



**Universidade de São Paulo**

**Biblioteca Digital da Produção Intelectual - BDPI**

---

Departamento de Física e Ciências Materiais - IFSC/FCM

Artigos e Materiais de Revistas Científicas - IFSC/FCM

---

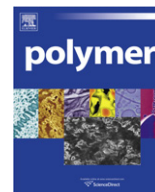
2011-09

# Hydrophobic methacrylic copolymers containing azobenzene moieties

---

Polymer, Oxford : Elsevier, v. 52, n. 21, p. 4703-4708, Sept. 2011  
<http://www.producao.usp.br/handle/BDPI/49702>

*Downloaded from: Biblioteca Digital da Produção Intelectual - BDPI, Universidade de São Paulo*



## Hydrophobic methacrylic copolymers containing azobenzene moieties

Rafaela C. Sanfelice, Felipe J. Pavinatto, Marcos R. Cardoso, Cleber R. Mendonça, Débora T. Balogh\*, Osvaldo N. Oliveira Jr.

Instituto de Física de São Carlos, Av. Trabalhador São-carlense 400, CP 369, CEP 13560-970, São Carlos, SP, Brazil

### ARTICLE INFO

#### Article history:

Received 4 May 2011

Received in revised form

19 August 2011

Accepted 21 August 2011

Available online 26 August 2011

#### Keywords:

Azobenzene

Fluorinated polymers

Polymer synthesis

### ABSTRACT

The functionalization of polymer materials to produce hydrophobic surfaces is an important goal for a number of applications, especially those associated with self-cleaning and anti-adherent surfaces. Azopolymers are known for photoisomerization property that can lead to photoinduced anisotropy, photomechanical effect and surface modification with surface-relief gratings. In this study, we combine the low surface energy property of perfluoroalkyl methacrylates with the photoinduced characteristics of azopolymers, by fabricating cast films of copolymers of 2,2,2 trifluoroethyl methacrylate (TFEMA) or 2,2,3,3,4,4,5,5 octafluoropentyl methacrylate (OFPMA) and 4'-[N-ethyl-N-(2-methacryloxy-ethyl)]amine-4-nitro-azobenzene (DR13MA). The intended structures of the copolymers synthesized using radical polymerization was confirmed with Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR). The polymers had much higher thermal stability than conventional azopolymers, and formed hydrophobic surfaces with a water contact angle of ca. 96°. These hydrophobic azopolymers were amenable to the formation of surface-relief gratings at room temperature resulting from an all-photonics mass transport process, which opens the way for a number of new applications to be designed.

© 2011 Elsevier Ltd. All rights reserved.

### 1. Introduction

Fluorinated polymers have been studied due to their lower surface energy which makes them suitable for applications in coatings and dielectrics for transistors, antireflection coatings, water repellent coatings, anti-adherent and self-cleaning surfaces [1–4]. They have high thermal stability, low moisture absorption, weather resistance, low refractive index and high transparency [5,6]. Fluorinated acrylates and methacrylates exhibit all these properties with the advantage of being soluble in common organic solvents and easily synthesized. This has motivated studies on the effects from perfluoroalkyl side-chains on the surface properties of acrylates/methacrylates [7,8], in addition to investigation of surface properties of latex and core-shell particles [9–12]. If the intended application requires additional, specific properties, one may exploit blending and/or copolymerization to combine the characteristics of fluorinated polymers with other types of polymer. For example, polymers containing an azobenzene moiety, also known as azopolymers, are suitable for optical applications owing to the *trans-cis-trans* photoisomerization process [13]. Besides the photoinduced anisotropy when polarized light is used, photoisomerization

can impart light-induced changes in surfaces that lead to large-scale mass transport and the formation of surface-relief gratings [14]. Photomechanical effects of contraction and expansion of azopolymers films are also believed to result from the photoisomerization process [15]. These effects induced by photoisomerization can be useful in applications such as optical storage, optical switching and waveguides.

In this study, we exploit the properties of low surface energy of perfluoroalkyl methacrylates and the photoinduced properties of azopolymers, by producing via radical polymerization copolymers of 2,2,2 trifluoroethyl methacrylate (TFEMA) or 2,2,3,3,4,4,5,5 octafluoropentyl methacrylate (OFPMA) with 4'-[N-ethyl-N-(2-methacryloxy-ethyl)]amine-4-nitro-azobenzene (DR13MA) in different proportions.

### 2. Experimental

The random copolymers were synthesized by radical polymerization in solution at 70 °C for 72 h in sealed glass ampoules. The chemical structures of the monomers used and copolymers synthesized are shown in Fig. 1. A mixture of methyl-ethyl-ketone (MEK) and dimethylformamide (DMF) (3:1, v/v) was used as solvent and AIBN was the initiator. The monomers 4'-[N-ethyl-N-(2-methacryloxyethyl)]amine-4-nitro-azobenzene (DR13MA, **1**), 2,2,2-trifluoroethyl methacrylate (TFEMA, **2**) and 2,2,3,3,4,4,5,5

\* Corresponding author.

E-mail address: [balogh@ifsc.usp.br](mailto:balogh@ifsc.usp.br) (D.T. Balogh).

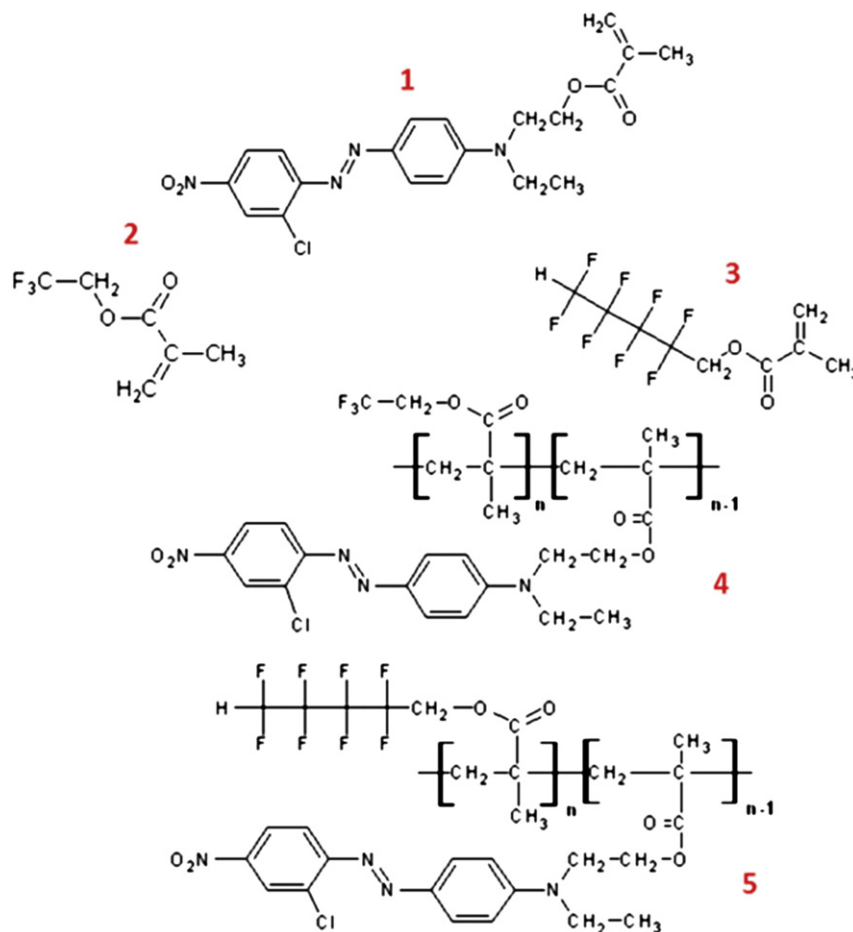


Fig. 1. Chemical structures of the monomers and the corresponding copolymers prepared.

octafluoropentyl methacrylate (OFPMA, **3**), were purchased from Aldrich and used without purification. The reactions were performed using feed ratios of 10, 20 and 30% by weight of the azo-monomer DR13MA, based on the weight of the fluorinated monomers. The copolymers were purified by precipitation and washings in ethanol 90%. The polymers were characterized by proton nuclear magnetic resonance (NMR), infrared (FTIR) and ultraviolet–visible spectroscopies (UV–Vis.). The molecular weight distributions were obtained by size exclusion chromatography (HPSEC) in tetrahydrofuran at 35 °C and 1 mL/min flow rate using an Agilent 1100 chromatographic system with a refraction index detector and polystyrene standards. Glass transition temperatures were determined by Differential Scanning Calorimetry (DSC) with heating range of 20 °C/min under a nitrogen flow of 50 mL/min from ambient to 180 °C in two heating cycles.

Thermogravimetric (TG) measurements were performed at the temperature interval from 25 °C to 800 °C with heating range of 20 °C/min under nitrogen flow of 40 mL/min. Water contact angles were measured in a KSV CAM200 tensiometer at room temperature. Films of the copolymers were cast from 5 g/L solutions in chloroform onto glass slides at 40 °C and maintained at this temperature until complete evaporation of the solvent. Surface-relief gratings were inscribed with an interference pattern of 2 μm of period produced by an Argon ion laser operating at 488 nm (irradiance of 100 mW/cm<sup>2</sup> and p:p polarized light). To obtain the interference pattern, the laser beam was split into two components. The first one impinged directly on the sample, while the second was reflected onto the sample by a mirror. AFM images were recorded in a Digital Nanoscope IIIa Microscope using the tapping mode.

**Table 1**  
Copolymers compositions and molecular weights.

Copolymer	Feed Ratio (mol% azo) <sup>a</sup>	Feed Ratio (wt% azo) <sup>a</sup>	% wt azo (NMR) <sup>a</sup>	%wt azo (Vis.) <sup>a</sup>	Mn (g/mol)	Mw (g/mol)	PDI	M <sub>RU</sub> <sup>b</sup>	DP <sub>n</sub>	Yield (%)
TFEMA-co-DR13MA(10%)	5	11	11	10	9300	13,000	1.4	180	51	53
TFEMA-co-DR13MA(20%)	9	20	21	23	8800	13,000	1.5	192	46	40
TFEMA-co-DR13MA(30%)	11	23	30	29	12,000	21,000	1.7	198	44	43
OFPMA-co-DR13MA(10%)	7	9	9	11	10,000	15,000	1.4	306	33	54
OFPMA-co-DR13MA(20%)	13	17	15	21	37,000	67,000	1.8	311	119	44
OFPMA-co-DR13MA(30%)	15	20	17	31	11,000	17,000	1.5	314	35	67

<sup>a</sup> Based on the total repeating units.

<sup>b</sup> Molecular weight of the repeating units.

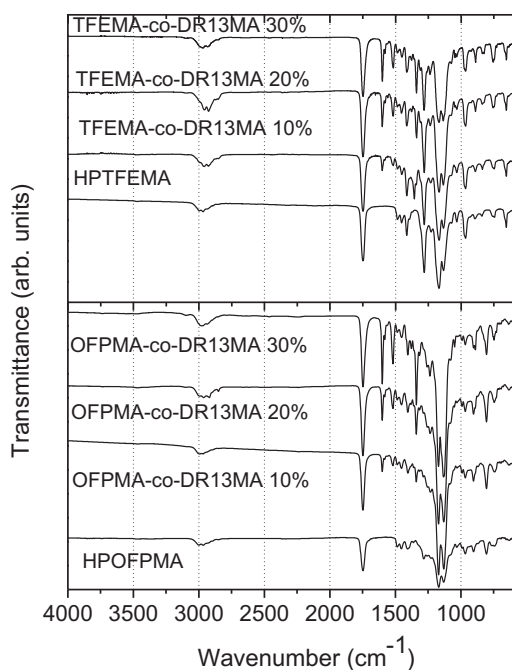


Fig. 2. FTIR spectra of cast films of all polymers prepared.

### 3. Results and discussion

Two copolymers, poly-{2,2,2-trifluoroethyl methacrylate-co-4'-[N-ethyl-N-(2-methacryloxyethyl)]amine-4-nitro-azobenzene (TFEMA-co-DR13MA, **4**) and poly-{2,2,3,3,4,4,5,5 octafluoropentyl-methacrylate-co-4'-[N-ethyl-N-(2-methacryloxyethyl)] amine-4-nitro-azobenzene (OFPMA-co-DR13MA, **5**), with 10, 20 and 30% nominal azo contents, were prepared along with the corresponding fluorinated homopolymers for comparison. The copolymers were obtained with a rather good yield (40–67%) as shown in Table 1.

The FTIR spectra of cast films deposited onto sodium chloride windows in Fig. 2 feature the vibrations of both repeating units of the copolymers TFEMA, OFPMA and DR13MA. These include the methyl and methylene stretching at 2950, 2920 and 2850  $\text{cm}^{-1}$ ; carbonyl ester stretching at 1740  $\text{cm}^{-1}$ ; and C–O ester deformation at 1230  $\text{cm}^{-1}$  and 1135  $\text{cm}^{-1}$ . Absorption bands of C–F groups from TFEMA and OFPMA repeating units appear at 1280 and 1170  $\text{cm}^{-1}$  in the spectra of all copolymers and fluorinated homopolymers. Absorption bands characteristic only of DR13MA appears at 1600 (aromatic ring), 1580 (nitro group attached to aromatic ring), 1516 (aromatic ring) and 1340  $\text{cm}^{-1}$  (nitro group) in all copolymers. These absorption bands, which are absent in the spectra of the homopolymers, have their intensity increased with increasing nominal azo content in the copolymers.

In order to illustrate the change in intensity, Fig. 3A and B show the spectra normalized with respect to the most intense band (at 1170  $\text{cm}^{-1}$ ), with an enlarged region for the aromatic ring absorption (1650–1500  $\text{cm}^{-1}$ ). These results confirm that polymers containing both the fluorinated and azo units, in different compositions, were successfully prepared.

Fig. 4A shows the NMR spectra for TFEM copolymers while the spectra for the OFPM copolymers are shown in Fig. 4B, with the corresponding proton assignments in the insets. Signals of both repeating units could be observed for all copolymers, confirming the intended structures. The amount of azo groups incorporated can be quantitatively determined through techniques such as NMR and UV–vis. spectroscopy, and both were used for this purpose. The ratio between the areas of the peaks in the region highlighted in the figure, corresponding to the methylene group neighbor to the CF<sub>3</sub> groups (numbered 1 and 2 in the insets of Fig. 4A and B, respectively) and the aromatic proton of the azobenzenic repeating unit (numbered 10 and 11, respectively, in Fig. 4A and B), allowed us to calculate the copolymers composition. The results are shown in Table 1.

The composition was also calculated from the content of azo repeating units using visible spectroscopy measurements. The fluorinated units do not absorb in the visible region. An analytical

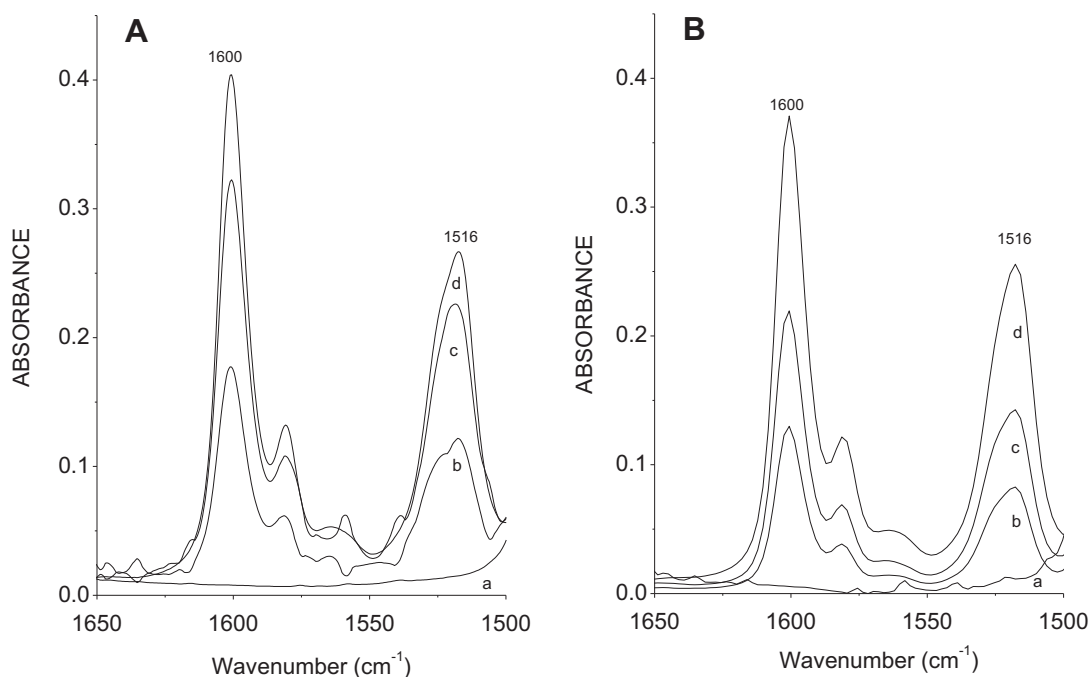


Fig. 3. Aromatic ring absorption region of FTIR spectra for samples containing TFEMA (A) and OFPMA (B) repeating units. The lower case letters correspond to the spectra of homopolymers (a) and copolymers with (b) 10% azo content, (c) 20% azo content and (d) 30% azo content.

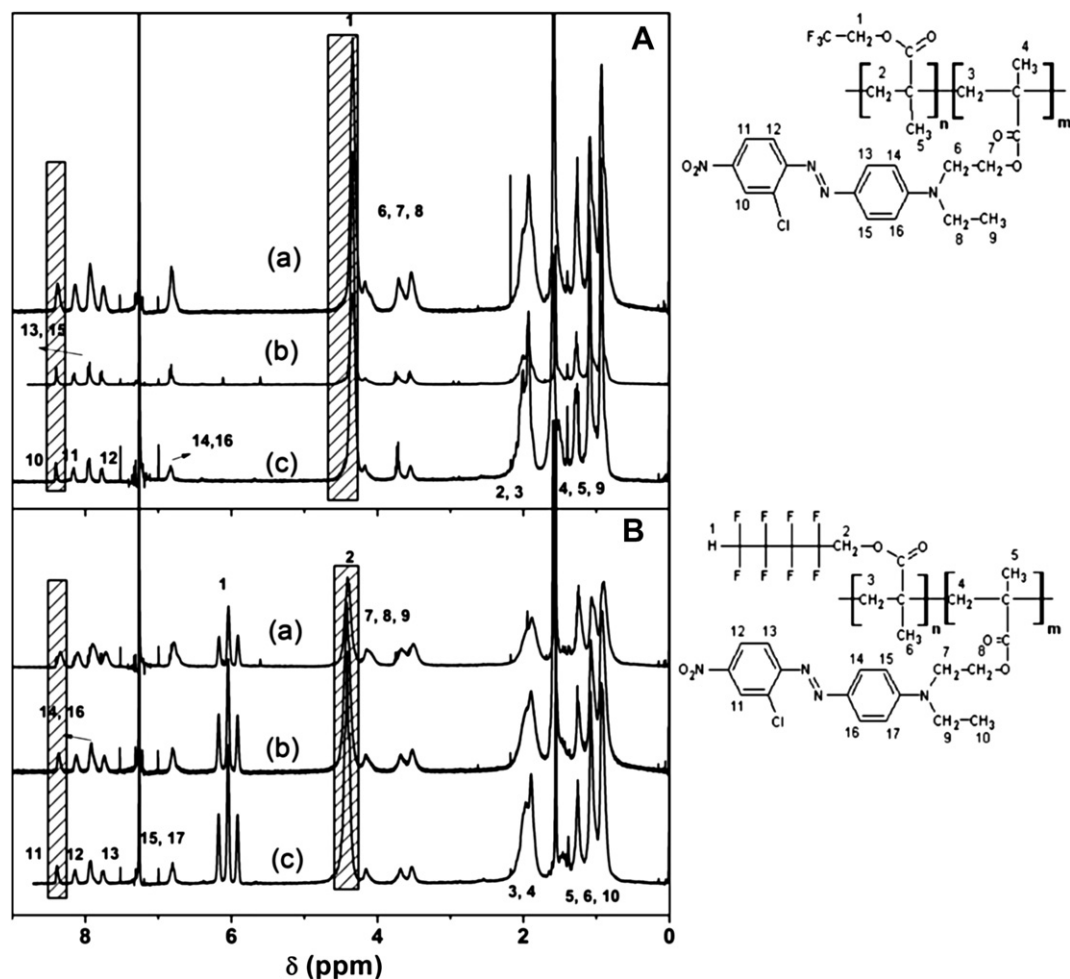


Fig. 4.  $^1\text{H}$ NMR of copolymers containing TFEMA (A) and OFPMA (B) repeating units. The lower case letters correspond to the spectra of copolymers with (a) 10% azo content, (b) 20% azo content and (c) 30% azo content.

curve was built with the azomonomer, assuming that the extinction coefficient of the polymers would be similar to the monomer, in spite of the small blue shift in the polymers spectra compared to the monomer spectrum. The spectra of the azomonomer chloroform solutions are shown in Fig. 5, and the content of repeating units was calculated with the equation in Fig. 5, also taking into account the absorption spectra for the copolymers in Fig. 6. The

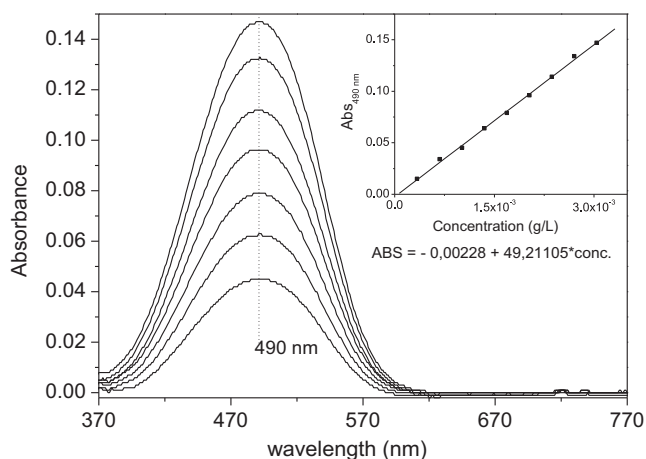


Fig. 5. Visible spectra of solutions of DR13MA in chloroform in different concentrations. The inset shows the analytical curve and the equation obtained by linear fitting.

results in Table 1 indicate good agreement between the polymer composition determined by NMR and visible spectroscopy, except for the copolymers OFPMA-co-DR13MA(20%) e OFPMA-co-DR13MA(30%). Furthermore, the compositions differ slightly from the feed ratios used, especially for the copolymers with more azo units.

The molecular weight distributions (MWD) for the copolymers determined with HPSEC are shown in Fig. 7. The averages calculated relative to the polystyrene standards are given in Table 1, together with the polydispersity index (PDI) and the degree of polymerization

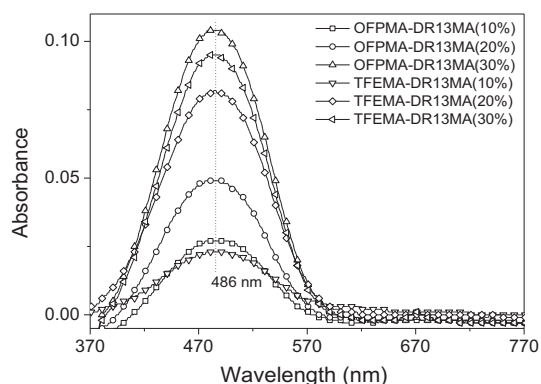
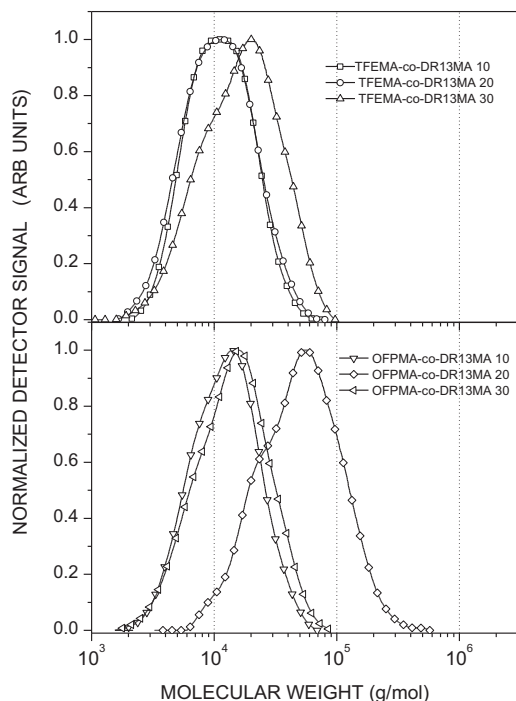


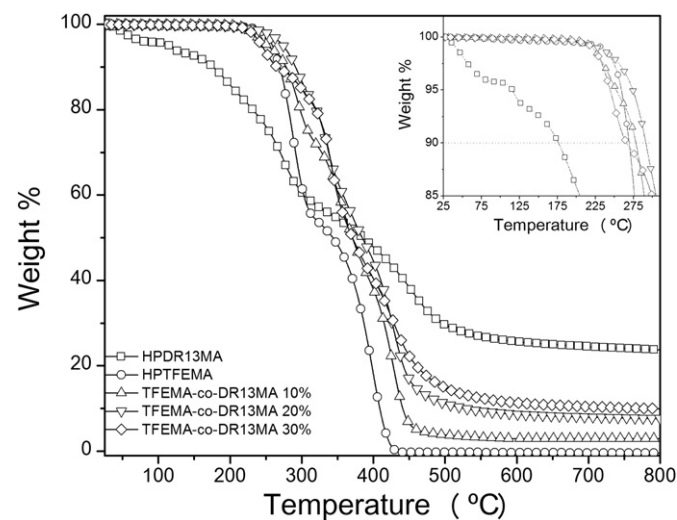
Fig. 6. Visible spectra of copolymers in chloroform solutions.



**Fig. 7.** Molecular weight distributions (MWD) of the copolymers obtained by HPSEC in THF.

(DP). The MWD profiles for the copolymers TFEMA-co-DR13MA (10%), TFEMA-co-DR13MA(20%), OFPMA-co-DR13MA(10%), OFPMA-co-DR13MA(30%) are quite similar, featuring a single peak at 11,000 g/mol for TFEMA copolymers and 15,000 g/mol for OFPMA copolymers, representing polymer chains with approximately 50–55 units for both types of copolymers. However, the copolymers TFEMA-co-DR13MA(30%) and OFPMA-co-DR13MA(20%) displayed a small shoulder at around 10,000 g/mol and 20,000 g/mol, and peaks at ca. 20,000 g/mol and 50,000 g/mol, respectively. These differences can be explained by a change in the experimental procedure for these two samples, which were occasionally shaken during the polymerization, while the others were left to stand still during the whole period of polymerization.

The thermal stability of the copolymers and homopolymers was evaluated by thermogravimetry, to verify if fluorinated repeating



**Fig. 8.** Thermogravimetric curves of TFEMA-co-DR13MA along with the homopolymers HPTFEMA and HPDR13MA.

**Table 2**

Thermogravimetric data of all copolymers and homopolymers. Glass transition temperatures ( $T_g$ ) are also showed.

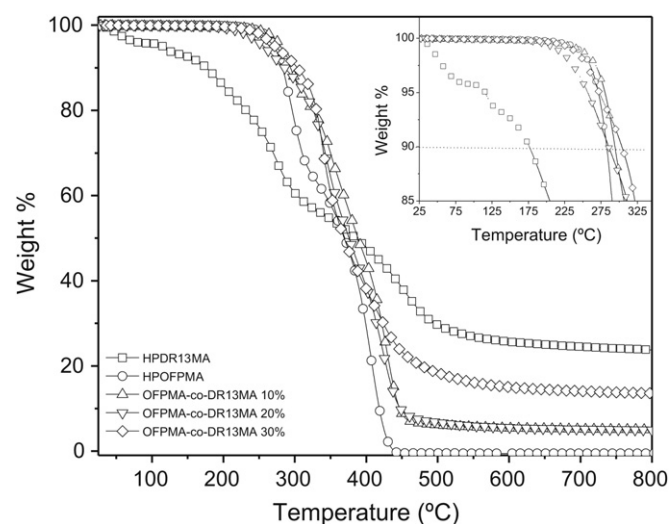
Sample	$T_i$ (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	$T_f$ (°C)	Ash (%)	$T_g^a$
HPDR13MA	50	178	386	564	24	–
HPTFEMA	250	269	344	432	0.4	74
TFEMA-co-DR13MA(10%)	245	279	370	454	3	71
TFEMA-co-DR13MA(20%)	220	292	386	492	8	66
TFEMA-co-DR13MA(30%)	225	266	370	519	10	82
HPOFPMA	263	283	369	446	0.5	– <sup>b</sup>
OFPMA-co-DR13MA(10%)	263	294	388	462	5	– <sup>b</sup>
OFPMA-co-DR13MA(20%)	225	283	388	462	5	– <sup>b</sup>
OFPMA-co-DR13MA(30%)	250	305	369	501	14	58

<sup>a</sup> Measured in the second heating cycle.

<sup>b</sup> Could not be determined.

units could improve stability. The stability of the azobenzene homopolymer (HPDR13MA) is poor with a two-step weight loss depicted in Fig. 8, with decomposition starting at  $T_{id} = 50$  °C and a 10% weight loss at 180 °C (Inset of the figures and Table 2). The fluorinated homopolymers have higher thermal stability, also with a two-step weight loss with  $T_{id}$  around 220 °C and 10% weight loss at 270–280 °C. HPOFPMA is slightly more stable than HPTFEMA (Fig. 9). Thus, the copolymers had higher thermal stability than pure HPDR13MA, as expected. Nevertheless, no clear trend with the azo content could be observed for  $T_{id}$ ,  $T_{10\%}$ ,  $T_{50\%}$  and  $T_f$  values. However, the ash content increased with increasing azo content, which means that the polymer became less combustible when the azo content increased. Glass transition temperatures ( $T_g$ ) could only be determined by DSC for the TFEMA copolymers and homopolymer and for the OFPMA-co-DR13MA(30%). The values are listed in Table 2, and were taken at the middle half of the transitions which were significantly large (at least 20 °C). No direct correlation between  $T_{gs}$  and the copolymers composition or molecular weight could be drawn. The physical appearance (rubbery) of the other polymers suggests that their  $T_g$  are near or sub-ambient, except for the homopolymer of DR13MA.

The cast films of the copolymers on glass slides had water contact angle (WCA) of ca. 96°, with no significant difference among the copolymers, as shown in Table 3. The fluorinated homopolymers and the copolymer OFPMA-co-DR13MA 10% did not form good quality films, and could not be analyzed. Low contact angles ( $\theta < 45^\circ$ ) are indicative of wetting and angles lower than 20 are indicative of excellent wetting [16]. Water is used to probe if

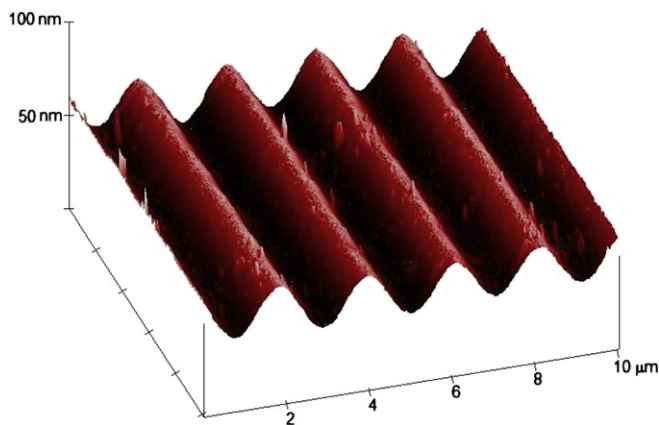


**Fig. 9.** Thermogravimetric curves for OFPMA-co-DR13MA and the homopolymers HPOFPMA and HPDR13MA.

**Table 3**  
Water contact angle values.

Film	WCA <sup>a</sup> (°)
TFEMA-co-DR13MA(10%)	97.0 ± 0.5
TFEMA-co-DR13MA(20%)	96.0 ± 1.0
TFEMA-co-DR13MA(30%)	95.0 ± 0.5
OFPMA-co-DR13MA(20%)	96.0 ± 1.0
OFPMA-co-DR13MA(30%)	97.0 ± 1.0

<sup>a</sup> Average of three measurements.



**Fig. 10.** AFM image of surface-relief grating on a TFEMA-co-DR13MA(30%) film.

a surface is hydrophobic (angle > 90°), hydrophilic ( $\theta < 45^\circ$ ) or intermediate ( $45^\circ < \theta < 90^\circ$ ) [17], and therefore all copolymers studied here were hydrophobic.

The ability of azopolymers to form surface-relief gratings, by exploiting the azobenzene photoisomerization process, was already established for HPDR13MA [18]. In order to show that the copolymerization with fluorinated units does not affect this ability, surface-relief gratings were inscribed on cast films of TFEMA-co-DR13MA(30%) and OFPMA-co-DR13MA(30%). An interference pattern of 2 μm period was produced by an argon laser beam impinging on the film surface. The AFM image of the grating recorded in the TFEMA-co-DR13MA(30%) in Fig. 10 demonstrates that even with a relatively low concentration of azobenzene units (less than 20 mol%) the mass transport took place, and good quality, 25 nm deep surface-relief gratings were formed. A similar result was obtained with the OFPMA-co-DR13MA(30%) film. Considering the parameters used for fabricating the grating, including the laser intensity, one may infer that the surface-relief gratings result from mass transport is an all-photonic process [14].

#### 4. Conclusions and perspectives

Copolymers of two fluorinated methacrylates with azobenzene moieties were produced with three compositions, with the copolymerization of the six copolymers being confirmed by FTIR and NMR spectra. The content of azobenzene repeating units determined with both visible and NMR spectra was in good agreement with the feed ratio. The thermal stability of the copolymers was similar to that of fluorinated homopolymers, but much higher than for the azobenzene homopolymer. Cast films from these copolymers were hydrophobic. Mass transport induced during the photoisomerization process of the azobenzene repeating units occurred in the two copolymers containing less than 20 mol% of azobenzene units, as indicated by the formation of surface-relief gratings.

The possible combination of thermal stability, hydrophobicity and surface-relief gratings demonstrated here for cast films of fluorinated-azobenzene copolymers opens a number of new avenues. One may now envisage the fabrication of nanostructured films, e.g. using the Langmuir-Blodgett (LB) [19] technique in order to exploit the control of film architectures, and tune the properties of the polymer surfaces to reach superhydrophobicity.

#### Acknowledgments

The authors are grateful for the financial support of Capes, CNPq, FAPESP and INEO/CNPq (Brazil).

#### Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.polymer.2011.08.032.

#### References

- [1] Chuang C-S, Cheng J-A, Huang Y-J, Chang H-F, Chen F-C, Shieh H-PD. Organic thin-film transistors with color filtering functional gate insulators. *Appl Phys Lett* 2008;93(053305).
- [2] Alessandrini G, Aglietto M, Castelvetro V, Ciardelli F, Peruzzi R, Toniolo L. Comparative evaluation of fluorinated and unfluorinated acrylic copolymers as water-repellent coating materials for stone. *J Appl Polym Sci* 2000;76:962–77.
- [3] Katano Y, Tomono H, Nakajima T. Surface property of polymer films with fluoroalkyl side chains. *Macromolecules* 1994;27:2342–4.
- [4] Roussel F, Saidi S, Guittard F, Geribaldi S. Thermophysical properties of fluorinated acrylate homopolymers: mixing and phase separation. *Eur Phys J E* 2002;8:283–8.
- [5] Saidi S, Guittard F, Guimon C, Geribaldi S. Low surface energy perfluoroalkyl acrylate copolymers for surface modification of PET. *Macromol Chem Phys* 2005;206:1098–105.
- [6] Zhou D, Teng H, Koike K, Koike Y, Okamoto Y. Copolymers of methyl methacrylate and fluoroalkyl methacrylates: effects of fluoroalkyl groups on the thermal and optical properties of the copolymers. *J Polym Sci Part A: Polym Chem* 2008;46:4748–55.
- [7] Honda K, Morita M, Otsuka H, Takahara A. Molecular aggregation structure and surface properties of poly (fluoroalkyl acrylate) thin films. *Macromolecules* 2005;38:5699–705.
- [8] Saidi S, Guittard F, Guimon C, Geribaldi S. Fluorinated comblike homopolymers: the effect of spacer lengths on surface properties. *J Polym Sci Part A: Polym Chem* 2005;43:3737–47.
- [9] Ha J-W, Park IJ, Lee S-B. Antireflection surfaces prepared from fluorinated latex particles. *Macromolecules* 2008;41:8800–6.
- [10] Ha J-W, Park IJ, Lee S-B, Ki D-K. Preparation and characterization of core-shell particles containing perfluoroalkyl acrylate in the shell. *Macromolecules* 2002;35:6811–8.
- [11] Zhang C, Chen Y. Investigation of fluorinated polyacrylate latex with core-shell structure. *Polym Int* 2005;54:1027–33.
- [12] Thomas RR, Lloyd KG, Stika KM, Stephens LE, Magallanes GS, Dimonie VL, Sudol ED, El-Aasser MS. Low free energy surfaces using blends of fluorinated acrylic copolymer and hydrocarbon acrylic copolymer latexes. *Macromolecules* 2000;33:8828–41.
- [13] Oliveira Jr ON, Santos Jr DS, Balogh DT, Zucolotto V, Mendonça CR. Optical storage and surface-relief gratings in azobenzene-containing nanostructured films. *Adv Coll Interf Sci* 2005;116:179–92.
- [14] Oliveira Jr ON, Li L, Kumar J, Tripathy SK. In: Sekkat Z, Knoll W, editors. Surface relief grating in azobenzene-containing films in photoreactive organic thin films, chapter 4. San Diego: Academic Press; 2002.
- [15] Tanchak OM, Barrett CJ. Light-induced reversible volume changes in thin films of azo polymers: the photomechanical effect. *Macromolecules* 2005;38:10566–70.
- [16] ASTM: D7334 – 08. Standard practice for surface wettability of coatings, substrates and pigments by advancing contact angle measurement.
- [17] ASTM: D7940 – 08. Standard test method for measurement of surface tension of solid coatings, substrates and pigments using contact angle measurements.
- [18] Mendonça CR, Dhanabalan A, Balogh DT, Misoguti L, Dos Santos Jr DS, Pereira-da-Silva MA, Giacometti JA, Zilio SC, Oliveira Jr ON. Optically induced birefringence and surface relief gratings in composite Langmuir-Blodgett (LB) films of poly[4'-[[2-(methacryloyloxy)ethyl]ethylamino]-2-chloro-4-nitroazobenzene]HPDR13 and cadmium stearate. *Macromolecules* 1999;32:1493–9.
- [19] Petty MC. Langmuir-Blodgett films: an introduction. Cambridge University Press; 1996.