillator strength in the u.v. region with relaxation frequency  $\omega_{uv}$ . The infra-red term in equation

(4) is neglected as it makes a negligible contribution to the final quantity<sup>17</sup>. The constants  $C_{un}$  and  $\omega_{uv}$  are calculated using the equations

$$(n^2 - 1) = (n^2 - 1)\omega^2/\omega_{uv}^2 + C_{uv} \quad (5)$$

where  $n$  is the refractive index of the substance at frequency  $\omega$ . The refractive index data for PMMA in the visible region are available from the literature<sup>18</sup>. The refractive indices of the samples studied were determined using a silica substrate on an ellipsometer operating at 6328 Å. The values obtained for atactic and syndiotactic PMMA are virtually identical; however, the value for isotactic PMMA was 0.04 higher than the others. Combining these data with those from the literature using the above theory, it was possible to calculate the values of  $C_{uv}$  and  $\omega_{uv}$  listed in Table 2. The Hamaker constants can then be derived using equations (2)–(5). The values obtained are listed in Table 3.

### Conclusions

Both the contact angle measurements and the Hamaker constant calculations indicate that isotactic PMMA should interact less strongly with the substrate than either atactic or syndiotactic PMMA. This is completely the reverse of the observed trend. It would therefore appear that the greater adhesion in the case of isotactic PMMA must be a consequence both of its stereochemical structure and probably of specific 'chemical' interactions with the polar substrate. In isotactic PMMA, all the methyl groups lie on one side of the chain and the polar groups on the other, leading to the formation of a relatively stable helical structure. Changes in the tacticity have a signi-

ficant effect on the glass transition temperature and hence mobility of the chain backbone. The glass transition temperature of the isotactic polymer ( $T_g \approx 321$  K) is significantly lower than that for either syndiotactic or atactic PMMA ( $T_g \approx 433$  K). The greater adhesion in the isotactic PMMA is probably a consequence of strong interactions between the aligned polar side chains and the substrate and also of the greater mobility allowing the formation of favourable dipolar substrate interactions.

### Electron beam degradation

For an ideal electron resist all the chains in the exposed region should undergo random scission leading to fragments of the same molecular weight. Several studies have reported the molecular weight distribution of degraded material.

### Analysis of degraded polymer

The g.p.c. traces of the polymer obtained before degradation were normalized to the trace of the material obtained after electron beam exposure. The difference between these curves reflects the degradation and cross-linking of the polymer as a consequence of electron beam exposure. The atactic PMMA behaves similarly to that reported by other workers<sup>5–8</sup>, the main peak shifting to a molecular weight of approximately one-fifth of its original value and having approximately the same molecular weight distribution as the starting material (Table 4). The behaviour of the stereospecific polymers is rather different (Figures 1–3). In both syndiotactic and isotactic PMMA the amplitude of the signal associated with the chain extended material (high molecular weight fraction) is increased relative to that observed in the case of the atactic PMMA. The molecular weight distribution of the degradation product in the case of the isotactic material is also significantly broader than that observed in the other two polymers. Analysis of the pyrolysis of various tactic forms of PMMA have indicated that there are differences in the monomer to methyl group factors obtained from mass spectroscopy associated with the effects of tacticity on the ester decomposition. These data have been interpreted in terms of the extent to which depolymerization to form monomer occurs compared with ester decomposition<sup>19</sup>. The tendency to form methyl groups is greatest with the isotactic polymer and the generation of a significant proportion of ester radicals would probably explain the observation of chain extension with this polymer.

### Development, sensitivity and contrast of tactic PMMA

Development curves were measured in the normal way.

Table 2 Values of  $C_{UV}$  and  $\omega_{UV}$  for PMMA

Polymer	$C_{UV}$	$\omega_{UV} \times 10^{16}$ (rad s <sup>-1</sup> )
Atactic PMMA	1.192	1.879
Isotactic PMMA	1.308	1.965
Syndiotactic PMMA	1.192	1.879
Fused silica	1.098	2.033

Table 3 Hamaker constants

System	Hamaker constant $\times 10^{20}$ (J)
Fused silica—atactic PMMA—air	-0.0162
Fused silica— <i>isotactic</i> PMMA—air	0.400

Table 4 Molecular weight characteristics of exposed polymer

Polymer	Fraction	Percentage of total	$M_w \times 10^5$	$M_n \times 10^5$	$M_w/M_n$
Normal PMMA	Undegraded	27.5	2.05	1.19	1.72
	Degraded	71.76	0.461	0.28	1.64
	Crosslinked	0.7	4.1	3.8	1.07
Isotactic PMMA	Undegraded	36.4	3.28	1.43	2.29
	Degraded	61.1	0.85	0.35	2.42
	Crosslinked	2.3	28.3	18.11	1.56
Syndiotactic PMMA	Undegraded	67.6	2.46	1.63	1.509
	Degraded	26.5	0.585	0.317	1.845
	Crosslinked	6.90	12.74	6.94	1.83

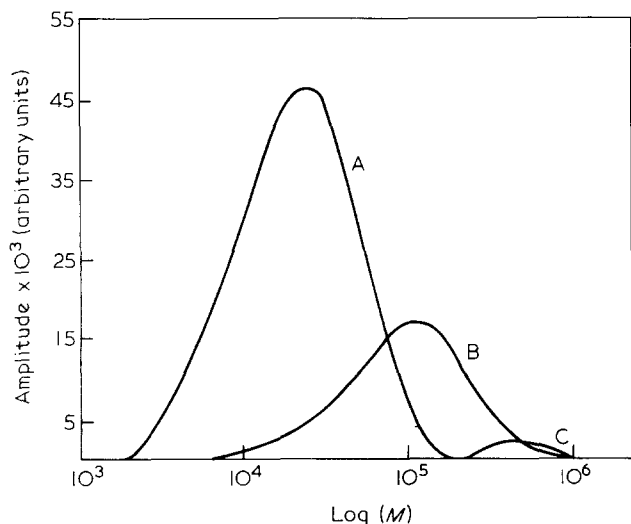


Figure 1 Molecular weight distribution, resolved into three components, for normal PMMA: A, degraded material, B, undegraded material; C, crosslinked material

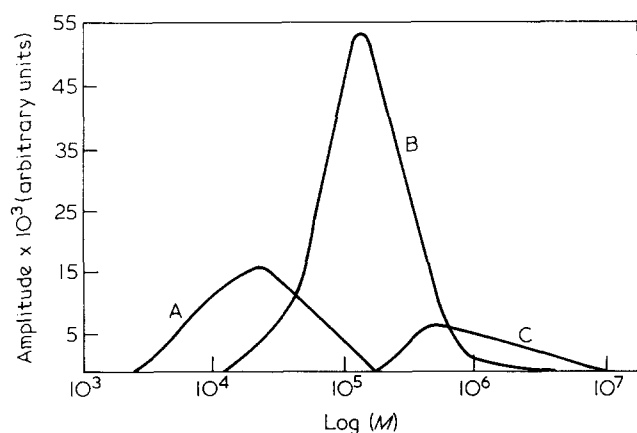


Figure 2 Molecular weight distribution, resolved into three components, for syndiotactic PMMA: A, degraded material; B, undegraded material; C, crosslinked material

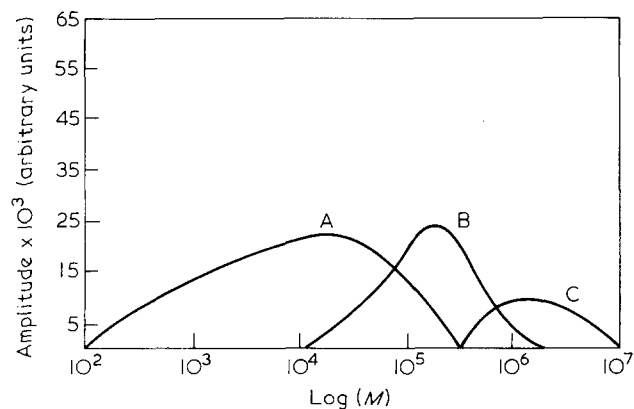


Figure 3 Molecular weight distribution, resolved into three components, for isotactic PMMA: A, degraded material; B, undegraded material; C, crosslinked material

The sensitivity of the resist was determined as the minimum dose required to obtain complete removal of the resist and was obtained from normalized plots (Figure 4) of the film thickness against the logarithm of the exposure. The contrast as defined by Taylor *et al.*<sup>20</sup> was computed from  $\log(D_0/D_i)^{-1}$ , where  $D_0$  is the extrapolated dose for complete exposure and  $D_i$  is the extrapo-

lated dose for full thickness. The results for the PMMAs studied are presented in Table 5.

### Conclusions

The degradation and the development characteristics for the tactic polymers are significantly different from those of atactic PMMA. The sensitivity of syndiotactic and atactic PMMA are very different from those of the isotactic polymer. It has been suggested<sup>5</sup> that a correlation exists between the sensitivity and the glass transition temperature. Isotactic PMMA has low  $T_g$  (321 K) and hence higher chain mobility when compared with syndiotactic ( $T_g = 433$  K) and atactic PMMA ( $T_g = 403$  K). It would appear that the nature of the radical generated and also its mobility are both a function of tacticity and will lead to differences in the electron resist behaviour.

### GENERAL COMMENTS AND CONCLUSIONS

Changes in reaction conditions during the preparation of PMMA resist are likely to induce corresponding variations in the tacticity of the polymer. Since PMMA stereospecific blocks have the potential of aggregation and the formation of stereocomplexes, changes in tacticity may lead to larger effects than might at first be attributed to changes in the backbone sequence structure. Since adhesion, sensitivity, nature of fragments generated and gamma are all a function of tacticity, control of the tacticity of PMMA resists would appear desirable. This paper illustrates the extremes of such variations and indicates the possible connection between certain of the

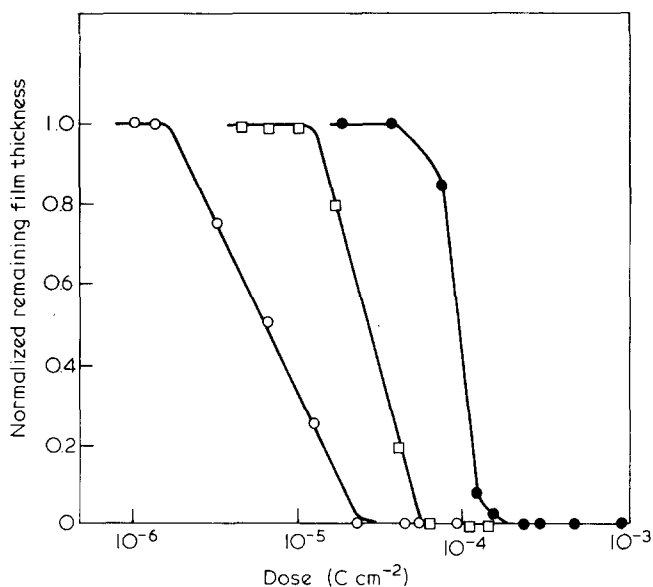


Figure 4 Development curves for PMMA:  $\circ$ , isotactic;  $\square$ , atactic;  $\bullet$ , syndiotactic

Table 5 Development characteristics of PMMA films

Polymer	Sensitivity at 25 keV ( $C\ cm^{-2}$ )	$M_w \times 10^{-4}$	$M_w/M_n$
Atactic PMMA	$6 \times 10^{-5}$	1.70	12.3
Isotactic PMMA	$2 \times 10^{-5}$	0.91	18.1
Syndiotactic PMMA	$2 \times 10^{-4}$	3.70	16.6

failure modes identified during resolution studies and local variations in polymer composition.

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