

# P[CF<sub>3</sub>(CF<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>MA-co-MMA] and P[CF<sub>3</sub>(CF<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>MA-co-BA] Copolymers: Reactivity Ratios and Surface Properties

ROBERT D. VAN DE GRAMPPEL, JAN VAN GELDROP, JOZUA LAVEN, ROB VAN DER LINDE

Laboratory of Polymer Chemistry and Coatings Technology, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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**ABSTRACT:** This study aimed at reducing the surface energy of coatings by copolymerization of commonly used monomers with fluorine-containing monomers. Copolymers of 1,1-dihydroperfluoroheptyl methacrylate (FHMA) and methyl methacrylate (MMA) or butyl acrylate (BA) are prepared by low-conversion polymerization in solution. Using <sup>1</sup>H-NMR data and nonlinear least-squares data fitting, reactivity ratios of these systems at 80°C are determined to be  $r_{\text{FHMA}} = 1.31$ ,  $r_{\text{MMA}} = 0.76$ , and  $r_{\text{FHMA}} = 3.15$ ,  $r_{\text{BA}} = 0.38$ , respectively. We assume that the penultimate unit effect plays an important role in these systems. Introduction of the perfluoroalkyl side chain lowers the polymer surface energy significantly; copolymers of MMA and FHMA show a reduction in total surface energy of about 50 % at a content of 15 mol % FHMA as compared with pure PMMA. The attainable reduction in surface energy is much larger than with, for example, Teflon. This is due to the preferential adsorption of the —CF<sub>3</sub> groups of the fluoroalkyl side chain, if compared to that of the —CF<sub>2</sub>— groups of Teflon. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 159–165, 2001

**Key words:** reactivity ratios; nonlinear least-squares data fitting; perfluoroalkyl side chain; copolymers; surface energy

## INTRODUCTION

The incorporation of perfluoroalkyl moieties into organic polymers affords significant influence on the properties of polymeric materials. As a result of this incorporation, a lowering of the surface tension is obtained. Based on the low surface tension, application of perfluoroalkyl-containing polymers as thermostable materials or elastomers for coatings has been very successful.<sup>1,2</sup> However, a drawback of perfluorinated polymers is their poor solubility in common organic sol-

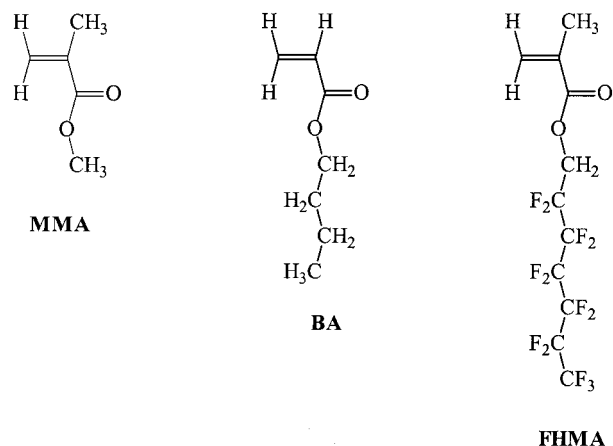
vents, which renders them intractable materials. This problem can be overcome by copolymerization of perfluorinated acrylates and methacrylates with nonfluorine-containing monomers such as acrylates, methacrylates, or styrene.<sup>3–8</sup>

It is known that reactivity ratios of the monomers are the parameters which control the composition of the copolymer, and, hence, knowledge of their values is of paramount importance to control the copolymer process. Despite the industrial interest, up to now, only a few investigations have been carried out on the reactivity ratios of these copolymer systems. In some cases, Alfrey–Price parameters have been determined for perfluorinated acrylates and methacrylates, suggesting a strongly electro-negative character of the fluorinated side chain.<sup>9–12</sup>

Correspondence to: R. D. van de Gramppe (r.v.d.gramppe@tue.nl).

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**Figure 1** Chemical structures of the monomers used.

An accurate method to estimate reactivity ratios is the determination of the copolymer composition for low-conversion polymerizations at different monomer feed compositions. According to the terminal copolymerization model,<sup>13</sup> the data can be fitted by the copolymer equation for instantaneous copolymer composition:

$$F = \frac{r_1 f^2 + f(1-f)}{r_1 f^2 + 2f(1-f) + r_2(1-f)^2}$$

where  $F$  is the instantaneous mol fraction of monomer 1 in the polymer;  $f$ , the molar fraction of monomer 1 in the monomer feed; and  $r_1$  and  $r_2$ , the reactivity ratios. Nonlinear least-square (NLLS) methods have to be used for a proper estimation of  $r_1$  and  $r_2$ .<sup>14</sup>

In this article, the reactivity ratios are determined for the radical copolymerization of methyl methacrylate (MMA) or butyl acrylate (BA) with 1,1-dihydroperfluoroheptyl methacrylate (FHMA) (Fig. 1) in order to obtain better insight into the distribution of FHMA units in the corresponding copolymers. In addition, we studied the influence of the incorporation of FHMA on the surface properties for thin films of copolymers of MMA–FHMA. In combination with acrylates or epoxides, these copolymers could have potential applications in self-stratifying materials.

## EXPERIMENTAL

### Materials

MMA (Aldrich, Zwynrecht, The Netherlands), BA (Aldrich), and FHMA (ACR Technologies B.V.

Amsterdam, The Netherlands) were distilled from CaH<sub>2</sub> under a reduced nitrogen atmosphere and stored at  $-20^\circ\text{C}$ . Azobisisobutyronitrile (AIBN, Merck, Amsterdam, The Netherlands) was recrystallized from methanol, dried *in vacuo*, and stored at  $-20^\circ\text{C}$  prior to use. Benzoyl peroxide (BPO, Merck) and butyl acetate (BuOAc, Aldrich) were used as received.

### Methods

All reactions were carried out in an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. <sup>1</sup>H-NMR spectra were recorded on a Varian VXR 300 spectrometer operating at 299.9 MHz. CDCl<sub>3</sub> was used as a solvent. The CHCl<sub>3</sub> peak at 7.24 ppm was used as an internal standard. Copolymers with a molar fluorine composition of 50% or higher were dissolved in perfluorobenzene with a small quantity of *d*<sub>6</sub>-benzene as a locking solvent. Glass transition temperatures were measured by a Perkin–Elmer Pyris 1 DSC equipment with a scan speed of 10°C/min.

### Determination of Reactivity Ratios

Free-radical polymerizations were carried out in a 25 wt % BuOAc solution, using 2 mol % (based on monomers) BPO as an initiator. Typically, a mixture of 3.569 g (27.85 mmol) of BA and 7.749 g (18.53 mmol) of FHMA and 0.244 g (1.01 mmol) of BPO in 30 mL BuOAc was subjected to three freeze–pump–thaw cycles to remove oxygen. Polymerizations were performed at 80°C for a period of 5–10 min to keep the conversion below 5%. Copolymerizations were quenched by precipitation in methanol. The precipitated copolymer was dried *in vacuo* at 65°C (MMA–FHMA) or at 40°C (BA–FHMA) and stored under atmospheric pressure at room temperature.

### Preparation of Copolymers for Contact Angle Measurements

A separate series of copolymers of MMA–FHMA was prepared for the contact angle measurements. To minimize composition drift, reactions were carried out as follows: A reaction vessel was charged with 30 mL of BuOAc and degassed for 30 min with nitrogen. The solvent was heated to 80°C, and a mixture of the two monomers (total of 10 g) (Table IV) with AIBN (2 mol % on monomer concentration) was added slowly over a period of 15 min. After complete addition, the reaction mixture was precipitated in cold methanol to avoid

**Table I** Feed Ratios ( $f_{\text{MMA}}$ ) and Copolymer Compositions ( $F_{\text{MMA}}$ ) of MMA-FHMA in BuOAc at 80°C

$f_{\text{MMA}}$	$F_{\text{MMA}}$	$f_{\text{MMA}}$	$F_{\text{MMA}}$
0.7302	0.6668	0.3810	0.3236
0.7291	0.6757	0.3812	0.3200
0.7295	0.6741	0.3801	0.3200
0.7299	0.6734	0.3804	0.3318
0.7299	0.6786	0.3806	0.3201

any further polymerization. The obtained polymer was dried at 65°C *in vacuo*.

### Preparation of Coatings

Samples for contact angle analysis were prepared by spin coating polymer solutions onto glass plates. Solutions of the methacrylic copolymers were prepared with a concentration of 300 mg in 3 g of toluene or hexafluoroisopropanol, depending on the fluorine concentration of the polymer. The obtained solutions were filtered through a 0.2 μm Teflon filter prior to spin coating (1500 rpm for 60 s). After spin coating, the polymer films were annealed for 2 h at 125°C in an air-circulation oven.

### Contact Angle Measurements

Advancing contact angles were obtained using the direct observation tangent technique, using a

home-built setup. With a microsyringe, a droplet of the wetting agent was applied on the surface using a Harvard syringe pump. The droplet was monitored by a CCD camera and analyzed using Scion Image software. The contact angle was measured both at the left and right sides using distilled water and methylene iodide (>99%, Merck) as wetting agents.

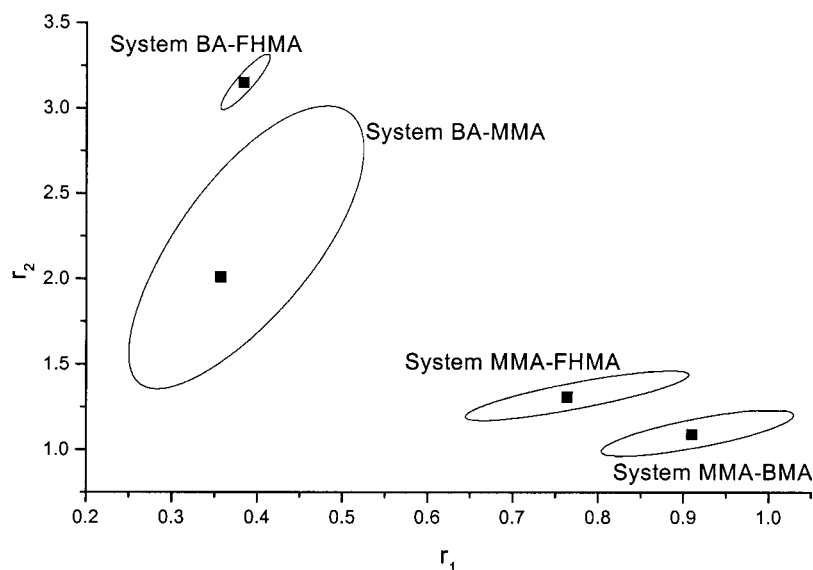
## RESULTS AND DISCUSSION

Copolymerizations of FHMA and MMA were performed five times at each of the two optimal feed compositions for MMA:  $f'_{\text{MMA}} = 0.75$  and  $f''_{\text{MMA}} = 0.38$  as calculated from the Tidwell–Mortimer criteria<sup>15</sup>:

$$f'_{\text{MMA}} \approx \frac{2}{2 + r_1} \quad f''_{\text{MMA}} \approx \frac{r_2}{2 + r_2}$$

The values for  $r_1$  (MMA) = 0.75 and  $r_2$  (FHMA) = 1.22 were previously determined in a number of exploratory experiments. The average molar fraction of MMA ( $F_{\text{MMA}}$ ) was calculated from <sup>1</sup>H-NMR data using the relation

$$F_{\text{MMA}} = \frac{2A}{2A + 3B}$$



**Figure 2** Reactivity ratios and the 95% joint confidence intervals for the reactivity ratios for the systems MMA-FHMA, BA-FHMA, MMA-BMA,<sup>17</sup> and BA-MMA.<sup>18</sup> For the system BA-MMA, the published <sup>1</sup>H-NMR data are recalculated using the NLLS fitting method.

**Table II Feed Ratios ( $f_{BA}$ ) and Copolymer Compositions ( $F_{BA}$ ) of BA–FHMA in BuOAc at 80°C**

$f_{BA}$	$F_{BA}$	$f_{BA}$	$F_{BA}$
		0.6004	0.3371
0.8404	0.6532	0.6004	0.3407
0.8405	0.6532	0.6006	0.3388
0.8395	0.6569	0.6003	0.3332
0.8439	0.6549	0.6000	0.3384

where  $A$  and  $B$  represent the total peak areas of the  $\text{CH}_3\text{O}$  signal (MMA) at 3.6 ppm and  $\text{CH}_2\text{O}$  signal (FHMA) at 4.4 ppm, respectively. Results of the copolymerizations are given in Table I. In all cases, conversions (determined gravimetrically) were below 5% to avoid composition drift. Reactivity ratios were calculated using a nonlinear least-squares (NLLS) fitting method<sup>16</sup> assuming a relative error of 5% in the copolymer compositions. This resulted in  $r_{\text{MMA}} = 0.76$  and  $r_{\text{FHMA}} = 1.31$ . Reactivity ratios and their 95% joint confidence intervals are shown in Figure 2, together with literature values for the copolymer systems MMA–BMA<sup>17</sup> and BA–MMA.<sup>18</sup>

Reactivity ratios for the system FHMA–BA were determined in a similar way as described above. Optimal feed ratios were  $f'_{BA} = 0.60$  and  $f''_{BA} = 0.84$ , estimated from preliminary values of  $r_1$  (BA) = 0.38 and  $r_2$  (FHMA) = 3.05. The molar fraction of BA was calculated from proton NMR data using the relationship

$$F_{BA} = \frac{C}{C + B}$$

where  $C$  and  $B$  represent the total peak area of the  $\text{CH}_2\text{O}$  signal (BA) at 4.0 ppm and the  $\text{CH}_2\text{O}$  signal (FHMA) at 4.5 ppm, respectively. Copoly-

merization data are given in Table II. The NLLS parameter estimation with a relative error of 5% in the copolymer compositions leads to  $r_{BA} = 0.38$  and  $r_{\text{FHMA}} = 3.15$ .

In Table III, the newly determined reactivity ratios are compared to those belonging to the systems MMA–BMA and BA–MMA. In Figure 2, the 95 % joint confidence intervals for the reactivity ratios of these systems are displayed. The joint confidence interval of the reactivity ratio of MMA–BA is larger in comparison with the others because the experimental design of Tidwell and Mortimer was not used to reduce the confidence interval. No overlap is present between the various confidence intervals, implying that the reactivities observed are significantly different from each other.

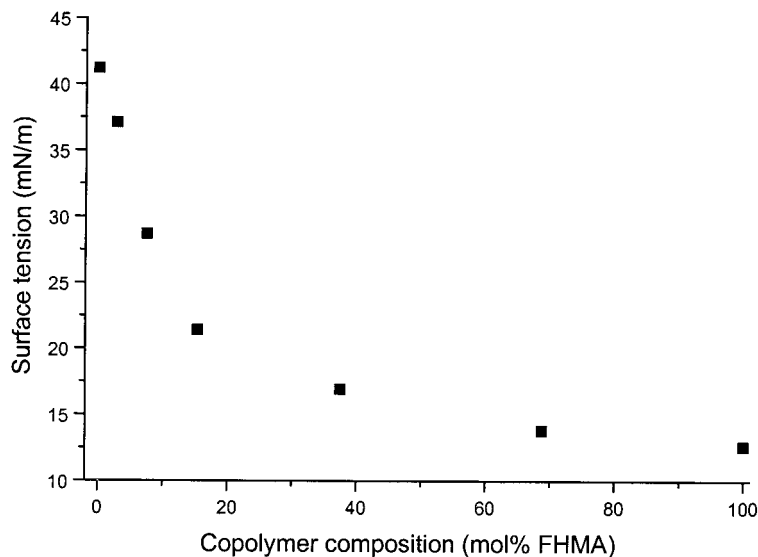
Comparison of the reactivity ratios of the system MMA–FHMA and of MMA–BMA indicates that the replacement of the alkyl group in BMA by a perfluoroalkyl group enhances, to some extent, the monomer reactivity, resulting in a lower value of  $r_1/r_2$ . The same conclusion can be drawn from a comparison of the systems BA–FHMA and BA–MMA. The increase in reactivity may be ascribed to the relatively high electronegativity of the  $\text{CH}_2(\text{CF}_2)_5\text{CF}_3$  group, although its electron-withdrawing influence is decreased by the insulating capacity of the  $\text{OCH}_2$  spacer.<sup>19</sup> On the other hand, the difference in chain length may also influence the reactivity ratio. Therefore, we assume that the penultimate unit effect, as described by Heuts et al.,<sup>20</sup> plays an important role in this system. For the system MMA–FHMA, the product  $r_1r_2$  equals about 1, indicating a nearly ideal copolymerization. Figure 2 clearly shows that introduction of FHMA results in larger  $r_2$  values, whereas  $r_1$  decreases or remains equal. This points to a higher reactivity of the fluorinated radical toward its own monomer compared to MMA.

**Table III Reactivity Ratios of Acrylate and Methacrylate Monomers for the Systems MMA–FHMA, BA–FHMA, MMA–BMA, and BA–MMA**

Monomer 1	Monomer 2	$r_1$	$r_2$	$r_1/r_2$	Ref.
MMA	FHMA	0.76	1.31	0.58	This work
MMA	BMA	0.91	1.09	0.83	17 <sup>a</sup>
BA	FHMA	0.38	3.15	0.12	This work
BA	MMA	0.36	2.018	0.18	18 <sup>b</sup>

<sup>a</sup> Bulk polymerization at 50°C.

<sup>b</sup> Solution polymerization in toluene at 50°C; reactivity ratios recalculated by the NLLS fitting method.



**Figure 3** Surface energy (mN/m) of MMA–FHMA copolymers as a function of the molar fraction of FHMA.

### Surface Characterization

To study the influence of the incorporation of FHMA on the surface energy of the MMA copolymers, a series of polymers was prepared with different molar fractions of FHMA. All polymers were synthesized in solution (see Experimental), except for the homopolymer of FHMA, which was prepared in bulk. Copolymerizations were carried out under “starved” conditions using the reactivity ratios as determined above for MMA–FHMA. In this way, the chemical composition of the formed copolymers could be controlled, and, hence, the uniform distribution of the monomers into the polymer chains could be guaranteed.

The surface properties of the homopolymers and the five copolymers (2.8, 7.6, 15.3, 37.5, and 68.8 mol % FHMA) were examined by advancing contact angle measurements. Up to 15% of FHMA content, the contact angles for both distilled water and methylene iodide rose drastically and subsequently flattened off. Surface energies were calculated numerically using the harmonic-mean method of Wu.<sup>21</sup> According to this method, the harmonic-mean formula<sup>22</sup> for the interfacial tension is substituted in the Young’s equation, leading to

$$\gamma_l(1 + \cos \theta) = 4 \left( \frac{\gamma_l^d \gamma_s^d}{\gamma_l^d + \gamma_s^d} + \frac{\gamma_l^p \gamma_s^p}{\gamma_l^p + \gamma_s^p} \right)$$

where  $\gamma^d$  and  $\gamma^p$  are the contributions from dispersion interaction and polar interaction, respec-

tively, whereas  $\theta$  represents the contact angle of a droplet of the wetting liquid on the polymer surface measured within the liquid phase. The subscripts  $l$  and  $s$  refer to the wetting liquid and the solid polymer surface, respectively. After substituting the contact angles of the two wetting liquids into the equation above, two relationships are obtained with  $\gamma_s^d$  and  $\gamma_s^p$  as unknown parameters. The solution of these equations results in the dispersive and polar contributions of the surface energy of the polymers synthesized. As suggested by Wu, distilled water and methylene iodide (H<sub>2</sub>O:  $\gamma = 72.8$  mN/m and  $\gamma^d = 22.1$  mN/m; CH<sub>2</sub>I<sub>2</sub>:  $\gamma = 50.8$  mN/m and  $\gamma^d = 44.1$  mN/m) were used as wetting agents.

As can be seen in Figure 3, the total surface energy for the MMA–FHMA copolymers decreases sharply with increasing FHMA content, resulting in a reduction of the surface energy by a factor of about 2 at an incorporation of 15 mol % of FHMA. Similar trends were observed for copolymers using styrene and fluoroalkyl-modified styrene.<sup>23,24</sup> This indicates a preferential orientation of the fluoroalkyl side chain to the air–polymer surface. It is important to note that the polymerization technique applied (see Experimental) implies that all copolymer chains have the same composition. Thus, the steep drop in surface tension is not due to a preferential adsorption of polymer chains containing extra FHMA units.

Table IV shows that the surface tension is extremely lowered by the incorporation of FHMA,



**Table IV** Contact Angles and Surface Energies for Different Copolymers of MMA–FHMA

Sample	Copolymer of FHMA–MMA		Contact Angles (°)		Surface Energies <sup>a</sup> (mN/m)		
	$f_{\text{FHMA}}$	$F_{\text{FHMA}}^b$	Distilled H <sub>2</sub> O	CH <sub>2</sub> I <sub>2</sub>	$\gamma_s$	$\gamma_s^d$	$\gamma_s^p$
1	0	0	80	41	41.2 <sup>c</sup>	31.1	10.1
2	2	2.8	83	50	37.2	27.4	9.8
3	5	7.6	94	65	28.7	22.1	6.6
4	10	15.3	104	80	21.4	16.8	4.6
5	25	37.5	110	91	17.0	12.8	4.2
6	50	68.8	117	99	13.7	10.9	2.8
7	100	100	120	102	12.6	10.5	2.1

<sup>a</sup> Calculated by the harmonic-mean method of Wu<sup>21</sup> for the contact angles from distilled H<sub>2</sub>O and CH<sub>2</sub>I<sub>2</sub>.

<sup>b</sup> Calculated by proton NMR.

<sup>c</sup> Ref. 26: 40.2–41.1 mN/m.

resulting in a reduction to 12.6 mN/m for the homopolymer of FHMA. This value for  $\gamma$  is of the same order of magnitude as reported for poly(1H,1H,2H,2H-tridecafluorooctyl methacrylate) (14.3 mN/m)<sup>25</sup> and considerably lower than the value of 20 mN/m found for polytetrafluoroethylene.<sup>26</sup> This difference strongly suggests that the perfluoralkyl side chains of poly(FHMA) adsorbed in the surface are orientated with the —CF<sub>3</sub> groups at the outermost surface. Schulman et al. demonstrated that the lowest surface energy is obtained by an ideal close-packed array of trifluoromethyl groups in the surface, resulting in 6 mN/m for *n*-perfluorodecanoic acid, CF<sub>3</sub>(CF<sub>2</sub>)<sub>8</sub>COOH.<sup>27</sup>

The value of the dispersive part of the surface energy of the copolymer (MMA–FHMA 6:1) (Table IV) is comparable to with that of polytetrafluoroethylene (PTFE,  $\gamma_{\text{PTFE}}^d = 18.4$  mN/m) and polydimethylsiloxane (PDMS,  $\gamma_{\text{PDMS}}^d = 19.0$  mN/m).<sup>26</sup> When this level of  $\gamma^d$  is a target in coatings applications, the copolymer system MMA–FHMA is preferred to these homopolymers since (i) copolymers of MMA–FHMA are soluble in common organic solvents up to an FHMA content of 40 mol %, (ii) they exhibit  $T_g$  values varying from 106°C for pure PMMA to 39.8°C for PFHMA, and (iii) they lead to this level of  $\gamma^d$  with an FHMA mol fraction of 0.15. Conversely, the application of PTFE is hampered by its low solubility in organic solvents, whereas PDMS suffers from a too low glass transition temperature.

## CONCLUSIONS

The reactivity ratios for the free-radical polymerization in a BuOAc solution for the systems

MMA–FHMA and FHMA–BA were determined to be  $r_{\text{FHMA}} = 1.31$ ,  $r_{\text{MMA}} = 0.76$  and  $r_{\text{FHMA}} = 3.15$ ,  $r_{\text{BA}} = 0.38$ , respectively. Incorporation of fluorine implies a small increase of reactivity of the monomer concerned. As judged from copolymers MMA–FHMA, the incorporation of FHMA decreases the surface energy, pointing to a preferential orientation of the fluorinated side group, especially of the —CF<sub>3</sub> group to the air–polymer surface.

Preliminary experiments<sup>28</sup> with combinations of fluorinated epoxides with nonfluorinated di(epoxide) systems in coatings application gave strong indications of a surface-enrichment with fluorinated compounds. Our current investigations are directed toward a more detailed understanding of the underlying driving forces and mechanism as studied by X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS).

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