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Application of a cold plasma process for polymerization and copolymerization of fluorinated and hydrogenated (meth)acrylates

F. Hochart, J. Levalois-Mitjaville, R. De Jaeger*

Laboratoire de Spectrochimie Infrarouge et Raman, CNRS UMR 8516, Bât. C5, Université des Sciences et Technologies de Lille,
59655 Villeneuve d'Ascq Cédex, France

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Abstract

The fluorinated monomers 1,1,2,2-tetrahydroperfluorodecyl acrylate (AC8) and methacrylate (MAC8), and an hydrogenated monomer isodecyl acrylate (ISO) were polymerized by using a low pressure Microwave (MW) plasma process. Reactions were carried out on monomer films (200–600 μm) and were monitored by ^{1}H NMR spectroscopy by following the evolution of the vinylic protons. Effects of inhibitor, photoinitiator, power of the MW generator, depth of films on the kinetics of homopolymerization were investigated. Our results show that a classical radical mechanism is respected and that the reactivity follows the order AC8 $>$ ISO $>$ MAC8. Copolymerization of AC8 with isodecyl acrylate was also studied and values of the reactivity ratios determined by the Fineman–Ross method. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Fluorinated acrylates and methacrylates; Polymerization; Microwave plasma

1. Introduction

A number of fluorine derivatives—monomers, oligomers or polymers—have been proposed for the coating of substrates such as textiles, papers, leather, wood, etc. in order to obtain oil- and water-repellent surfaces [1,2]. For this purpose, fluoroalkyl compounds and particularly the perfluoroalkyl(meth)acrylates, homo and copolymers, are actually the most effective [3,4].

Many publications and patents refer to the corresponding syntheses [5–17]. Copolymers are usually derived from monomer mixtures containing:

(i) fluorinated (meth)acrylates;

$$R_FXOC(O)C(R){=}CH_2 \qquad R = H, CH_3$$

in which R_F is a straight or branched perfluoroalkyl group and X, represents a spacer which may contain oxygen, sulfur or nitrogen atoms,
(ii) non fluorinated monomers containing one ethylene linkage and a further group to induce cross-linking reactions; and
(iii) occasionally, ionic monomers with water solubilizing anions.

These corresponding homo and copolymers are generally obtained by conventional solvent or emulsion polymerization techniques in the presence of catalysts—such as peroxy compounds or AIBN—in order to initiate the polymerization reaction. On the contrary, radical photopolymerization initiated by UV irradiation was used for example for:

(i) homopolymerization of the pure fluorinated monomers 2-(*n*-perfluoroctyl)ethylacrylate (AC8) ($R_F = -C_8F_{17}$, $X = -CH_2-CH_2-$, $R = H$) [18];
(ii) preparation of copolymers and terpolymers of methylmethacrylate-perfluoro octyl-*N*-methylsulfonamide ethylmethacrylate and or methoxy polyethyleneglycolmethacrylate [19];
(iii) curing of methacrylic macromers containing perfluoroether structures [20] and of fluorinated acrylic monomers eventually containing heteroatoms [21].

Recently, Boutevin and Coll investigated the radical copolymerization of AC8 and its methacrylic analog (MAC8) with morpholinoethyl methacrylate [7] and the radical homopolymerization of several fluoroacrylates differing from each other in the nature of the fluorinated chain and in the spacer length between this last and the ester group [22]. It was shown that:

(i) the reactivity of a fluorinated acrylate is higher than that of the methacrylate analog;

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* Corresponding author. Fax: +33-3-20-43-67-55.
E-mail address: roger.dejaeger@univ-lillel.fr (R. De Jaeger).

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(ii) contrary to its behavior in homopolymerization, MAC8 is more reactive than AC8 when it is copolymerized with morpholinoethylacrylate;
(iii) the reactivity of fluorinated monomers increases with the spacer length, probably due to the decrease of the electron withdrawing effect of the fluorinated chain.

Concurrently to all classical polymerization processes, the cold plasma technique nowadays takes an increasing place due to the growing demand of industries for more profitable and clean environment processes. Cold plasma are already used, as polymerization agents, in macromolecular chemistry. It has been shown that two types of polymerization reactions can occur: plasma-state polymerization and plasma-induced polymerization. In the first case, the polymerization occurs in a plasma in which electrons and other reactive species have enough energy to break any bond. By this way, any organic compound and even those without the necessary polymerizable function for a conventional polymerization can be used [23].

In the latter case, the plasma initiates polymerization at the surface of the liquid or solid monomer which contain, instead of the previous way, a polymerizable structure, such as double or triple bonds or cyclic structures. Most of the papers about plasma-induced polymerization concerns essentially volatile monomers, as (meth)acrylic acids, which were distilled and were sealed into ampoules before being plasma irradiated [24]. Comparatively, papers concerning plasma polymerization of heavy monomers coated onto glass plates are still rare [25]. On this subject, Epaillard and Coll have described the plasma polymerization of the hydrogenated monomers [26].

In this article, we present a fast and convenient synthetic method involving a low-pressure plasma process to prepare homopolymers derived from heavy monomers as AC8, MAC8 and isodecyl acrylate ($C_{10}H_{21}OC(O)CH{=}CH_2$). As well copolymers from these fluorinated and non-fluorinated monomers were obtained. Kinetics of the plasma homopolymerization reactions are compared, and the reactivity of AC8 and isodecyl acrylate in their copolymerization reaction is investigated.

2. Experimental

2.1. Materials

AC8 and MAC8 were kindly supplied by Elf Atochem. Isodecyl acrylate and the photoinitiator 2, hydroxy, 2 methyl propiophenone (Darocur 1173) were purchased from Aldrich. These monomers were stabilized with hydroquinone (<100 ppm). They were used either as received or the stabilizer was extracted twice with 10% aqueous NaOH, and dried over anhydrous magnesium sulfate.

Chloroform and 1,1,2 trichloro 1,2,2 trifluoroethane (Freon 113) were obtained from SDS and Prolabo, respectively. They were utilized as received. Argon (99.998%) was obtained from Air Liquide.

2.2. Plasma polymerization procedure

The microwave plasma was generated by an EUROPLASMA set-up composed of three parts. Excitation was provided by a microwave generator (2.46 GHz) with a tunable power from 0 to 600 W. The glow discharge was generated at the top of the chamber (volume: 27 l). The pumping system was composed of a primary pump (E2M28 PFPE, Edwards). The gas flow was controlled by Unit mass flow controllers.

2.3. Homopolymerizations

(Meth)acrylate monomers mixed with (or without) 2.5% (w/w) of the photoinitiator were coated onto glass plates to obtain liquid films of variable thickness. The coated plates were then introduced in the plasma reactor, the sample to generator window distance being 15 cm.

Before treatment, the reactor was evacuated (pressure: 40 Pa) and the gas flow rate (Argon) (500 sccm) adjusted. The discharge was then initiated by adjusting the power of the generator. After treatments for specific periods (0.5–15 min), the reactor was opened and the obtained films (AC8), powder (MAC8) or paste mixture (isodecyl acrylate) were removed from glass plates.

2.4. Copolymerization

Monomers AC8 and isodecyl acrylate, in various mole ratios with 2.5% (w/w) of Darocur were copolymerized by the same procedure. In order to compare their reactivity, several polymerizations were carried out under the conditions where polymerization are incomplete, i.e. for short times of treatment (30 s or 1 min). After plasma treatment, the products were dissolved in Freon 113 and the solutions poured in 250 ml of chloroform (for initial mole ratios $AC8/ISO > 1$) or methanol (for ratios $AC8/ISO < 1$) in order to precipitate the copolymers. Then, they were filtered and finally dried under vacuum.

2.5. Equipment

^1H NMR, ^{13}C and ^{19}F spectra were recorded in Cl_2FCCF_2Cl with C_6D_6 as external lock or $CDCl_3$ using a Bruker WP 300 NMR spectrometer. Molecular weights were obtained by means of steric exclusion chromatography on a Waters Millipore apparatus equipped with Shodex columns using THF as eluant. The calibration curve was established using standards polystyrene. Viscosity measurements were performed with a Ubbelolhde capillary viscometer at 20°C. The XPS analyses were performed with a LHS 10 system (Leybold AG). The X-ray source was operated at 13 kV, 20 mA using AlKα radiation (1486.6 eV). The vacuum during analyses was in the 10^{-6} Pa range. All

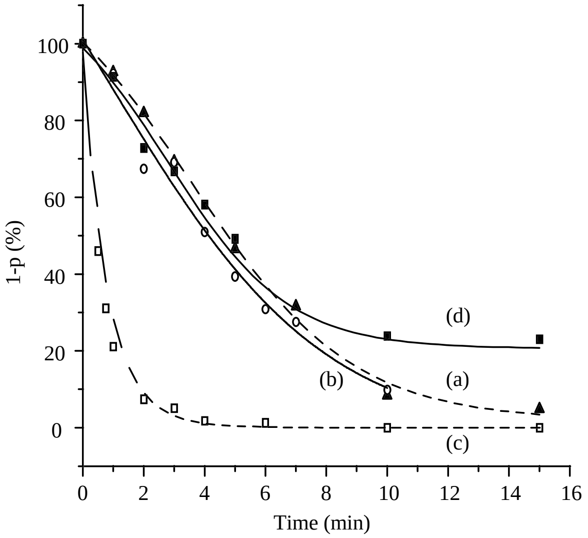

Fig. 1. Kinetics of homopolymerization in an Ar MW plasma of; (a) unwashed AC8; (b) washed AC8; (c) and (d) unwashed AC8 and MAC8 with 2.5% (w/w) initiator (flow rate = 500 sccm; $P = 100$ W; operating pressure = 120 Pa; thickness film = 190 μm).

the experiments were carried out at normal incidence relative to the plane film surface.

2.6. Characterization

PolyAC8: ^{1}H NMR (C_6D_6): δ 1.59–2.07 (m, 2H, (–CH_2–CH–)$_n$), 2.52 (brs, 3H, (–CH_2–CH–)$_n$ and (–CH_2–CF_2–)), 4.42 (brs, 2H, –O–CH_2–).

^{13}C NMR (C_6D_6): δ 30.3 (m, CH$_2$–R_F), 34.2 (m, (–CH$_2$–CH–)$_n$), 41.3 (m, (–CH_2–CH–)$_n$), 56.4 (d, –O–CH$_2$–), 107–123 (m, CF$_2$, CF$_3$), 173.8 (d, $-C=O$).

^{19}F NMR (C_6D_6): δ −6.2 (t, CF_3), −38.5 (s, CF_2–CF_2–CH_2–), −46.2 to −48.2 (m, –CF_2), −51 (s, CF_2–CF_3).

PolyMAC8: ^{1}H NMR (C_6D_6): δ 1.05 (brs, 3H, –CH_3), 1.83 (brs, 2H, (–CH_2–C(CH_3)–)$_n$), 2.36 (brs, 2H, (–CH_2–CF_2–), 4.17 (brs, 2H, –O–CH_2–).

^{13}C NMR (C_6D_6): δ 18.8 (m, CH$_3$), 30.2 (t, CH$_2$–R_F), 45.2 (s, (–CH_2–C(CH_3)–)$_n$), 54.3 (m, (–CH$_2$–CH–)$_n$), 56.7 (s, –O–CH$_2$–), 107–123 (m, CF_2, CF$_3$), 176.2 (d, $-C=O$).

^{19}F NMR (C_6D_6): analogous to ^{19}F NMR of polyAC8.

PolyISO: ^{1}H NMR ($CDCl_3$): δ 0.75–1.76 (m, 21H, (–CH_2–CH–)$_n$ and –C_9H_{19}), 2.26 (brs, 2H, (–CH_2–CH–)$_n$), 3.99 (brs, 2H, –O–CH_2–).

Copolymer AC8/ISO: ^{1}H NMR (C_6D_6): δ 0.95–2.06 [m, 2H, ((–CH_2–CH–)$_n$ AC8), 21H, ((–CH_2–CH–)$_n$ ISO) and –C_9H_{19}], 2.52 [brs, 3H, ((–CH_2–CH–)$_n$ and –CH_2–CF_2–AC8)), 1H, (–CH_2–CH–)$_n$ ISO], 4.14 (brs, 2H, –O–CH_2–ISO).

3. Results and discussion

When an inert gas (Ar) is submitted to a low-pressure (≤133 Pa) high frequency discharge (≥1 MHz), reactive species such as radicals, ions, free electrons, metastables and excited species are created. The latter relax to their ground energy levels emitting infrared, visible and UV radiations. All these reactive species, for which their concentration depend on the plasma conditions (power, pressure, etc.) can take part in gas-phase reactions or can interact strongly with a solid or liquid surface in contact with the plasma, usually via free radical chemistry.

3.1. Kinetic of homopolymerization of AC8 and MAC8

The fluorinated acrylic monomers AC8 and MAC8 coated on glass substrates, upon plasma exposition, give rise to films (AC8) and powders (MAC8) insoluble in hydrocarbon and chlorinated solvents, but soluble in Freon 113. Then, these uncross-linked films and powders were characterized by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy and XPS analysis. The NMR spectra are similar to those of the linear polymers obtained from the same monomers by conventional polymerization technique. Moreover, the surface atomic ratio nF/nC and nO/nC, for a polyAC8 film, determined by XPS were 1.35 and 0.18, respectively (theoretically 1.30 and 0.15). The good accordance between the experimental and the theoretical ratio nF/nC showed that, in this case, the Argon plasma does not lead to a surface defluorination.

In order to investigate and to improve their behavior in polymerization reaction induced by an Ar microwave plasma, it was worth studying the influence of different parameters—like the presence or absence of a stabilizing agent, an initiator and its concentration, the power of the plasma generator, the depth of the monomer films—on the kinetic of homopolymerization.

The experiments were monitored by ^{1}H NMR spectroscopy. For various treatment times, the ratio R between the relative intensities of $HC=CH_2$ (AC8) or $MeC=CH_2$ (MAC8) and CH_2O– groups was calculated. The latter was used as internal reference because it remains constant during the reaction. This ratio allows to evaluate the conversion rate p monomer to polymer and the amount $1-p$ of remaining (meth)acrylates:

$$1-p = 2R/3 \text{ for AC8} \qquad 1-p = R \text{ for MAC8}$$

The possible desorption of the monomer within the vacuum, was checked by weighing the glass plates coated with the monomer films before and after treatment. It was found that the weight loss was about less than 1% even after 10 min of treatment, certainly on account of the superficial polymerization. Therefore, it will be disregarded for the following.

The commercially available AC8 and MAC8 were stabilized with hydroquinone. Thus, in a first step, it was necessary to examine its influence to know if their purification prior to use was useful. In the same way, the effect of a photoinitiator (Darocur 1173) was assessed.

Fig. 1 shows the evolution of the remaining acrylates functions versus time of treatment for AC8 with (*1a*) and

Table 1
Disappearance rate of monomers AC8 and MAC8 in an Ar plasma (treatment time = 1 min; flow rate = 500 sccm; P = 100 W; operating pressure = 120 Pa; Darocur: 2.5% (w/w))

Monomer disappearance rate ($\times 10^2$ mol l^{-1} s^{-1})	
AC8 Washed	0.62
AC8 Inhibited	0.42
AC8 Inhibited + Darocur	4.06
MAC8 Inhibited + Darocur	0.50
ISO Inhibited + Darocur	1.54

without inhibitor (*1b*) and for inhibited AC8 and MAC8 in the presence of Darocur (*1c*, *1d*, respectively). These experiments were carried out under the same conditions (pressure, MW power, gas flow rate and position of the sample with respect to the plasma, film thickness). Results clearly indicate that the presence of the hydroquinone does not affect the kinetic of the polymerization of AC8, but that the addition of photoinitiator dramatically increases the polymerization rate (Table 1). Indeed in this case, more than 90% of the monomer are polymerized after 2 min and the reaction is achieved after 10 min. Interestingly, even without initiating reagent, after 10 min of treatment, more than 90% of the monomer are converted. This clearly demonstrates the role of the vacuum ultraviolet radiations in the plasma. Up to 6 min of treatment, conversion rates of MAC8 with and AC8 without photoinitiator are similar. However, even after 15 min, MAC8 is incompletely polymerized. This observation that a methacrylate is more difficult to homopolymerize than an acrylate is not surprising. It goes in the same way, as it has been previously demonstrated [27].

The required amount of photoinitiator for an improved polymerization was also estimated by following for a very short treatment time (1 min) the variation of $(1 - p)$ versus its weight percentage. A plateau value was reached, as shown on Fig. 2(a), for a concentration equivalent to 2.5% (w/w).

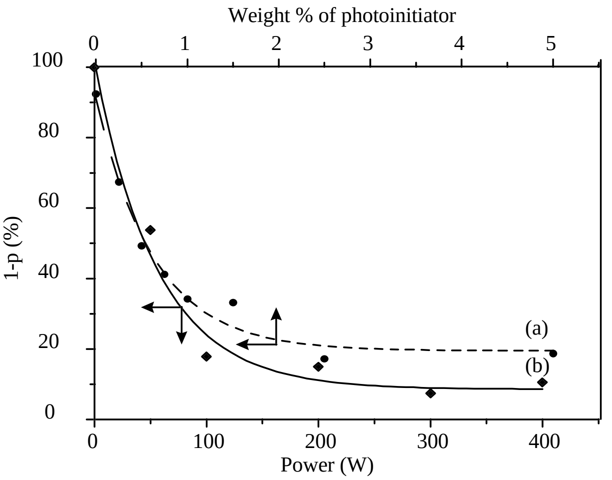

Fig. 2. Influence on the Ar MW plasma AC8 homopolymerization of the weight percentage of Darocur (a) and the power of generator (b) ($t = 1$ min; flow rate = 500 sccm; $P = 100$ W; operating pressure = 120 Pa; thickness film = 190 μm).

Likewise, the influence of the MW generator power was examined and a maximum conversion rate (80%) was obtained after 1 min of treatment at 100 W (Fig. 2(b)).

Finally, we investigated the effect, which is obtained when monomer films of variable thickness (100–550 μm) but of the same surface are exposed to an Ar plasma at $P =$ 100 W and $t = 1$ min. The amount of residual acrylate functions $1 - p$ (12% for 100 μm) increases with thickness to reach a limit (27%) for 350 μm. This can find an explanation in the fact that in a plasma initiated polymerization, the initiation of the reaction takes place especially at the exposed monomer film surface, contrary to the propagation which proceeds also in the bulk materials. Therefore, in the case of thick films, the initiation effect must decrease with the increase of the thickness and the polymerization rate must be strongly dependent on the migration of active species. It was checked that the completion of the polymerization could be obtained by increasing the treatment time or by switching off the MW generator and keeping the sample under vacuum in the reactor. A good compromise between film thickness, short treatment time and almost complete conversion was found for 190 μm film thickness, for which after 1 min of treatment, the conversion rate was higher than 80%.

All these experiments allowed us to find the optimal conditions for AC8 polymerization induced by an Ar MW plasma ($P = 100$ W, 2.5% (w/w) Darocur, 190 μm thickness). To confirm that AC8 polymerization in these conditions proceeded as expected by a normal radical mechanism, the evolution of the calculated amount of residual acrylates functions versus treatment time and the determination of the monomer disappearance rate for different concentrations of Darocur were investigated (Fig. 3). For both cases, linear plots were obtained which indicate that the disappearance rate is indeed proportional to the monomer concentration (first-order) and proportional to the square root of the photoinitiator concentration (half-order).

In the same conditions as for AC8 and MAC8, the behavior in an Ar MW plasma of isodecyl acrylate (ISO) (which is a hydrogenated monomer similar to AC8) was also studied. The results given in Table 1 allowed us to establish a relative reactivity scale in the order AC8 > ISO > MAC8.

3.2. Viscosity measurements

Due to the insolubility of polymers obtained from AC8 in most common organic solvents, size exclusion chromatography experiments were not possible except for the polyalkylacrylate (ISO). Therefore, intrinsic viscosity $[\eta]$ measurements in Freon 113 were carried out in order to compare fluorinated and non-fluorinated polymers obtained under the same conditions of treatment (exposure time and

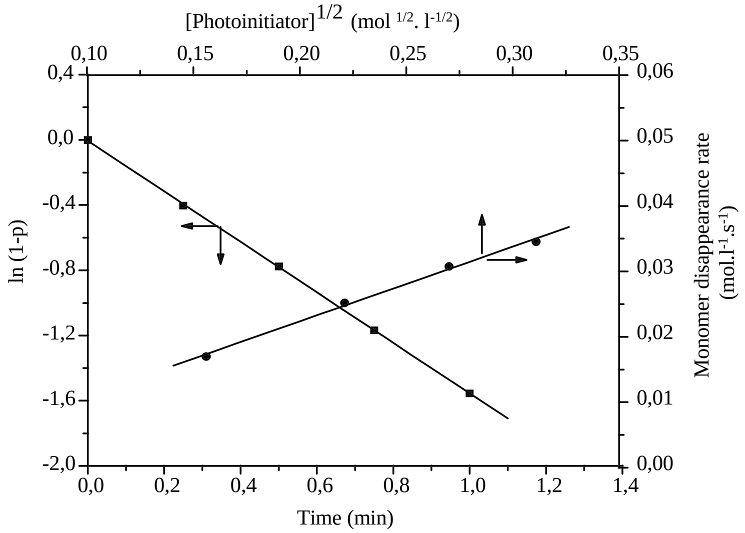

Fig. 3. Kinetic of disappearance of the monomer AC8 in an Ar plasma ($[\mathrm{Ac8}]_0 = 3.12$ mol l^{-2}; [Darocur]: 2.44–9.71 $\times 10^{-2}$ mol l^{-1}; flow rate = 500 sccm; $P = 100$ W; operating pressure = 120 Pa; thickness film = 190 μm).

power of the applied plasma, film thickness). Intrinsic viscosity values obtained for polyisodecyl acrylate (2.2 dl/g) were about two times higher than for polyfluoroacrylate (1 dl/g). The solvents used (Freon 113 for polyAC8–$CHCl_3$ for polyISO) were suitable for these polymer characterizations. The Huggins (k_H) and Kraemer (k_K) constants have normal values and the intersections of the linear plots corresponding to the Huggins and Kraemer equations:

$$\eta_{sp}/c = [\eta]_H + k_H[\eta]_H^2 c \quad (1)$$

$$\ln \eta_{rel}/c = [\eta]_k + k_K[\eta]_K^2 c \quad (2)$$

where c is the concentration, η_{sp} and η_{rel} are the specific and relative viscosity respectively, coincide ($[\eta]_H = [\eta]_k$) with limiting slopes related by $k_H + k_K\#1/2$. The molecular weight determined by SEC analysis in THF of the polyisodecyl acrylate ($[\eta] = 2.2$ dl/g) was $M_w = 2 \times 10^6$ with a polydispersity index $I = 7$.

3.3. AC8-isodecyl acrylate copolymers

The high market price of fluorinated monomers is a handicap for their use, and therefore it was interesting to investigate the possibility to prepare, by using the same process, a random copolymer containing the minimum amount of AC8 necessary to obtain a reasonable water repellency.

Copolymerization reactions involving AC8, generally proceed readily to give copolymers with a wide range of composition [7,28]. Thus, we opted to examine in detail the system AC8/isodecyl acrylate. To study the reactivity of each monomer in the copolymerization, AC8 and ISO were polymerized in various mole ratios in the presence of Darocur. The percentage of conversion, composition of copolymers and the ratio of AC8 and ISO in the copolymer in comparison to the initial ratio of the monomers was determined in the following way: The vinylic protons show characteristic ^{1}H signals in the range A $\delta = 5.50$–6.25 while the OCH_2 protons of both monomers and copolymer show a resonance in range B, $\delta = 4.14$–4.42. From a comparison of the intensity of the resonance signals in range A with the one in B of the crude reaction mixture, the percentage of conversion was determined. Then, the monomers in excess were extracted and the copolymers

Table 2
Composition, treatment time and percent of conversion for AC8-Isodcyl acrylate copolymerization (treatment time = 1 min; flow rate = 500 sccm; $P = 100$ W; operating pressure = 120 Pa; Darocur: 2.5% (w/w))

Initial ratio AC8/ISO	Feed ratioAC8/ISO	Product ratio AC8/ISO	Treatment time (s)	Percentage of conversion
9	10.36	7.45	30	36.47
4	4.21	3.54	30	28.7
3	3.11	2.86	30	32.8
3	3.10	2.91	60	52.95
1.5	1.45	1.64	30	25.62
0.66	0.625	0.77	60	30.60
0.33	0.315	0.38	60	29.07
0.11	0.096	0.16	60	25.75

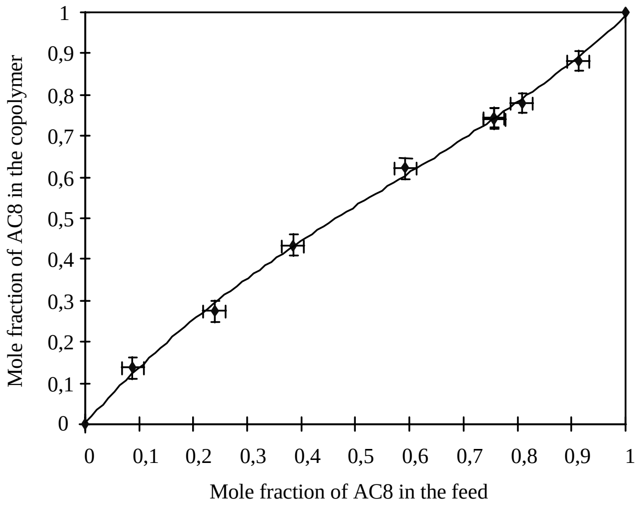

Fig. 4. Dependence of instantaneous copolymer composition on monomer feed composition for the AC8—isodecyl acrylate copolymerization.

investigated. Comparison of the signal intensity at $\delta = 4.42$ ppm, characteristic for the OCH_2 protons in polyAC8 and $\delta = 4.14$ ppm, characteristic of the OCH_2 protons in polyISO, allowed us to determine the instantaneous AC8/ISO mole ratios in copolymer feeds. The experimental data are given in Table 2.

The combination of both the data evaluations point out the dependence of the instantaneous copolymer composition on initial comonomer composition, which is graphically depicted in Fig. 4.

To provide a more thorough examination of the reactivity of AC8 in the system AC8/ISO, we have determined the reactivity ratios r_1(AC8) and r_2(ISO). These ratios calculated by the Fineman–Ross method are $r_1 = 0.75$ and $r_2 = 0.57$. Once more, these results are in accordance with the radical mechanism of these plasma initiated polymerizations. The polymeric radicals have reactivities of the same order of magnitude. Therefore, copolymers show a slightly higher fluoroacrylate content than that of the initial monomer feed up to an azeotropic composition AC8/ISO 65/35%.

4. Conclusion

This work indicates that polymers of 1,1,2,2-tetrahydroperfluorodecyl (meth)acrylates and isodecyl acrylate can be easily prepared by submitting films of these commercial monomers to an Argon microwave plasma even in the presence of a stabilizer.

Monitoring the progress of the polymerization reactions using ^{1}H NMR spectrometry allowed us (i) to describe them as a function of plasma parameters, (ii) to show that in the presence of Darocur as initiator the radical polymerizability increase in the order MAC8 < ISO < AC8, (iii) to confirm that polymerization of fluorinated acrylate proceeds by a radical mechanism.

Films of various thickness could be prepared and the experimental conditions used for the homopolymerization reactions of fluorinated and non-fluorinated acrylates have been transposed to the copolymerization of these monomers. Plasma treatments of AC8/ISO compositions with different feed ratios, associated with the ^{1}H NMR study of copolymers obtained at low conversion rates allowed us to give the corresponding monomer–copolymer compositions and to show the existence of an 65/35% azeotropic composition. Reactivity ratios were calculated by the Fineman–Ross method.

Acknowledgements

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