Radical copolymerization of acrylic monomers: 10. Copolymerization of *ortho*-methacryloyloxybenzoic acid with methyl methacrylate and vinyl chloride

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The radical copolymerization of *ortho*-methacryloyloxybenzoic acid with methyl methacrylate and vinyl chloride has been studied at low conversions. The reactivity ratios of these comonomeric pairs have been determined by the application of Fineman–Ross and Kelen–Tüdös methods. The values obtained indicate that both systems copolymerize at random. The copolymerization with methyl methacrylate is nearly ideal, but with vinyl chloride it deviates significantly from ideal behaviour, the growing radicals being much more reactive towards *ortho*-methacryloyloxybenzoic acid than towards vinyl chloride. Therefore, small amounts of the acrylic monomer drastically modify the microstructure of poly(vinyl chloride) chains. The microstructure of copolymers is analysed statistically and the thermal behaviour is studied by thermogravimetric analysis, taking into account the distribution of monomers along the copolymer chains..

(Keywords: copolymerization; *ortho*-methacryloyloxybenzoic acid; methyl methacrylate; vinyl chloride; thermal stability)

INTRODUCTION

The use of homopolymers and copolymers especially designed with functional active groups as lateral substituents of the main chain is a topic of increasing activity and interest. In this sense, the use of derivatives of salicylic acid as u.v. absorbers is well known[1] and several polymers and copolymers prepared from salicyclic acid and its derivatives have been synthesized in order to obtain macromolecular products with biological activity[2-8]. Copolymers of methacrylic acid and 3-vinylsalicylic acid present high activity against one type of bacterium, but none against another[5]. Although it has been found that the cytotoxicity of homopolymers is rather high, copolymers of methacrylic acid with 3-vinylsalicylic acid have been found to be non-toxic at concentrations as high as 1000 ppm[5]. Also these kinds of compounds are being used in the preparation of vesicular polymeric membranes in which it is very important to control the permeability when they are used for the separation of mixtures or the controlled release of drugs[9]. In this sense, copolymers have been prepared from 4-carboxyacrylanilide and methyl methacrylate, in an attempt to develop polymer membranes whose permeability to water-soluble compounds could be controlled in response to a pH change in the medium[10]. Polymer membranes based on acrylic copolymers (i.e. methyl methacrylate, acrylic and methacrylic acids and several acrylic aliphatic and aromatic esters) present good stability with respect to chemical, osmotic and mechanical stresses[11].

Generally, it can be considered that the characteristics and properties of macromolecular compounds synthesized from acrylic and vinyl monomers with organic functional groups depend on the chemical structure of the monomer[12], the stereoregularity of the polymers as well as on the composition and sequence distribution of comonomers in the macromolecular chains[8,13-15]. Hrabák *et al.*[16] have analysed the radical copolymerization of *ortho*-acryloyloxybenzoic and *ortho*-methacryloyloxybenzoic acids with unsaturated tertiary amines (*N*-methyl-*N*-phenyl-2-methyl methacrylate), in order to study the effect of mutual interactions between the carboxylic and amine groups of comonomers on the composition of copolymers. The present paper describes the radical copolymerization of *ortho*-methacryloyloxybenzoic acid with methyl methacrylate and vinyl chloride, determining for both systems the corresponding copolymerization parameters as well as the statistical parameters that describe the distribution of monomer units along the polymer chains in the whole range of compositions. Also the thermal behaviour of both copolymer systems is reported.

EXPERIMENTAL

Reactants

Ortho-methacryloyloxybenzoic acid (OM) was prepared by the reaction of salicylic acid with methacryloyl chloride as described elsewhere[17].

Methyl methacrylate (MMA), a commercial product, was washed with 5 wt% aqueous sodium hydroxide, dried over calcium chloride and twice distilled at reduced pressure.

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Table 1 Data for the copolymerization of OM with MMA in acetone solution at 60°C, initiated by AIBN

Feed, F_{OM}[a]	Copolymer, f_{OM}[a]	Time (min)	Conversion (wt%)	Conv./time (min^{-1})
0.800	0.84_3	120	9.60	8.0×10^{-2}
0.600	0.64_3	90	8.20	9.1×10^{-2}
0.400	0.47_3	90	10.07	11.1×10^{-2}
0.140	0.15_6	60	8.86	14.8×10^{-2}

[a] F_{OM} and f_{OM} are the molar fractions of *ortho*-methacryloyloxybenzoic acid in the monomer feed and in the copolymer samples, respectively

Table 2 Data for the copolymerization of OM with VC in acetone solution at 60°C, initiated by AIBN

Feed, F_{OM}	Copolymer, f_{OM}	Time (min)	Conversion (wt%)	Conv./time (min^{-1})
0.020	0.45_0	120	3.05	2.5×10^{-2}
0.050	0.60_0	120	3.25	2.7×10^{-2}
0.100	0.65_0	120	4.32	3.6×10^{-2}
0.200	0.76_0	120	4.86	4.0×10^{-2}
0.300	0.86_0	120	5.23	4.4×10^{-2}

Vinyl chloride (VC) was purified by repeat distillations in a high-vacuum line.

2,2'-Azobisisobutyronitrile (AIBN) was purified by fractional crystallization from methanol, m.p. 104°C.

Polymerization

Copolymerization reactions were made in acetone solutions at 60±0.1°C in Pyrex glass ampoules sealed off under high vacuum. Monomer and initiator concentrations were 0.5 mol l^{-1} and 0.3 mol%, respectively.

After the desired reaction time, the reaction mixture was added to hexane and the precipitated polymer was filtered off, washed with hot hexane to remove the *o*-methacryloyloxybenzoic acid and dried under vacuum until constant weight was attained.

Polymer characterization

Copolymers obtained from OM and MMA were analysed by n.m.r. spectroscopy using a Varian T-90 (90 MHz) spectrometer. The spectra were recorded at 60°C in 8% (wt/vol) hexadeuteroacetone and deuterochloroform solutions. Hexamethyldisiloxane (HMDS) was used as an internal reference standard.

Copolymers obtained from OM and VC were analysed by volumetric titration of chlorine following the method described by Schoniger[18] as well as by potentiometric titration of the chloride hydride released from the calcination of polymer samples in enriched oxygen atmosphere, using a solution of silver nitrate and electrodes of silver and silver-silver-chloride.

Thermogravimetric analysis

Programmed thermogravimetric analyses were performed with a Perkin-Elmer TGS-2 equipment coupled to a System-4 microprocessor programmer as the temperature control unit. Powdered samples (5–10 mg) were stacked in an open platinum sample pan and heated to 100°C for 60 min under dry nitrogen atmosphere with a nominal flow rate of 5 ml s^{-1}. After that, the samples were heated at a rate of 10°C min^{-1} until 500°C.

RESULTS AND DISCUSSION

The copolymerization of OM with MMA in acetone solution has been studied in a wide composition interval with molar fractions of OM ranging from 0.14 to 0.80 in the monomer feed. The reaction time was regulated to reach conversions about 10 wt% in order to satisfy the differential copolymerization equation[19]. *Table 1* presents data on the composition of the initial mixtures of comonomers and of the resulting copolymers. It is clear that the polymerization rate measured as conversion/time ratio increases with increase of MMA molar fraction in the monomer feed.

The composition of copolymers prepared from the OM–VC system are quoted in *Table 2*. It is noteworthy that, for this monomeric system, the copolymers obtained present an OM content significantly higher than the corresponding monomer feed. This behaviour is similar to that of several VC–acrylic ester systems reported in the literature[20–23]. From the slopes and intercepts of the straight lines obtained by the application of the Fineman–Ross[24] and Kelen–Tüdös[25] linear diagrams to both systems, the reactivity ratios and the corresponding average values quoted in *Table 3* were calculated.

The copolymer composition diagram obtained for the copolymerization of OM with MMA, which is near to the ideal behaviour, as well as the product of the corresponding reactivity ratios ($r_{OM}\times r_{MMA}=0.90$, very close to unity), indicate that this system copolymerizes predominantly at random, although the reactivity of growing radicals with MMA and OM ends, as measured by the ratios $1/r_{OM}$ and $1/r_{MMA}$, is somewhat higher towards OM than MMA monomer molecules. Therefore, the addition of OM molecules to growing polymer chains is slightly favoured in comparison with the addition of MMA for copolymers prepared at low conversions.

However, the behaviour of the OM–VC copolymerization system is rather different, since the composition diagram is very far from ideality. The values of $1/r_{OM}$ and $1/r_{VC}$ indicate that the reactivity of growing radicals towards OM molecules is much higher than that towards VC. Therefore, one can expect to see the formation of polymer chains with isolated VC units in long sequences of OM units for copolymers prepared at low conversions in a wide interval of feed compositions. Similar results have been reported in the literature for the free-radical copolymerization of methyl methacrylate with vinyl chloride[22,23,26].

In order to study the distribution of monomer units along the copolymer chains, several statistical parameters have been calculated. From the corresponding reactivity ratios and taking into account statistical relations, the so-

Table 3 Copolymerization parameters for OM–MMA and OM–VC systems

Monomers	Reactivity ratios	Parameters	
Methyl methacrylate	$r_{OM}=1.22\pm0.05$	$r_{OM}\times r_{MMA}=0.90$	$1/r_{OM}=0.82$
	$r_{MMA}=0.74\pm0.05$		$1/r_{MMA}=1.35$
Vinyl chloride	$r'_{OM}=11.60\pm0.05$	$r'_{OM}\times r_{VC}=0.12$	$1/r'_{OM}=0.09$
	$r_{VC}=0.01\pm0.02$		$1/r_{VC}=100$

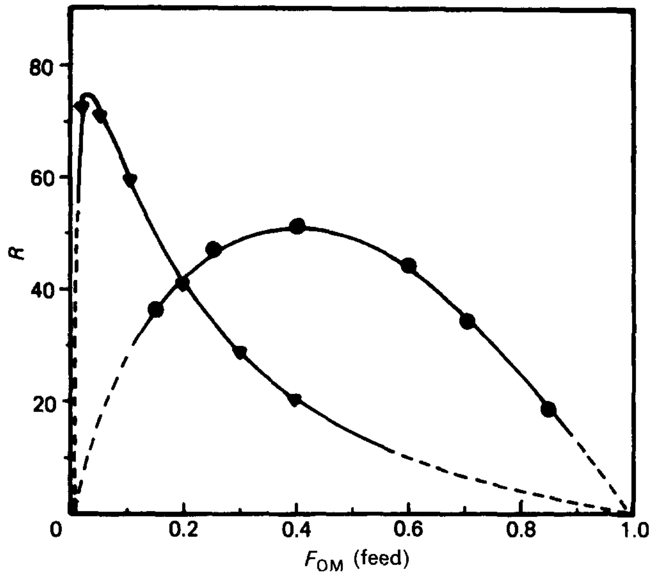

Figure 1 Run number R as a function of OM molar fraction in the monomer feed: (●) OM–MMA, (▼) OM–VC

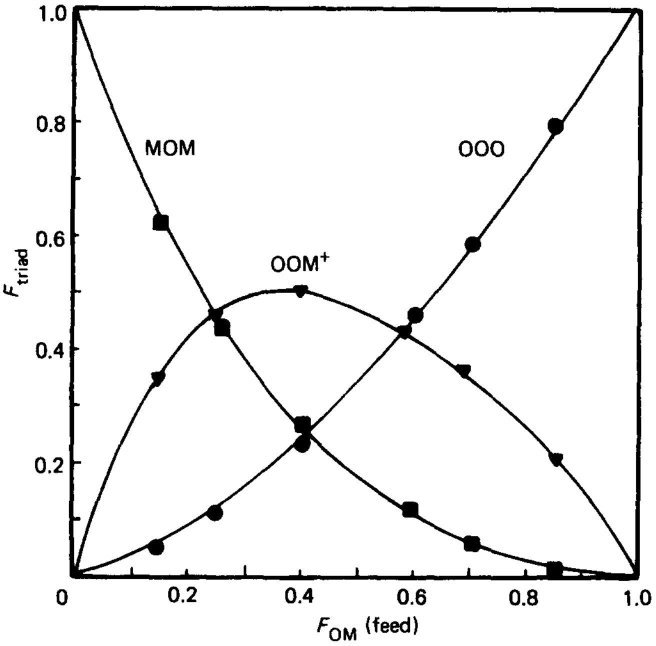

Figure 2 OM-centred triad distribution as a function of OM molar fraction in the feed, for the radical copolymerization of the OM–MMA system: (O) = OM units, (M) = MMA units, OOM$^+$ = OOM + MOO triads

called 'run number' R of Harwood[27] (the average number of monomer alternations in a copolymer per 100 monomer units), which provides a useful picture of sequence distribution in a copolymer chain, has been calculated for each copolymerization system. *Figure 1* shows the variation of R with OM molar fraction in the monomer feed for both copolymerization systems. The great difference in the diagrams obtained can be clearly seen. Whereas R reaches a maximum value of 51 at an OM molar fraction in the feed $F_{OM} = 0.40$ for the OM–MMA system, in the case of the OM–VC copolymers, R reaches a maximum value roughly equal to 74 for copolymers prepared with an OM molar fraction in the feed $F_{OM} \simeq 0.03$.

Figure 2 shows the statistical distribution of OM-centred triads along the copolymer chains according to the average molar composition of copolymer samples for the OM–MMA system. The diagrams obtained correspond adequately to a typical random distribution of monomeric units along the macromolecular chains, as a consequence of the small difference in the reactivity of growing radicals towards both kinds of monomers. This means that a homogeneous distribution of sequences is expected independently of the conversion reached, the composition of such sequences being dependent on the corresponding composition of the monomer feed.

However, as is shown in *Figure 3*, the situation is drastically different for the OM–VC copolymerization system. The diagrams obtained in this case indicate that the formation of homotriads of OM will be predominant in a wide interval of feed compositions and the probability of formation of OM-centred heterotriads with two VC units is practically zero for copolymers prepared with OM molar fractions higher than 0.4 in the monomer feed. This result clearly suggests that the presence of small amounts of OM in the reaction medium for a free-radical polymerization of VC drastically modifies the microstructure of the poly(vinyl chloride) macromolecular chains, giving rise to an appreciable modification of its physical and chemical properties.

Thermal behaviour

The study of the thermal degradative behaviour of statistical vinyl and acrylic copolymers has shown that, in general, the thermal behaviour of copolymers is intermediate between those of the corresponding homopolymers[28–32]. But in random copolymers the influence of the sequence distribution of monomer units is clearly shown, in such a way that the behaviour is different for an alternating copolymer and a random copolymer[33,34]. The thermal behaviour of PM–MMA copolymers has been studied by thermogravimetric analysis in a nitrogen atmosphere. The thermo-

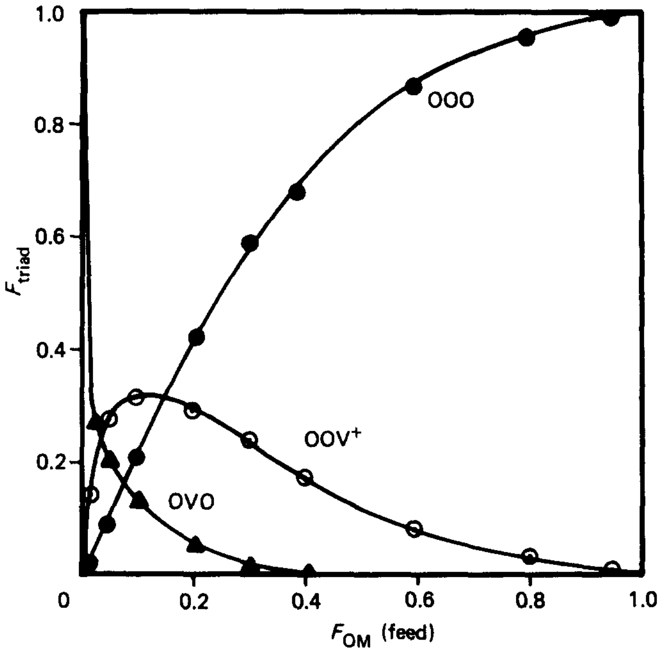

Figure 3 OM-centred triad distribution as a function of OM molar fraction in the feed, for the free-radical copolymerization of the OM–VC system: (O) = OM units, (V) = VC units, OOV$^+$ = OOV + VOO triads

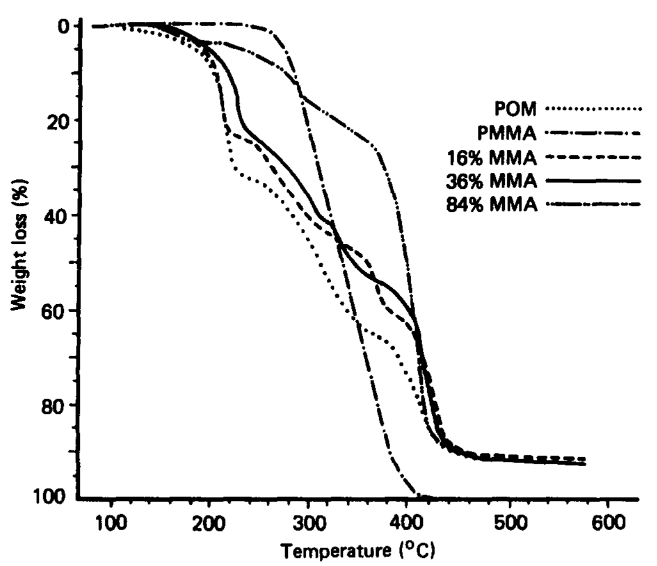

Figure 4 Thermogravimetric curves for OM–MMA copolymers

gravimetric (t.g.) curves for the weight loss of copolymers with a heating rate of 10°C min^{-1} and those of the corresponding homopolymers are shown in *Figure 4*. The curve of poly(OM) and also those of the copolymers can be classified into three or four distinct zones with weight loss percentages depending on the copolymer composition. But in all cases they tend to reach a constant weight, representing little carbonization of the remainder, independently of the copolymer composition. This does not happen with poly(MMA), for which the weight loss is total, as a consequence of the unzipping degradative mechanism.

Poly(*ortho*-methacryloyloxybenzoic acid) presents a thermogravimetric curve which indicates that there are three steps in the decomposition mechanism (*Figure 4*). The first step corresponds to a weight loss in the range of temperatures (140–200°C) with a relatively low activation energy ($E_a = 79$ kJ mol^{-1}), which has been attributed to the release of salicylic acid from isotactic sequences and the formation of cyclic anhydrides of glutaric-type structures along the macromolecular chains[35]. The second step has been attributed to the complete release of salicylic acid from the remaining syndiotactic sequences, with an activation energy $E_a = 163$ kJ mol^{-1}, and the third step corresponds to the decomposition of hydrocarbonated chains until carbonization.

The shape of the t.g. curves obtained for the copolymer samples studied indicates that this degradative mechanism remains for copolymers, since the lower the OM molar fraction in the copolymer, the lower the weight loss of the two steps of release of salicylic residues. However, the weight loss corresponding to these steps for copolymers prepared with a relatively low OM content is too great to be ascribed to the release of salicylic acid from two neighbouring OM units. Therefore, it can be possible that MMA units adjacent to OM units participate in the reaction of release of salicylic residues (in this case methyl salicylate) and the formation of cyclic anhydrides in the main chain. An intermolecular reaction can be ruled out because of the solubility of samples partially degraded in typical organic solvents for PMMA and POM. Also it is clear from the t.g. curves that the formation of anhydride structures gives rise to the thermal stabilization of MMA sequences, since for copolymers with such a low OM molar fraction as 0.16 the sigmoidal part of the t.g. curve that corresponds to MMA sequences is shifted to higher temperatures.

According to the sequence distribution of monomer units along the macromolecular chains (*Figure 2*), heterotactic triads with one OM unit predominate for copolymers prepared with low content of this monomer. Since the degradative mechanism assumes that the participation of two adjacent units is possible in the elimination of salicylic residues and the intramolecular cyclization to give the anhydride structures, the initial weight loss of copolymers with relatively low OM content could hardly be explained if MMA adjacent to OM units does not take part in the initial degradative process. Moreover, it has been demonstrated that in the copolymerization of several phenyl-substituted acrylates with MMA[36], the heterotactic triads with one phenyl acrylate unit are predominantly co-isotactic and a very similar behaviour can be expected for the OM–MMA system. This stereochemical arrangement is the most favourable to the elimination–cyclization reaction.

The study of the thermal behaviour of copolymers based on VC has claimed the attention of many investigators[37–40] since reactions can be easily produced in which the laterial functional groups of the main chain participate, giving rise in general to the formation of cyclic structures. Such reactions depend on the distribution of monomer sequences along the copolymer chains as well as on the chemical structure of the second monomer. Several investigators[39],[41–43] have described quantitatively the thermally induced cyclization of copolymers prepared from MMA and vinyl halides. In this sense, Zutty and Welch[41] have stated that random copolymers of MMA and vinyl chloride degrade at temperatures between 150 and 200°C, giving rise to the volatilization of methyl chloride through an intramolecular reaction involving adjacent VC and MMA units to form lactone rings. Under dynamic conditions the copolymers show three steps[40,44], which involve lactonization to give methyl chloride, dehydrochlorination and finally evolution of MMA monomer and breakdown products of the lactone ring structures. Moreover, Guyot *et al.*[42,43] and McNeill *et al.*[40] have shown that the copolymers are considerably less stable than PVC and the elimination of methyl chloride and subsequent lactonization appears to result from an exclusively intramolecular reaction of adjacent VC and MMA units at relatively low temperatures (100–120°C).

The t.g. curves for OM–VC copolymers with a heating rate of 10°C min^{-1} in a nitrogen atmosphere and those of the corresponding VC and OM homopolymers are shown in *Figure 5*. The shape of the t.g. curves is rather complex and all the copolymer samples analysed present initial weight loss at lower temperatures than POM and PVC, which indicates a clear effect of VC units in the release of salicylic acid residues. Since the formation of chlorine derivatives with salicylic residues is unlikely because of the chemical structure of the reactants, it is possible that the hydrochloric acid released from VC units could act as a catalytic agent for the elimination of salicylic acid from OM sequences.

The thermal behaviour of this copolymerization system is more easily visualized by the analysis of the weight loss rate as a function of temperature, which is illustrated in *Figure 6*. It can be clearly seen that the first step in the

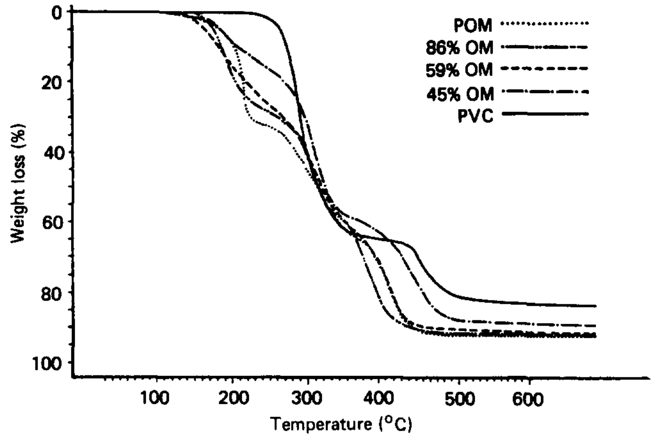

Figure 5 Thermogravimetric curves for OM–VC copolymers

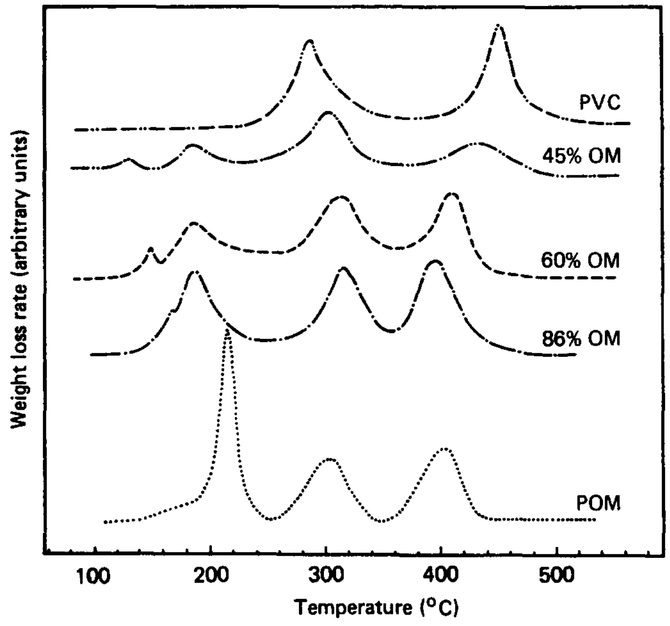

Figure 6 D.t.g. curves for OM–VC copolymers

release of salicylic residues from OM sequences (represented by a sharp peak with maximum at 210°C) is shifted to lower temperatures (185°C) for all the copolymer samples studied. Moreover, the diagrams show the appearance of a well defined peak over the temperature range 130–170°C which is shifted to lower temperatures with increasing VC content in the copolymer samples. Although it is difficult to relate this initial step with the sequence distribution of monomer units along the macromolecular chains, it seems to be probable that the VC units adjacent to OM units do not participate directly in the elimination–cyclization reaction since, for copolymers with a relatively low VC content, the VC units must be isolated in long sequences of OM units and a net peak at constant temperature in the range 130–170°C would be detected. However, the shift of the maximum observed in this range might be a consequence of a catalytic effect of small amounts of hydrochloric acid released from VC units at these temperatures, which could act as a catalyst, lowering the activation energy of the elimination–cyclization reaction. In order to clarify this point, further investigations are in progress.

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