

New acrylic titanium polymers: 2. Synthesis and characterization of organotitanium polymers

M. Camail*, M. Humbert, A. Margaillan and J. L. Vernet

Equipe d'Accueil 'Matériaux à Finalités Spécifiques', Laboratoire de Chimie Appliquée, Université de Toulon et du Var, BP132,83957, La Garde Cedex, France

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In this second part, we examined two possibilities for the synthesis of new acrylic organotitanium polymers that could be of great interest in the field of self-polishing antifouling coatings: copolymerization of acrylic organotitanium monomers with methyl methacrylate via free-radical initiation in organic solvents, or esterification of the acid functions of an available acrylic polymer with titanium tetraalkoxide. When a stoichiometric molar ratio Ti/COOH was used, a gel was formed. An excess of titanium tetraalkoxide had to be used to obtain an esterified polymer which was soluble in the usual organic solvents. The lowest excess value varied according to the nature of the alkoxide, the concentration and the nature of the polymer. An interpretation of this behaviour is proposed. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The major aim of our work is to succeed in the development of a new family of acrylic copolymers^{1,2} that could be used for self-polishing coatings. These coatings, whose role is to protect ships against marine fouling, contain a polymer as binder with hydrolysable functions. Most of the time, these functions are organotin derivatives^{3,4}, which are biocidal. Moreover, biocides such as cuprous oxide or zinc oxide are included in the formulation. The organotin compounds are released by hydrolysis in sea-water; the remaining polymeric backbone becomes appreciably water sensitive and is thus released as the other biocides. The result of this is a constant release of biocide obtained with self-polishing coatings⁵. The ecotoxicity of organotin compounds was established at the beginning of the 1980s⁶. As a result, these compounds are now partially forbidden, and one tries to find new solutions to protect ships against fouling.

With the purpose of developing self-polishing coatings free of toxicity, we studied the synthesis of new organotitanium acrylic polymers. Such polymers could be of interest for this application, because organotitanium compounds like titanium alkoxides are easily hydrolysed by water⁷, and are completely non-toxic for the marine environment.

In Part 1 of this work, we described the synthesis of five methacrylate titanium trialkoxides, among which three are new⁸. We studied their main features from a structural point of view, and we showed that they could be described by one to three structures. We determined that this kind of monomer, under radical copolymerization with methyl methacrylate, could lead to the kind of copolymer typically used in self-polishing coatings. We then studied the copolymerization of the different methacrylate titanium trialkoxides with methyl methacrylate, and this constitutes the first part of the present paper. According to the results we obtained, we explored another way to get organotitanium

acrylic copolymers and this constitutes the second part of the present paper. This second way consisted of preparing the polymers through esterification by titanium tetraalkoxides of acrylic copolymers containing a well-known ratio of acidic functions.

EXPERIMENTAL

Copolymerization of methacrylate titanium trialkoxides with methyl methacrylate

The synthesis of copolymers was conducted via free-radical initiation in organic solvents (toluene, methyl ethyl ketone) at 40 to 70°C using azobisisobutyronitrile (AIBN) or azobisisovaleronitrile (AIVN) as the free-radical initiator. The total monomer concentration was set between 0.5 and 2 mol l⁻¹.

All our copolymerization experiments led to insoluble final products, regardless of the nature of the alkoxy group.

Esterification of the acidic functions of (meth)acrylic polymers by titanium tetraalkoxides

The acrylic polymer Elvacite 2669, from ICI, is a tetrapolymer made of methacrylic acid, methyl methacrylate, ethyl acrylate and ethyl methacrylate. It is soluble in ether-alcohols (e.g. 2-methoxyethanol or 1-ethoxy-2-propanol) or in mixtures of ether-alcohols and aromatic solvents (like toluene or xylene) in 43:57 weight ratios. The acid number of the polymer is 124, and its $M_w = 60\,000$ g mol⁻¹.

The methacrylic polymer Elvacite 2550, from ICI, is a terpolymer made of methacrylic acid, methyl methacrylate and butyl methacrylate. It is soluble in aromatic solvents (toluene, xylene) and its acid number is 17 and its $M_w = 121\,000$ g mol⁻¹.

In a typical experiment, the polymer was solubilized in a convenient solvent. Under vigorous stirring, titanium tetraalkoxide was added straight to the solution, the flask was closed, and the mixture was allowed to react at room

* To whom correspondence should be addressed

temperature. The reaction was very fast and was easily detected by the changes in the appearance of the mixture. Two kinds of behaviour were observed:

- (1) When titanium tetraalkoxide was in default compared with the acidic functions or when a stoichiometric molar ratio Ti/COOH was used ($Ti/COOH \leq 1$), a gel was obtained. This tridimensional product was insoluble in common organic solvents, regardless of the nature of the alkoxy group.
- (2) When a sufficient excess of titanium tetraalkoxide was added to the solution ($Ti/COOH > 1$), an intermediate gel was formed, which evolved more or less quickly to a homogeneous and stable solution. This 'sufficient excess' was dependent on several parameters that will be discussed later. The total solids set for the experiment was calculated from:

$$TS = 100 \times \frac{\text{polymer} + Ti(OR)_4}{\text{polymer} + Ti(OR)_4 + \text{solvent}} \text{ in wt\%}$$

Polymer characterization

All the solutions that were obtained after esterification of the acrylic polymer by titanium tetraalkoxide were analysed by Fourier transform infrared (FTi.r.)

spectroscopy. FTi.r. spectra were acquired with an Ati-Unicam spectrophotometer ($4000-400 \text{ cm}^{-1}$). Liquid solutions were applied on a KBr window and the analysis was performed on the film that was obtained after evaporation of the solvent.

An example of esterification is given with the FTi.r. characterization of the reactants as well as of the final product. In that example, 1.0 g of Elvacite 2669 was solubilized in 14.0 g of 2-methoxy ethanol, and then 5.0 g of titanium tetra(2-ethylhexoxide) were added to the solution. This corresponded to a molar ratio $Ti/COOH = 4$ and to a total solid of 30 wt%. The mixture gave rise to a homogeneous solution under vigorous stirring. Figure 1 displays the following three spectra (wavenumbers in cm^{-1}):

FTi.r. of Elvacite 2669 (Figure 1a): 2985, 2950, 2842: ν_{CH_2, CH_3} ; 1477, 1449, 1388: δ_{CH_2, CH_3} ; 1731: $\nu_{C=O}$ (esters); 1700 (shoulder): $\nu_{C=O}$ (acid).

FTi.r. of $Ti(OEH)_4$ (Figure 1b): 2958, 2928, 2872, 2858: ν_{CH, CH_2, CH_3} ; 1460, 1378: δ_{CH, CH_2, CH_3} ; 1068: ν_{C-O} ; 661: ν_{Ti-O}

FTi.r. of the final product (Figure 1c): 3700 to 3100: ν_{OH} ; 2958, 2928, 2858: ν_{CH, CH_2, CH_3} ; 1460, 1379: δ_{CH, CH_2, CH_3} ; 1732: $\nu_{C=O}$ (esters); 1556: ν_a COO; 1455: ν_s COO; 1040: ν_{C-O} ; 666: ν_{Ti-O} .

Cross-linked gels could not be analysed by such a technique as solvent was held trapped in the mixture.

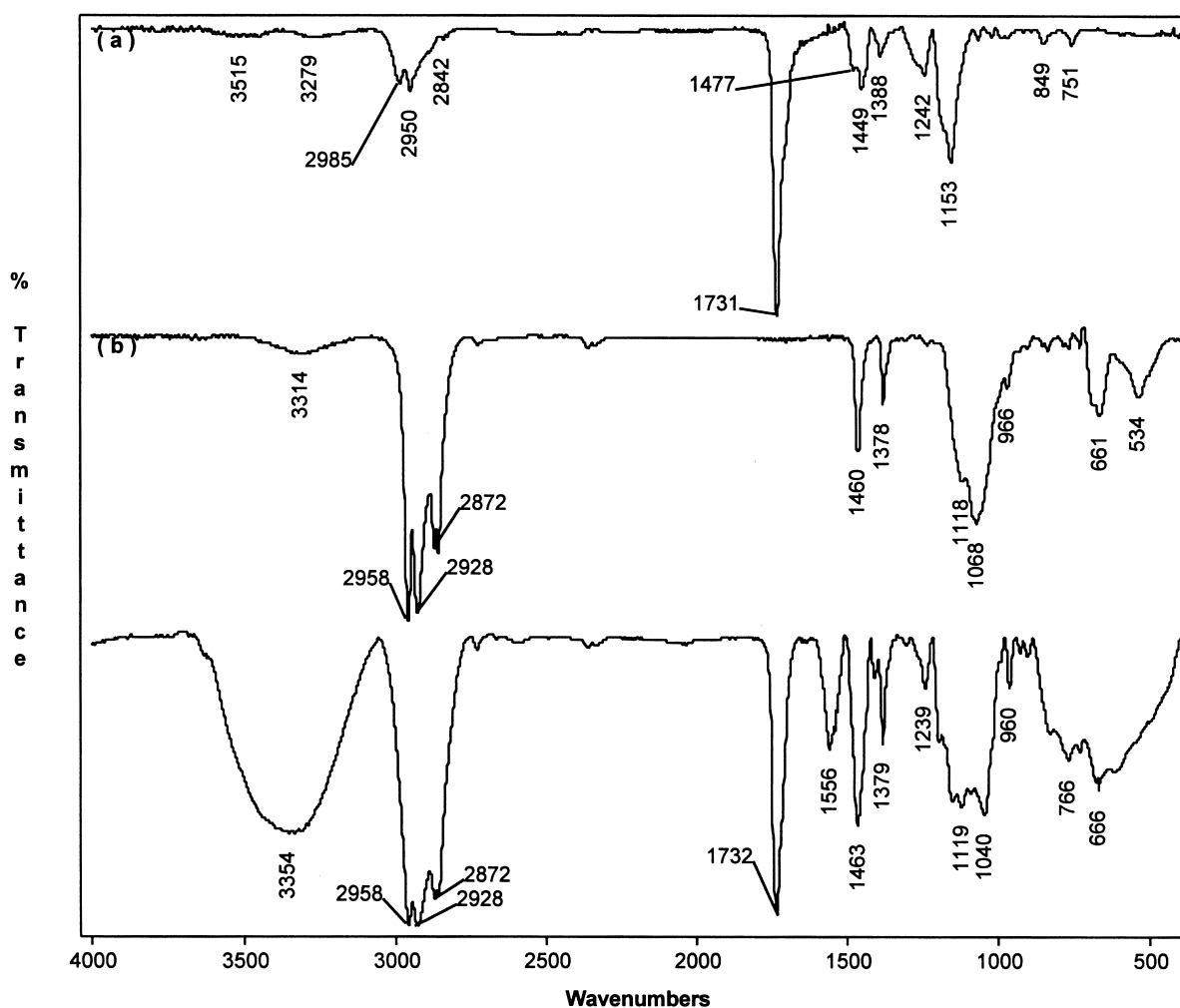


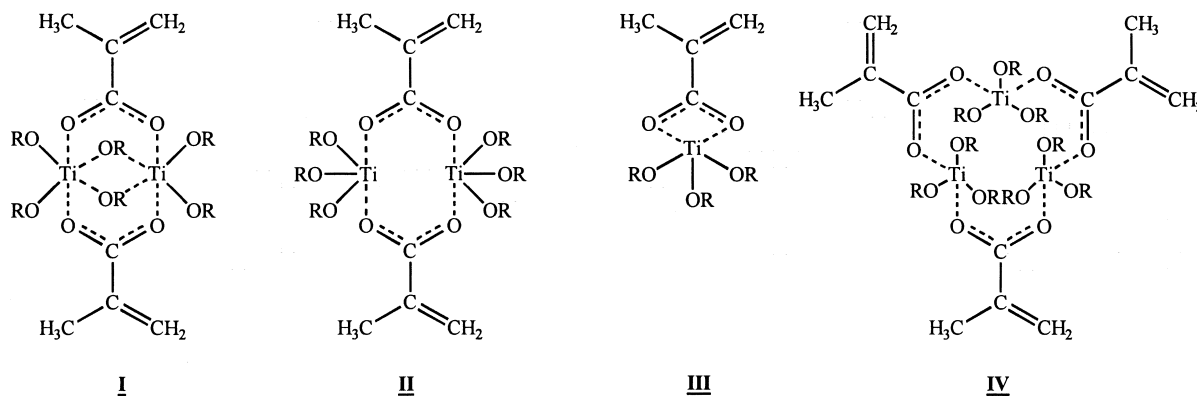
Figure 1 FTi.r. spectra of: (a) Elvacite 2669; (b) $Ti(OEH)_4$; (c) solution composed of Elvacite 2669 in 2-methoxyethanol esterified by $Ti(OEH)_4$ with a molar ratio $Ti/COOH = 4$ and a total solid of 30 wt%

RESULTS AND DISCUSSION

Copolymerizations

The aim of our experiments was to obtain statistical copolymers from methyl methacrylate and methacrylate titanium trialkoxides via free-radical initiation.

The methacrylate titanium trialkoxides were synthesized earlier, their preparation was the aim of Part 1. In this part, we also studied the structural behaviour of these five compounds. According to the nature of the alkoxy group, we showed from i.r. and n.m.r. studies that four types of structures could be proposed to describe the methacrylate titanium trialkoxides:



The butoxide derivative ($R = \text{Bu}$) exists in the form **I**, while the four other compounds are described by equilibrium between structures **II** and **III** ($R = \text{iPr}$, 2-ethylhexyl), or between structures **II**, **III** and **IV** ($R = \text{tAm}$, tBu).

The most important aspect of this study was the fact that, whatever the nature of the alkoxy group, at least one bridged structure was present in each compound. Therefore, it appeared that these oligomeric species acted as cross-linking junctions for the polymeric compounds prepared. The result was a tridimensional network as shown in *Figure 2*, in which we took the example of a dimeric species.

As at least one oligomeric species was systematically present, the five methacrylate titanium trialkoxides gave rise to cross-linked materials when copolymerized with methyl methacrylate.

In order to understand this result, we tried to obtain those copolymers by another method.

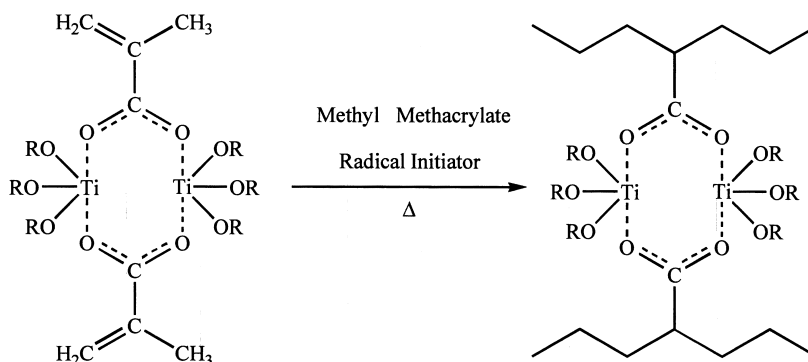


Figure 2 Tridimensional structures responsible for the formation of cross-linked products after copolymerization with methyl methacrylate

Esterification of available acrylic polymers

It was possible to form acrylic polymers that would contain a definite ratio of carboxylate titanium trialkoxides functions by the esterification of the acrylic functions of an available acrylic polymer with titanium tetraalkoxide. Such a reaction was assumed to take place as follows:



P represents the polymer backbone.

In other words, the aim here was to carry out reactions

that were similar to those that were done with methacrylic acid and titanium tetraalkoxides for the monomer synthesis (see Part 1). Nevertheless, as the alcohol ROH could not be removed from the mixture by distillation, the reaction could be incomplete. Moreover, perhaps this reaction could not take place as the acidic functions were hidden and not so easily available as in methacrylic acid. Finally, one was uncertain about the coordination mode of the carboxylate ligand that would be formed, as well as about the influence of the nature of the alkoxy group.

Molar ratio $\text{Ti}/\text{COOH} \leq 1$

When the reactions of esterification were carried out with a stoichiometric molar ratio between titanium tetraalkoxide and acidic functions ($\text{Ti}/\text{COOH} = 1$) or with a molar default of titanium tetraalkoxide ($\text{Ti}/\text{COOH} < 1$), we observed the instantaneous formation of tridimensional gels. The appearance of these gels was very similar to the appearance of the final products of the reactions of copolymerization. The

nature of the alkoxy group had no influence, and the only parameter that seemed to be essential was the molar ratio $Ti/COOH \leq 1$.

We made a comparison with copolymerization reactions, because the same features between the polymerization products and the esterification ones were observed. Let us assume that the same kind of phenomenon had taken place and had given rise to the formation of identical products. This was essential because the polymer skeleton existed prior to the reaction of esterification in one case and was built up during the reaction of copolymerization in the other case. Therefore, the species which was responsible of the formation of the network was present whatever the method of synthesis. Moreover, as the gel formation occurred just when the titanium tetraalkoxide was added to the polymer, this species was certainly responsible for the observed phenomenon. Taking into consideration the mechanism we supported to explain the formation of gels during the reactions of copolymerization, we assumed that the reaction of esterification occurred as shown on *Figure 3*.

Unfortunately, the i.r. analysis of the gels, that would have allowed us to define their structure at the level of the chemical bond between the carboxylate group and the titanium atom, was not carried out because the solvent is trapped into the gel.

Molar ratio $Ti/COOH > 1$

We were very surprised by the behaviour of the mixtures for which the reaction of esterification was carried out with a sufficient excess of titanium tetraalkoxide compared with the acidic functions ($Ti/COOH > 1$): after the formation of a temporary gel, the mixture slowly and progressively evolved to a homogeneous solution, that was stable if kept in a closed vessel.

FTi.r. analysis of the solutions (*Figure 1*). The i.r. analysis of a thin film obtained from the evaporation of the solvent of such a solution gave interesting elements in the understanding of the phenomenon that occurred. The spectra (e.g. see *Figure 1c*) systematically displayed the following features: the band (shoulder around 1700 cm^{-1}) for the carboxylic acid functions of the initial polymer disappeared, whereas the bands for the Ti–O and C–O vibrations of the titanium alkoxide were still present⁹. A broad band between 3000 and 3800 cm^{-1} corresponding to the O–H vibration of an alcohol was the sign that the reaction occurred and that an alcohol was formed. Moreover, one could observe a set of two new bands between 1400 and 1600 cm^{-1} . These bands were assigned to the $\nu_a(COO)$ ($\approx 1550\text{ cm}^{-1}$) and the $\nu_s(COO)$ ($\approx 1450\text{ cm}^{-1}$) vibrations of the carboxylate groups¹⁰.

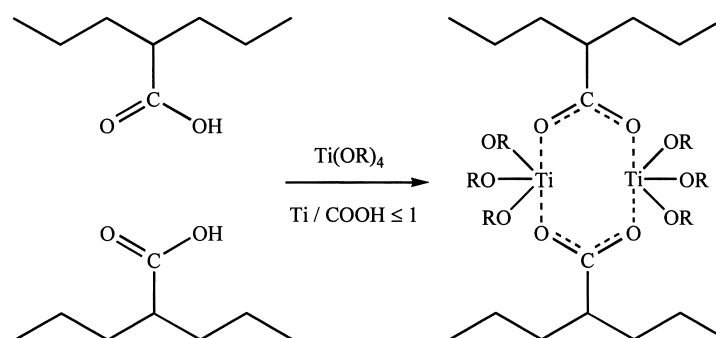


Figure 3 Progress of the esterification of acid functions of a polymer by titanium tetraalkoxide with a molar ratio $Ti/COOH \leq 1$

This doublet was evidence that the chemical reaction had taken place, giving rise to the formation of a covalent bond between the carboxylate function and the titanium atom. The value of their frequency separation $\Delta\nu = \nu_a - \nu_s$ was close to 100 cm^{-1} , which indicated that the carboxylate group was linked to the titanium in a bidentate, chelating mode of coordination^{10,11}.

In conclusion, this i.r. spectra showed that the acidic functions of the polymer were esterified by the titanium tetraalkoxide, this reaction giving rise to the liberation of an alcohol and to the formation of carboxylate titanium trialkoxide functions.

Evolution of the molar ratio $Ti/COOH$. It was interesting to examine the behaviour of the mixtures according to the value of the molar ratio $Ti/COOH$, all other parameters being unchanged. Between a mixture with a stoichiometric molar ratio $Ti/COOH = 1$, that led to a very dense gel, and a mixture with a high excess of titanium tetraalkoxide (e.g. $Ti/COOH = 14$), one could observe a continuous evolution of the behaviour of the mixtures. While increasing the molar ratio $Ti/COOH$, the gel formed became less and less dense. A definite molar ratio $Ti/COOH$ allowed one to obtain not a gel but a solution. However, this solution became a gel again when the stirring is stopped. A new increase of the molar ratio $Ti/COOH$ then gave rise to a stable solution.

We defined as a threshold the smallest molar ratio $Ti/COOH$ giving rise to an homogeneous and stable solution of esterified polymer. The value of this threshold was valid for a precise set of parameters, which were:

- the nature of the titanium tetraalkoxide,
- the total solids (in wt%),
- the nature of the initial polymer on which the esterification reactions were performed.

Then, we studied the evolution of the threshold when one of these parameters was modified.

Nature of the titanium tetraalkoxide. According to the nature of the alkyl chain of $Ti(OR)_4$, we observed a variation in the threshold we found (see *Table 1*). For linear alkyl chains, the longer the chain, the lower the threshold. Therefore, when the alkyl chain of titanium tetraalkoxide was four carbon atoms or more, it was easier to break the gel, whereas this was very difficult when this number decreased. The best results were obtained with $Ti(OEH)_4$.

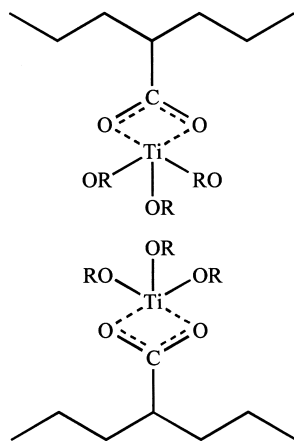
The role of spacer between polymer chains seemed to be essential. Indeed, when the titanium tetraalkoxide was able to space out the macromolecular chains, the formation of titanium-carboxylate bridges was restricted or even

Table 1 Variation of the threshold Ti/COOH according to the nature of the alkyl chain of Ti(OR)₄. Example of the esterification of Elvacite 2550 in toluene (total solids: 20 wt%)

Titanium tetraalkoxide	Threshold 'Ti/COOH'
Ti(OEt) ₄	13/1
Ti(OPr) ₄	12/1
Ti(OiPr) ₄	17/1
Ti(OBu) ₄	7/1
Ti(OEH) ₄	3/1

Table 2 Esterification reaction with titanium butoxide and titanium 2-ethyl hexoxide of both Elvacite 2550 and Elvacite 2669 when modifying the total percentage solid weight

Total solid (wt%)	Elvacite 2550 in toluene		Elvacite 2669 in 2-methoxyethanol	
	Ti(OEH) ₄	Ti(OBu) ₄	Ti(OEH) ₄	Ti(OBu) ₄
20	3/1	7/1	2.5/1	3/1
30	4/1	7/1	2.5/1	3/1
50	7/1	13/1	3/1	5/1

**Figure 4** Bidentate chelated structures obtained when the esterification of the polymer was performed with a sufficient excess of titanium tetraalkoxide

prevented. Consequently, the tridimensional structure did not possess sufficient interactions to exist, and vigorous stirring was enough to break the network and give rise to a solution. Therefore, the higher the total steric hindrance of the titanium tetraalkoxide, the easier it was to prevent the medium from forming bridged structures.

Polymer concentration (total solids). With the two titanium tetraalkoxides Ti(OR)₄ giving rise to solutions with the smallest molar ratio Ti/COOH, we studied the esterification reaction of both Elvacite 2550 and Elvacite 2669 when modifying the total percentage solid weight. Results are shown in Table 2, with titanium butoxide and titanium 2-ethyl hexoxide.

According to these results, a higher amount of titanium tetraalkoxide was necessary when increasing the concentration. The reasons seemed to be more linked to the speed of mixing the titanium tetraalkoxide with the polymer than to a structural factor. The higher the viscosity of the mixture, the longer it was for the titanium tetraalkoxide to diffuse into it.

Nature of the polymer. The excess of titanium tetraalkoxide necessary for breaking a gel was more important

when the polymer was Elvacite 2550 than when it was Elvacite 2669. A major reason for such a difference was the nature of the solvents in which experiments were performed: toluene for Elvacite 2550, 2-methoxyethanol for Elvacite 2669. This latter solvent interacts more with titanium alkoxides than toluene, which could induce a better shielding effect.

Role played by the excess of titanium tetraalkoxide

In previous paragraphs, we described what phenomenon we observed when the esterification of acrylic polymers was carried out:

- formation of gels denoting the presence of a tridimensional structure,
- evolution from gels to solution when acting with a minimum excess of titanium tetraalkoxide that we called the threshold,
- increase of this value with the concentration of the mixture.

Our purpose is now to try to rationalize these observations by suggesting a mechanism for the evolution from the gelified structure to the solution of polymer.

We showed in Figure 3 how a molar ratio Ti/COOH ≤ 1 could lead during esterification to tridimensional networks: by the formation of bidentate bridging carboxylate functions, polymer chains were cross-linked, and the result was an insoluble final product.

The addition of titanium tetraalkoxide in excess succeeded in breaking these bridges and gave rise to solutions in which macromolecular chains regained their relative mobility. We analysed the i.r. spectra of thin films prepared from these solutions and showed that, in these solutions, carboxylate ligands were systematically linked to the titanium atom in a bidentate chelating coordination mode. Obviously, such a coordination mode releases intermolecular interactions, as shown in Figure 4.

In this structure, the titanium tetraalkoxide molecules linked to lateral chains -CO₂Ti(OR)₃ were not represented, as we did not define exactly what these structures were. However, we can determine the experimental observations that support the existence of structures in which titanium tetraalkoxide molecules were strongly linked to these lateral chains:

- the evolution from the tridimensional bridged structure (Figure 3) to the chelated structure (Figure 4) needed addition of titanium tetraalkoxide;
- this change was possible only if the molar ratio of titanium tetraalkoxide in the mixture was higher than a minimal value ('threshold') which was always greater or equivalent to twice the number of acidic functions of the initial polymer;
- when the esterification was carried out, the intermediate formation of a gel in the mixture showed that the bridged structure was transitionally formed (kinetic control) before evolving to the chelated structure (thermodynamic control indicating a stabilization due to the excess of titanium tetraalkoxide);
- any other solvent (toluene, xylene, diethyl formamide, dimethyl sulfoxide) was able to fulfil the role played by the titanium tetraalkoxide in the formation of chelated structures.

This hypothesis enabled us to explain the dependency of the change in the bridged structure in the chelated structure under the action of titanium tetraalkoxide on the nature of

the alkoxy group, the concentration of the polymer and the nature of the polymer.

Copolymerization with the presence of excess titanium tetraalkoxide

We found that the esterification with a stoichiometric molar ratio Ti/COOH gave rise to identical gels to those resulting from the reactions of copolymerization. As the esterification carried out with an excess of titanium tetraalkoxide allowed us to obtain a solution of the polymer, we wanted to know if the polymerization in the presence of an excess of titanium tetraalkoxide could lead to such a solution.

Therefore, we performed copolymerizations with an excess of titanium tetraalkoxide; this excess was chosen

according to the threshold which was found during the reactions of esterification. Moreover, experiments were systematically carried out with a stoichiometric molar ratio Ti/COOH.

We observed that, in all cases, the experiments led to gels when the molar ratio was Ti/COOH = 1, whereas they led to homogeneous solutions when an excess of titanium tetraalkoxide was present. The fact that the alcohol resulting from the reaction of esterification of methacrylic acid with titanium tetraalkoxide was or was not kept in the mixture, had no influence on the final product. Therefore, it seemed that the presence of an excess of titanium tetraalkoxide was a necessary and sufficient condition to avoid the formation of a tridimensional network during reactions of copolymerizations.

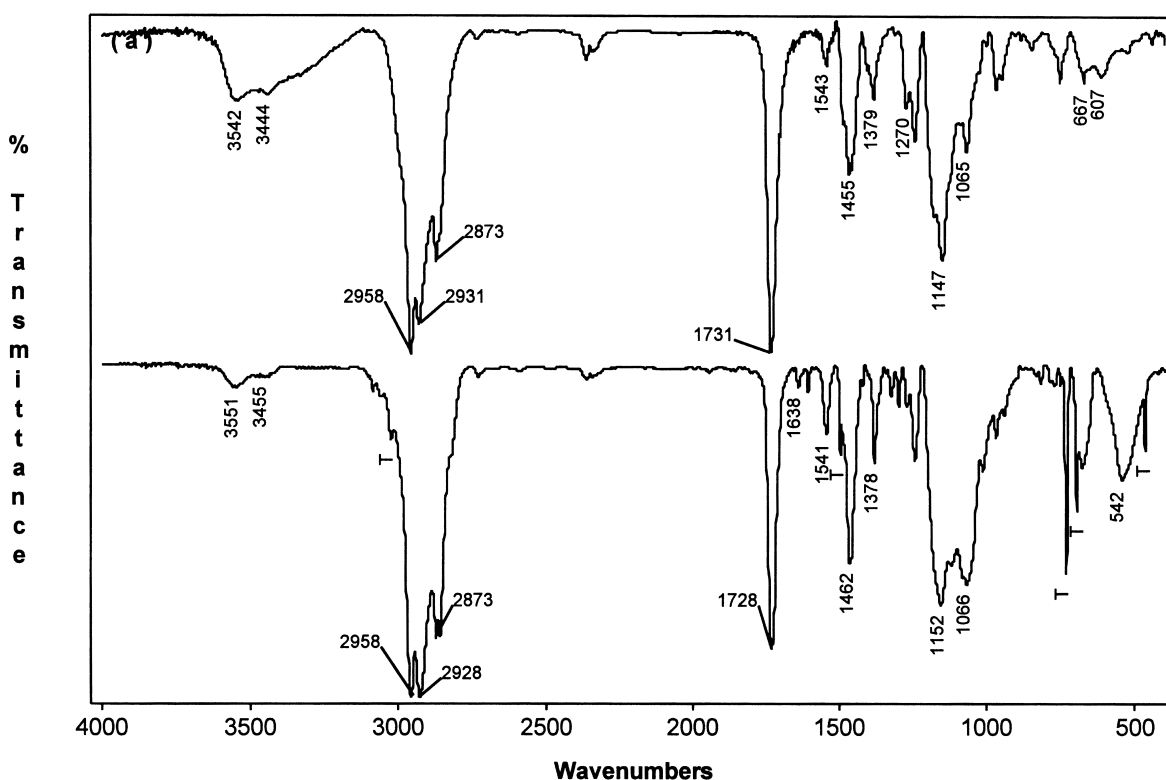


Figure 5 FTIR spectra of an esterified Elvacite (a) compared with a copolymerized mixture when a sufficient excess of Ti(OR)₄ was present (b). 'T' indicates some bands of the solvent (toluene)

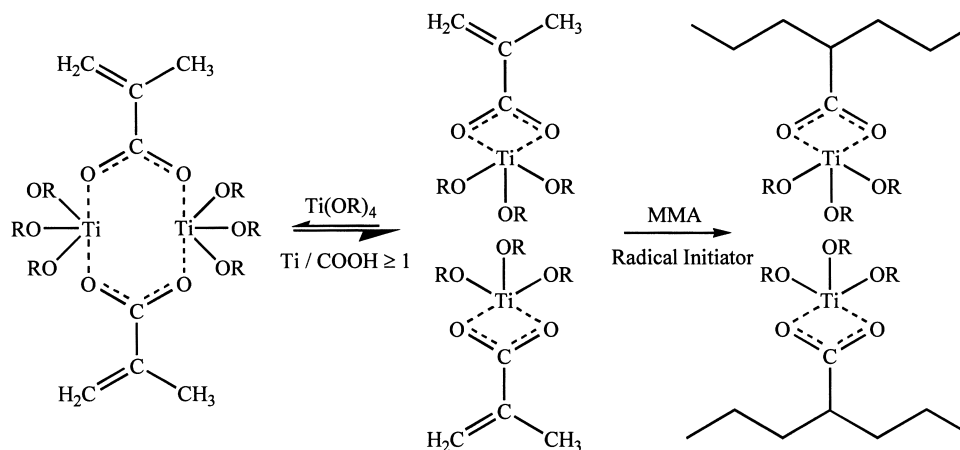


Figure 6 Prevention of the formation of bridged structures by the addition of a sufficient excess of Ti(OR)₄ before copolymerization with methyl methacrylate

The i.r. spectra of these copolymerized products displayed characteristic bonds of carboxylate ligands in a bidentate, chelating coordination mode (see *Figure 5b*). We deduced from this information that the structure responsible of the formation of a tridimensional network was not present at all in the mixture: when an excess of titanium tetraalkoxide was added to a methacrylate titanium trialkoxide, the latter gave with the former a non-bridged structure; when copolymerized with methyl methacrylate, such a structure gave rise to solutions, and the formation of gel was then prevented, as shown *Figure 6*.

CONCLUSION

The aim of our work was to prepare a new family of acrylic polymers containing organotitanium functions. The first possibility to obtain such polymers was to carry out the copolymerization of a methacrylate titanium trialkoxide with methyl methacrylate. The second way to get these polymers was to carry out the esterification of the acid functions of an available acrylic polymer by the use of titanium tetraalkoxide.

In these two ways, our experiments showed that the presence of an excess of titanium tetraalkoxide was an essential condition to obtain liquid products. We studied the progression of the smallest molar ratio Ti/COOH needed, which we called threshold, with the total solids (wt%). We made a comparison of the influence of the nature of the alkoxy groups on the value of the threshold. The length of the alkoxy chain was a deciding parameter for obtaining the non-bridged polymer chains: a titanium tetraalkoxide with a longer chain decreased the probability to form bridged species.

We noted that all the final products contained carboxylate ligands in a bidentate, chelating coordination mode. The formation of tridimensional networks when the molar ratio

Ti/COOH was a stoichiometric one could therefore be attributed to the presence of bridges made of bidentate, bridging carboxylate ligands.

The addition of an excess of titanium tetraalkoxide made possible the break of these bridges and favoured isolated structures in which the carboxylate ligands were in a bidentate, chelating coordination mode.

To summarize, we found a convenient way to get organotitanium acrylic polymers that could be of great interest for non-toxic self-polishing antifouling coatings, and for other applications.

ACKNOWLEDGEMENTS

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