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The use of NIR-FT-Raman spectroscopy for the characterization of polymer-supported reagents and catalysts

B. Altava, M. I. Burguete, E. García-Verdugo, S. V. Luis* and M. J. Vicent

Departamento de Química Inorgánica y Orgánica, E.S.T.C.E. Universitat Jaume I, E-12080 Castellón, Spain

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Abstract—The NIR-FT-Raman spectroscopy represents a very useful tool for the qualitative, semiquantitative and quantitative characterization of functional polymers being used for the preparation of resin-supported reagents and catalysts. This characterization is clearly complementary to the generally obtained using FT-IR techniques. The simplicity of the Raman sampling techniques makes them very suitable for the use with highly crosslinked, insoluble polymers and overcomes, many often, the limitations raised by the presence of polar functional groups. Even some polar functional groups such as the chloromethyl or thiol groups are easily analyzed using the FT-Raman spectroscopy. The use of this technique allows not only the analysis of the functional moieties present but also the appropriate characterization of the polymeric matrix in polystyrene–divinilbenzene resins. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

After the initial report by Merrifield on the solid phase synthesis (SPS) of peptides there has been a continuously growing interest in this field.[1] Since then a number of different applications have evolved such as the SPS of peptides,[2] oligonucleotides,[3] oligosacharides and other compounds,[4,5] the development of supported reagents and catalysts,[6,7] different environmental and biomedical applications,[8,9] and, finally, in last years, combinatorial chemistry.[10] The advantages of the use of insoluble functionalized polymers are generally associated with a simplification of the work-up, specially separation processes, the possibility of their recycling and reuse, the reduction of the environmental impact and the capacity of being used in continuous flow systems or in automated synthesis. Nevertheless, the use of insoluble funtionalized polymers in organic chemistry presents some disadvantages. Probably one of the most important ones is the rather limited range of analytical techniques available. NMR techniques are central today for the structural characterization of organic compounds and much effort has been concentrated on the development of appropriate gel-phase or solid-phase NMR techniques.[11,12] Those techniques present, however, some limitations which make difficult their general use. Accordingly, techniques such as elemental analysis,[13] chemical titration,[14] atomic absorption,[15] plasma analysis,[16] EDAX-semiquantitative analysis,[17] and IR spectroscopy, probably the most general technique up to now,[18] continue being mainly used to characterize the structures of the functional sites in polymeric reagents and catalysts, and there is a continuous need for the development of new analytical tools.

FT-Raman is a technique that provides structural information that is complementary to that obtained from FT-IR experiments.[19,20] Nevertheless, NIR-FT-Raman studies on functional polymers have been scarce up to now.[21,22] In general, it is considered that FT-IR is best suited for the characterization of supported species since many functional groups are polar and give place to the appearance of strong absorption bands in the IR. Accordingly, the presence or absence of those groups can be assessed, sometimes even quantitatively,[12a] by monitoring the corresponding bands. It has to be taken into account, however, that some of those groups show also bands in the Raman spectra, even if they are of lower intensity, and that some groups are more active in Raman than in IR. On the other hand, the nature of the sampling techniques for Raman spectroscopy makes it a no interfering and non-destructive technique very suited for the study of solid, insoluble materials.[20]

Additionally, the characteristics of some of the organic functional groups more active in Raman can provide a direct way for the study of the polymeric network that is acting as the support, in particular for PS–DVB resins that are the most used. This is an important aspect in the study of polymer-supported species, as many works have shown how the polymeric matrix can play an essential role in determining the final properties of the supported reagents and catalysts.[7d,23]

Here we present results that show how NIR-FT-Raman

Keywords: catalysts; infrared spectra; Raman spectra; polymer support; polymerization; supported reagents.

* Corresponding author. Tel.: +34-964-728239; fax: +34-964-728214; e-mail: luiss@qio.uji.es

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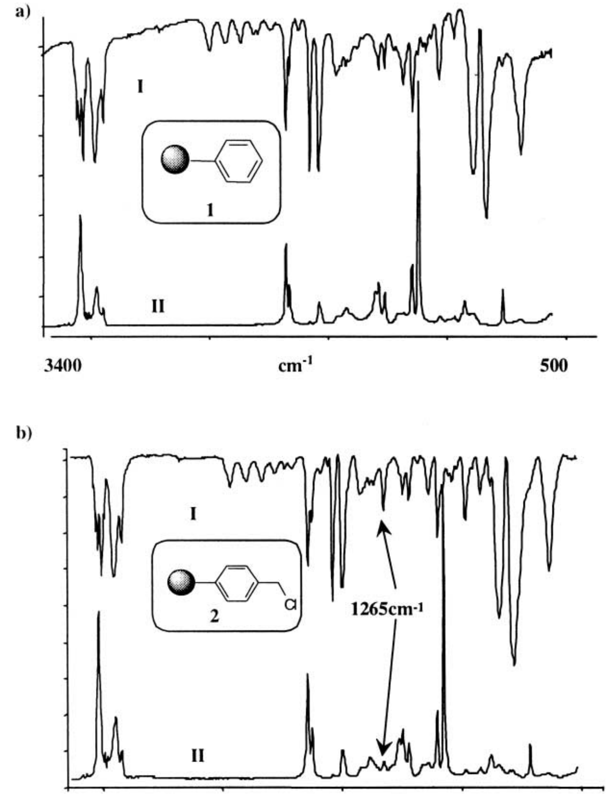


Figure 1. (a) FT-IR (I) and FT-Raman (II) spectra of a 1% crosslinked PS/DVB resin. (b) FT-IR (I) and FT-Raman (II) spectra of a 1% crosslinked Merrifield resin.

spectroscopy can become a very useful tool for the characterization of polymer-supported species.

2. Results and discussion

2.1. Qualitative analysis

One important advantage of NIR-FT-Raman spectroscopy is that no manipulation of the resins is needed for recording their spectra. It is a non-destructive technique that requires a minor amount of sample. At first, general observation is that moisture does not interfere in the Raman spectra whilst a strong interference occurs in the FT-IR. The Raman spectrum for PS–DVB (1% of crosslinking) is displayed in Fig. 1a (II) along with its FT-IR (I). The C_{sp2}–H stretching vibrations (3100–3000 cm^{-1}) appear as a single strong band in the FT-Raman instead of the triple band observed in the FT-IR. On the other hand, the aliphatic C_{sp3}–H stretching vibrations are of lower intensity. Two bands at ca. 1600 cm^{-1} are observed for the benzene skeleton vibrations, while distinct bands related to the benzene substitution patterns are observed in the 1300–600 cm^{-1} region (see Table 1). The more intense band is observed at 1001 cm^{-1} and corresponds to the vibrations of monosubstituted and *meta*-disubstituted benzenes.[19,28]

Table 1. Assignment of FT-Raman bands for substituted benzene rings[19]

Monosubstituted benzene	*para*-Disubstituted benzene
1620–1585 cm^{-1} (m)	1525–1480 cm^{-1} (vw)
1590–1565 cm^{-1} (m)	650–630 cm^{-1} (m)
1040–1016 cm^{-1} (m)	
1010–990 cm^{-1} (vs)	
630–605 cm^{-1} (m)	

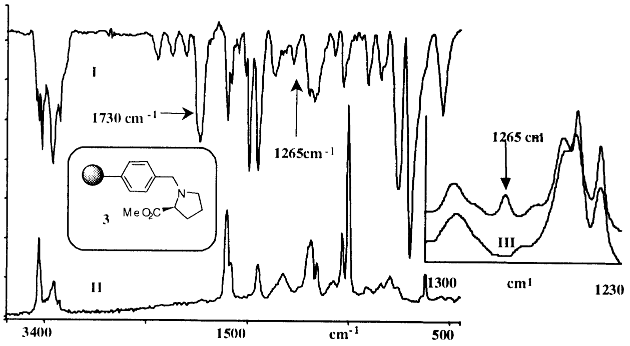


Figure 2. FT-IR (I) and FT-Raman (II) spectra of polymeric proline **3**. The inset shows an expansion in the 1230–1300 cm^{-1} region of the Raman spectra for resins **3** and **2**.

Fig. 1b shows the FT-IR (I) and the NIR-FT-Raman (II) spectra for a chloromethylated resin (**2**) (1% crosslinked, 1.1 mmol of Cl/g). As can be seen, even the presence of a polar group such as this can be detected in the FT-Raman spectrum using the weak band at 1265 cm^{-1} corresponding to the $-CH_2-$ 'wag vibration', as no other bands interfere in this region. Reactions on the Merrifield polymer can be monitored through the disappearance of the 1265 cm^{-1} band both at the FT-Raman and FT-IR spectra. Nevertheless, the presence of other bands that appear in this region precludes an accurate use of the FT-IR for this purpose. This is illustrated in Fig. 2 where the FT-IR and FT-Raman spectra of a polymeric proline derivative (**3**) are shown. This resin (**3**) was prepared by direct reaction of the proline methyl ester with polymer **2**.[23a,24] Complete substitution of the chloride was determined by elemental analysis and clearly corresponds with the complete disappearance of the band at 1265 cm^{-1} in the FT-Raman spectrum (see the expansion of the 1300–1100 cm^{-1} region in Fig. 2). On the contrary, a band, which must correspond to the new functional group, is observed in the FT-IR spectrum in this region. Even an assessment of the chloride content can be obtained by a direct observation of the intensity of this band. This is illustrated in Fig. 3 (a and c) that shows the 1300–1100 region of the NIR-FT-Raman spectra for commercial Merrifield resins with different chlorine contents. Fig. 3a displays the spectra for resins with a 1% DVB content and functionalization degrees of 0 (i), 1.19 (ii) and 1.60 (iii) mmol Cl/g. In Fig. 3c polymers with a 2% of DVB and functionalization degrees of 0 (i), 1.0 (ii), 2.1 (iii) and 4.3 (iv) mmol Cl/g are represented. The C–Cl band at 678 can also be observed in Fig. 3b and d.

In some instances, the functional groups introduced can be more active in Raman than in IR. This is the case of the preparation of the polymer-supported radical initiator (**4**) from a chloromethylated SMOP resin (poliethylene–polystyrene 3 mmol Cl/g).[25,26] The incorporation of the moiety containing the CN group is easily followed in the Raman spectrum through the appearance of the band at 2241 cm^{-1} and the disappearance of the chloride band at 1265 cm^{-1} (see Fig. 4a). Another example is given in Fig. 4b that

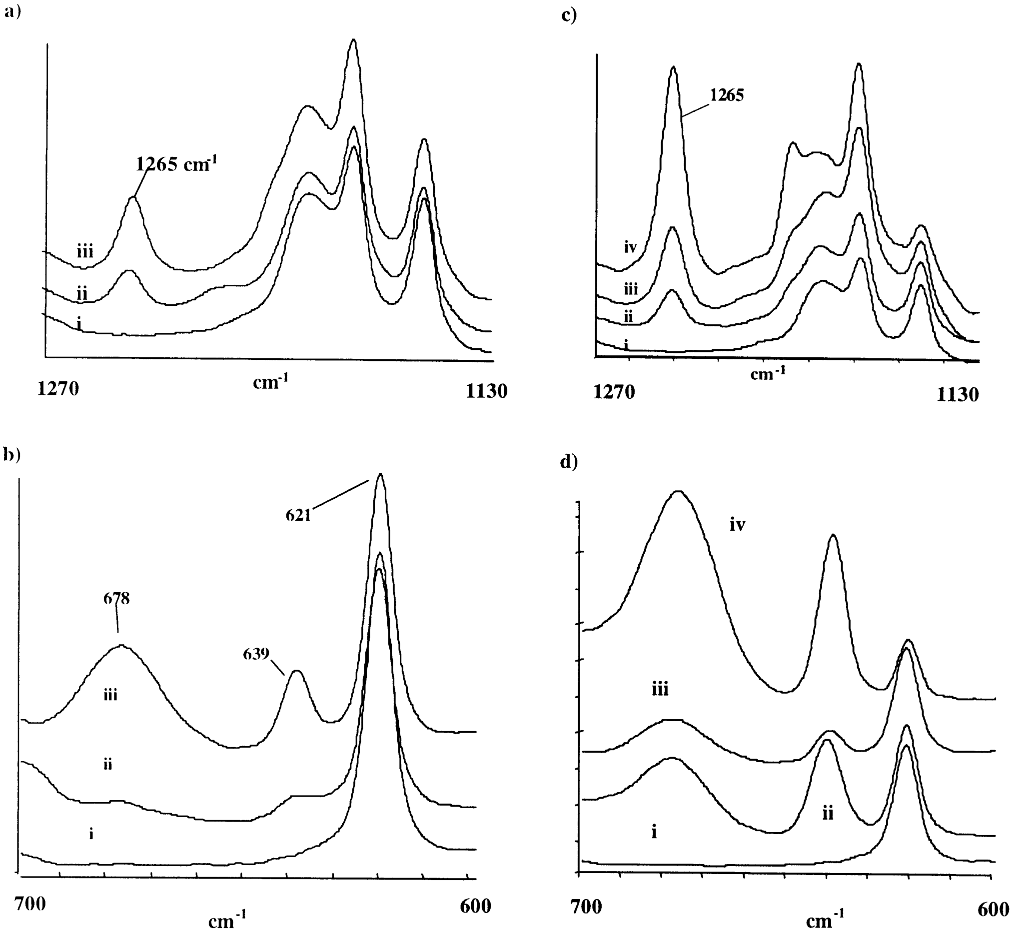


Figure 3. 1100–1300 cm^{-1} (a) and 600–700 cm^{-1} (b) regions of the FT-Raman spectra for different 1% crosslinked Merrifield resins: (i) PS–DVB used as a reference; (ii) 1.1 mmol Cl/g (iii) 1.6 mmol Cl/g. 1100–1300 cm^{-1} (c) and 600–700 cm^{-1} (d) regions of the FT-Raman spectra for different 2% crosslinked Merrifield resins. (i) PS–DVB used as a reference; (ii) 1.1 mmol Cl/g; (iii) 2.1 mmol Cl/g; (iv) 4.3 mmol Cl/g.

shows the NIR-FT-Raman spectrum of the polymeric tosyl hidrazone **5** prepared in several steps from resin **1**.[27] When compared with the starting material, the FT-Raman spectrum shows the expected features as are the increment of the intensity of the CH stretching bands, as well as of the band at 643 cm^{-1} corresponding to *para*-substituted benzenes. Additionally, the C═N band can be clearly observed at 1677 cm^{-1} whilst in the FT-IR this band is

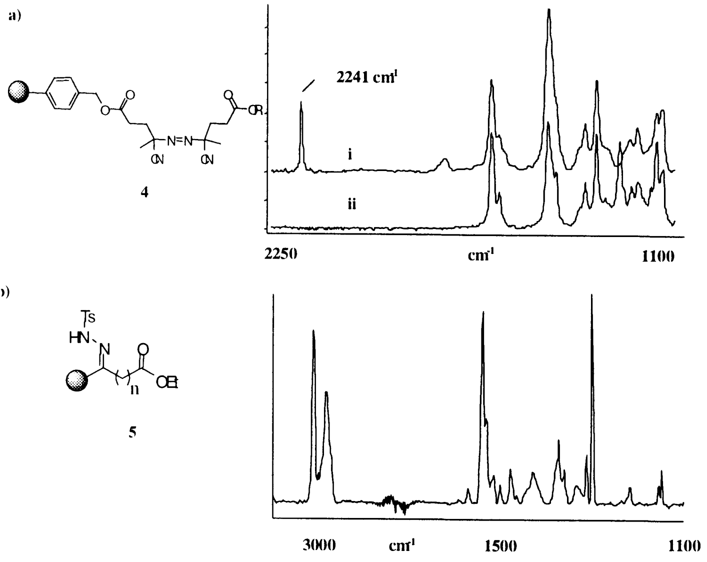


Figure 4. (a) FT-Raman spectra of a chloromethylated SMOP resin (3 mmol Cl/g) (ii) and after conversion into functional polymer **4** (i). (b) FT-Raman spectra of a 1% crosslinked resin functionalized with tosyl hydrazone groups **5**.

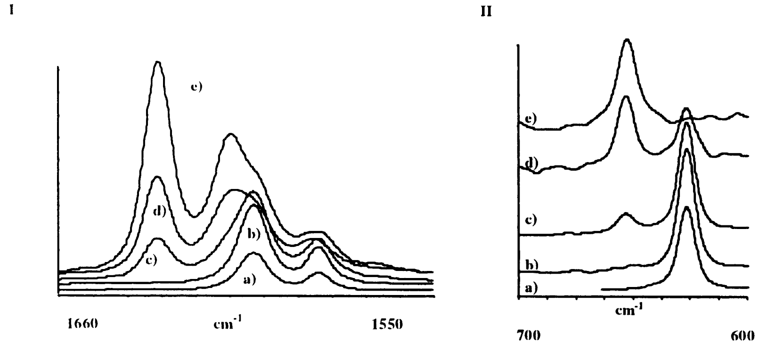
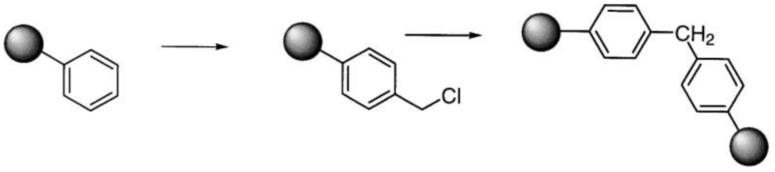


Figure 5. FT-Raman spectra (1660–1550 cm^{-1} and 700–600 cm^{-1} regions) of PS/DVB resins with different crosslinking degrees: (a) 1% DVB; (b) 2% DVB; (c) 20% DVB; (d) XAD-2 resin; (e) XAD-4 resin.



Scheme 1.

obscured by the presence of the strong C=O band of the ester group.

The usefulness of the FT-Raman spectroscopy is even clearer when the analysis of the matrix is considered. This analysis is necessary in order to understand the properties of polymer-supported reagents and catalysts and, in particular, some of the changes occurring upon immobilization. The presence of distinct bands for differently substituted benzenes (see Table 1) allows to distinguish the incorporation of aromatic rings with different substitution patterns and to study the crosslinking degrees of the polymers. The degree of crosslinking is always an essential structural factor that determines many of the macroscopic properties of the functional polymers.[23] The intensity of the bands corresponding to *para*-substituted benzenes (Table 1) can be used as a qualitative indication of the crosslinking degree for PS–DVB resins. Thus, for instance, Fig. 5 shows the 500–700 and the 1500–1700 cm^{-1} regions of the FT-Raman spectra for different commercial resins. The nominal DVB contents for those polymers are 2% (a), 20% (b), ca. 50% (XAD-2, c) and ca. 80% (XAD-4, d). As shown, the increase in the crosslinking degree is reflected in an increase of the intensity of the 645 cm^{-1} band (*para*-substitution) relative that of the 621 cm^{-1} band (*mono*-substitution). The increase of crosslinking is also reflected in the intensity of a band at 1631 cm^{-1}. This band corresponds to remaining vinyl groups from DVB monomers incorporated through only one vinyl moiety.[28] The use of those bands as a crosslinking indication must be used, however, carefully as commercial DVB samples contain both *meta* and *para* isomers.

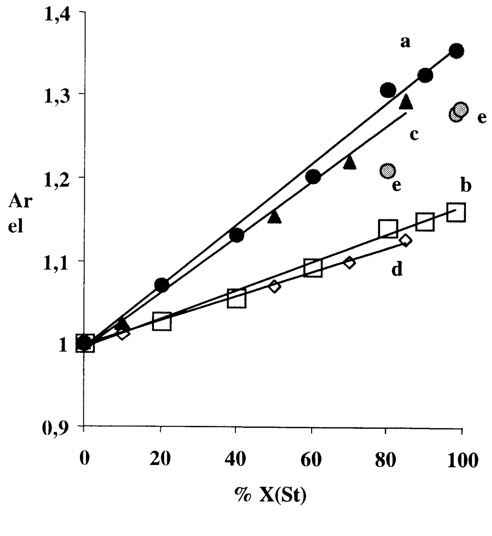
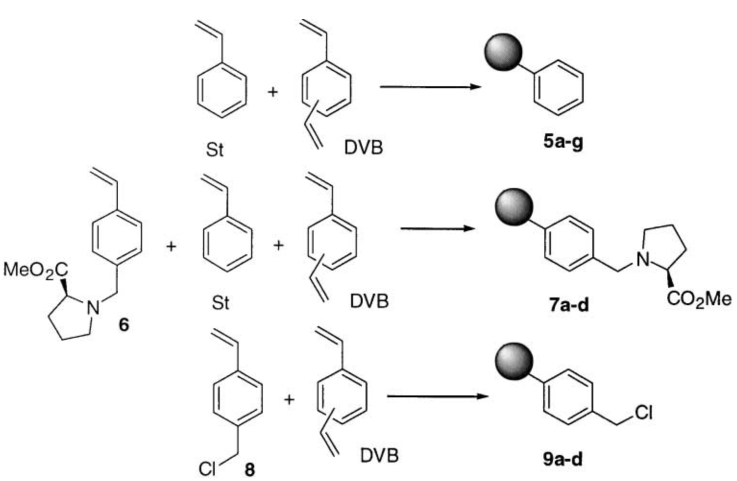


Figure 6. Correlation between the St content and the absorbance of bands at 1031 or 621 cm^{-1}, using the bands at 1270 (1135–1240 cm^{-1} region) for normalization. (a) PS–DVB ●: mol fraction of St vs $A_{1031+1270/1270}$ ($y = 3.708x + 0.995$, $r^2 = 0.995$). (b) PS–DVB □: mol fraction of St vs $A_{621+1270/1270}$ ($y = 1.740x + 0.994$, $r^2 = 0.998$). (c) PS–DVB ▲: mol fraction of St vs $A_{1031+1270/1270}$ ($y = 3.408x + 0.992$, $r^2 = 0.994$). (d) PS–DVB ◇: mol fraction of St vs $A_{621+1270/1270}$ ($y = 1.485x + 0.997$, $r^2 = 0.998$). (e) The values for some commercial PS–DVB resins are shown in shadowed circles for line a.

A simple analysis of the FT-Raman spectra of the chloromethylated resins is one of the more simple and fast methods to monitor how chloromethylation of the PS–DVB resins is very often accompanied by additional crosslinking (see Scheme 1). Thus, for resins with the same nominal crosslinking degree, the intensity of the band corresponding to *para*-dialkyl-substituted benzenes at 640 cm^{-1} clearly increases for higher functionalisation degrees (see Fig. 3b and d).[29]

2.2. Quantitative analysis

Quantitative analyses of functional polymers can also be carried out with the use of FT-Raman spectroscopy.[30] For that purpose, according to the general methodologies used in this field or in IR spectroscopy, best results were obtained when the normalized areas of the bands of interest are



Scheme 2.

Table 2. Composition of the monolithic polymers used for FT-Raman calibrations

Polymer	St		F.M.[a]	Porogenic mixture[b]		Yield (%)
	n_{VB}/n_t[c]	n_{DVB}/n_t[c]	$n_{M.F.}/n_t$[c]	Toluene	1-Dodecanol	
5a	90	10	–	10	50	>99
5b	80	20	–	10	50	>99
5c	60	40	–	10	50	>99
5d	40	60	–	10	50	>99
5e	20	80	–	10	50	>99
5f	10	90	–	10	50	>99
5g	–	100	–	10	50	>99
7a	10	80	10 (**6**)	10	50	>99
7b	20	70	10 (**6**)	10	50	>99
7c	50	40	10 (**6**)	10	50	>99
7d	70	20	10 (**6**)	10	50	>99
9a	–	90	10 (**8**)	10	50	>99
9b	–	50	50 (**8**)	10	50	>99
9c	–	60	40 (**8**)	10	50	>99
9d	–	10	90 (**8**)	10	50	>99

[a] F.M.=Functional monomer.

[b] % wt over the total.

[c] Molar ratios, $n_t = n_{VB} + n_{DVB} + n_{M.F.}$

considered instead of the intensities. In this way we have always used the following general equation:

$$(A_x + A_r)/A_r \tag{1}$$

where A_x is the area of the band considered as characteristic of the functional group to be determined and A_r is the area of the band that is used as a reference.

The simplest case we can consider is that of unfunctionalized PS–DVB polymers. As can be seen in Fig. 6 (a and b) a very good linear relationship ($r^2 > 0.99$) can be found for the vinylbenzene content and the absorbance at 1031 or 621 cm^{-1} in synthetic PS–DVB samples. Those polymers were prepared as monoliths by quantitative bulk polymerization (yields higher than 99%, see Scheme 2, Table 2) of mixtures of styrene (St) and commercial divinylbenzene (DVB).[31] In this case the bands for monosubstituted benzenes can be used for St while the 1130–1245 cm^{-1} region was used for normalization. The ability to analyze the polymeric monoliths without the need of any treatment of those materials further illustrates some of the advantages of the use of FT-Raman spectroscopy above mentioned. In the same figure, in gray, are collected some data obtained for commercial PS–DVB beads prepared by suspension polymerization, with nominal St contents of 99, 98, and 80%. The expected general trends are observed for those commercial materials, but important deviations are observed in some instances. For resins with low nominal St contents, the crosslinking degrees calculated according to our method are significantly higher. There could be differences in how the nominal crosslinking degrees are calculated or defined, but this could not account for such differences. The preferential incorporation of DVB into the beads formed through suspension polymerization can be responsible for the differences found. In the field of functional polymers it is very often considered, unfortunately, that the composition of the final resin always reflects the initial monomeric composition, even in polymerizations for which yields are not quantitative. This has not to be, obviously, the case, and this consideration just reflects the lack of simple, accessible analytical techniques for a complete characterization of functional polymers and highlights the utility that FT-Raman techniques can provide for

Table 3. Experimental and calculated compositions for proline derived resins **7**

Entry		St (% molar)	DVB (% molar)	**6** (% molar)	% N	Loading (mmol/g)
1	**7e**[a]	70	20	10	1.16	0.83
2	HP1[b]	40	40	20	2.30	1.64
3	HP2[c]	62.2	17.8	20	2.30	1.64
4	**7e**[d]	60.3	19.7	20	2.30	1.64
5	**7f**[e]	70	20	10	1.60	1.14
6	**7f**[d]	61.6	24.9	13.5	1.60	1.14

[a] Composition of the monomeric mixture. Yield for the suspension polymerization: 60%.
[b] Calculated composition of the polymer considering the preferential incorporation of DVB.
[c] Calculated composition of the polymer considering that the St/DVB ratio in the resin is the same as the one employed for the monomeric mixture.
[d] Calculated composition from FT-Raman and elemental analysis.
[e] Composition of the monomeric mixture. Yield for the suspension polymerization: 83%.

this purpose. In the case of highly crosslinked polymers, the use of FT-Raman seems to suggest the presence of VB, even in very minor amounts, for XAD-4. The detection of this component had not been possible using other techniques.[28a]

A good linear relationship was also observed, in our synthetic resins, for the DVB content. However, attempts to correlate, using this methodology, the DVB contents of synthetic and commercial PS–DVB resins were less successful. This had to be expected because of the complex monomeric composition of commercial DVB and the changes in composition that can occur as a consequence of the purification protocol. The possible incorporation of DVB in the polymeric matrix through one or two of the vinyl group, further increased the complexity for this component.[28]

According to the former considerations, the St content can be easily determined in PS–DVB resins by FT-Raman and this technique can be also applied for resins containing other functional monomers. Fig. 6 (c and d) shows the results obtained using the same methodology for polymers prepared by quantitative bulk polymerization of St, DVB and *N*-(4-vinylbenzyl) proline methyl ester (see Scheme 2 and Table 2), a class of materials that have been shown to be of great interest for the preparation of supported chiral catalysts.[23a,24] As can be seen, a very reasonable agreement is observed, and the same equation can be essentially used for the calculation of the St content. This is necessary for the calculation of the crosslinking degrees in polymers of this class for which the polymerization yields were not quantitative. It is worthy to mention here, again, that in the preparation of polymer-supported chiral catalysts the nature and degree of crosslinking are key factors in determining their activity and selectivity.

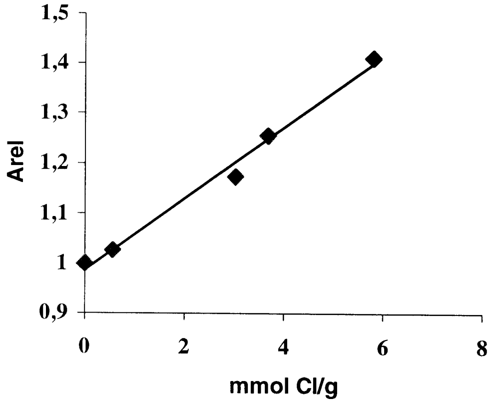


Figure 7. Correlation between the chlorine content and the absorbance of the C–Cl band at 1265 cm^{-1}, using the bands in the 1135–1240 cm^{-1} region for normalization. ($y = 0.072x + 0.993$, $r^2 = 0.989$).

This is clearly exemplified by the results obtained for polymers containing proline functionalities **7** prepared by suspension polymerisation of the corresponding monomers. Thus, for instance, when a composition of 70% of St, 20% of DVB and 10% of **6** (molar ratios) was used as the monomeric mixture and a 3% (w/w relative to the monomers) of AIBN was introduced as the initiator, a 60% yield of the corresponding functionalized polymer was obtained. Elemental analyses of this material showed a high nitrogen content relative to that expected from the monomeric composition. Combustion analysis gave a content of 2.3% of nitrogen that corresponds to a loading of 1.64 mmol/g instead of the theoretically calculated value of 0.83 mmol/g (1.16% theoretical nitrogen content). This reveals a preferential incorporation of the monomer **6** into the polymeric skeleton. Nevertheless, the elemental analysis does not allow in knowing the St/DVB ratio in the polymer. Several compositions can be adjusted to those values, two of which are represented in Table 3. The first hypothesis (HP1) considers the preferential incorporation of DVB, whilst the second one (HP2) considers that the St/DVB ratio is the same present at the monomeric mixture. Obviously, the crosslinking degrees, and so the properties, of both polymers should be very different. The use of the FT-Raman allows to solve this question very easily. The St content of this polymer calculated using the absorption at 1031 cm^{-1} and the parameters obtained using the data from Fig. 6c (St, DVB, 4-vinylproline polymers), was 60.3%, similar to the value calculated using the absorption at 621 cm^{-1} (60.1%). Rather interestingly, those values are quite close to those calculated using directly the parameters obtained from simple St/DVB resins. Thus, for instance, using the equation calculated from data shown in Fig. 6a, a value of 55% St was obtained. Taking into account the systematic errors that can be associated to this kind of techniques, the difference observed is not very high and suggests that for a rapid semi-quantitative analysis of the St content in functionalized PS/DVB resins the most simple correlations obtained for unfunctionalized resins can be used.

A second example is given in entries 5 and 6 of Table 3. Starting from the same monomeric composition as before

Table 4. Determination of chlorine content in commercial Merrifield resins by FT-Raman

Entry	C.D. (%)[a]	Loading Cl (mmol Cl/g)	Loading (mmol Cl/g)[b]
1	1	1.19[c]	1.12
2	1	≈1.60[d]	1.4
3	2	≈1.00[d]	1.4
4	2	≈4.30[d]	4.5
5	2	≈2.10[d]	1.9

[a] C.D.=Cross-linking degree.
[b] Loading calculated using FT-Raman.
[c] Exact loading of the Merrifield resin gave by manufacturer.
[d] Nominal loading of the Merrifield resin given by manufactures without analysis of the individual batch. According to manufacturer's instructions the nominal Cl content given for resin in entry 3 is only very approximate.

(70% St, 20% DVB, 10% **6**) and using a 6% of AIBN as the initiator, an 83% yield of resin **7** was obtained. Using the data obtained from elemental analysis and FT-Raman, the composition shown in Table 3 (entry 6) could be calculated. This composition shows that an essentially complete incorporation of **6** and DVB occurs in the formation of this polymer.

The quantitative analysis of chloromethylated resins provides another clear example of the utility of FT-Raman techniques for the rapid, simple and non-destructive analysis of this kind of materials. Using the general methodology as before, several monolithic chloromethylated polymers were prepared quantitatively starting from monomeric mixtures having different DVB/**8** ratios (see Scheme 2, Table 2).

Fig. 7 shows the existence of a very good correlation between the chlorine content and the absorbance of the C–Cl band at 1265 cm^{-1}, using the bands in the 1135–1240 cm^{-1} region for normalization. This allows the calculation of the chloromethyl functionalization in unknown samples in a fast way. Some results are gathered in Table 4 for commercial Merrifield resins whose nominal loadings are also given. A very good agreement is observed, in particular if we take into account the very approximate values of the nominal loadings usually given by the manufactures. As can be seen in the entry 1, the agreement is much better when the actual value of the loading is known.

3. Conclusions

In summary, the present results reveal that FT-Raman techniques are a very powerful tool for the analysis of polymer-supported reagents and catalysts. In particular, FT-Raman spectroscopy provides a non-destructive non-interfering method for the simple and rapid analysis of the functionalized polymers. Data obtained from this technique can give valuable information no only on the functional group present but also on the nature of the polymeric matrix of the support. Both, the functional group and the polymeric network play a key role in determining the final properties of the supported species and have to be analyzed in detail in order to understand those properties. Qualitative, semi-quantitative and quantitative analysis can be obtained using data from FT-Raman spectra. The simplicity of the FT-Raman spectroscopy and spectra facilitates the quantitative use of this technique for materials such as those considered in the present work. In general, very good lineal relationships can be found when selecting the appropriate bands for the groups under study and for reference purposes. According to the former, FT-Raman spectroscopy should become a routine technique for the study of polymer-supported reagents and catalysts.

4. Experimental

4.1. General polymerization procedure to obtain polymers 5a–d

Polymerisation mixture: Azobisisobutyronitrile (1 wt% relative to the monomers) was dissolved in 4 wt parts of a mixture consisting of styrene (St) and divinylbenzene (DVB), using the molar ratios shown in Table 2. The porogenic solvents, a mixture of toluene/1-dodecanol (1:5), were admixed slowly to the monomers. The total weight of the porogenic mixture was 6 parts. A glass mould was filled with the polymerization mixture, purged with nitrogen in order to remove the oxygen and placed in a vertical position into a water bath. The polymerization was allowed to proceed for 24 h at 80°C. The resulting monolithic polymer was washed with THF in a soxhlet to remove the porogenic solvents and any other soluble compounds that remained into the polymer to obtain. **5a–d** in almost quantitative yields for the different polymeric mixtures.

4.2. General polymerization procedure to obtain polymers 7a–d

Polymerisation mixture: Azobisisobutyronitrile (1 wt% relative to the monomers) was dissolved in 4 wt parts of a mixture consisting of styrene (St), crosslinker agent DVB and monomer **6** using the molar ratios shown in Table 2. The porogenic solvents, a mixture of toluene/1-dodecanol (1:5), were admixed slowly to the monomers. The total weight of the porogenic mixture was 6 parts. A glass mould was filled with the polymerization mixture, purged with nitrogen in order to remove the oxygen and placed in a vertical position into a water bath. The polymerization was allowed to proceed for 24 h at 80°C. The resulting polymer was washed with THF in a soxhlet to remove the porogenic solvents and any other soluble compounds that remained into the polymer to obtain **7a–d** in quantitative yields for the different polymeric mixtures. IR (KBr): peak present at 1737 cm^{-1}.

4.3. Polymerisation procedure to obtain polymer 7e

A solution of monomer **6** (722 mg, 2.39 mmol), styrene (2.05 g, 19.7 mmol), divinylbenzene (80% solution of DVB in ethylvinylbenzene, 903 mg, 5.56 mmol), and AIBN (208 mg) in benzene (CAUTION) (20 mL) and THF (20 mL) was added to a well stirred solution of poly-(vinylalcohol) (1 g) in water (100 mL) in a three-necked flask, equipped with a thermometer, condenser and a mechanical stirrer, under an Ar atmosphere. The poly(vinylalcohol) solution was prepared by stirring the initially formed suspension at 50°C and filtering off the insoluble parts. After stirring for 1 h at 0°C (ice-bath) to homogenize the suspension, the apparatus was placed into a heat-bath at 80°C, and the suspension was stirred for 24 h. The resulting polymer beads were washed with THF in a Soxhlet and dried (vacuum. 60–70°C) to give the polymer **7e** in 60% yield. IR (KBr): peak present at 1737 cm^{-1}. Anal. calcd for $[(C_{10}H_{10})_{0.20}(C_8H_8)_{0.70}(C_{15}H_{19}O_2N)_{0.10}]$: N, 1.2; found N, 2.3; loading: 1.64 mmol/g.

4.4. Polymerization procedure to obtain polymer 7f

7f was prepared as it is described above but using AIBN (6% of the monomer weight) as initiator to give the polymer **7f**. 82% yield. IR (KBr): peak at 1737 cm^{-1}. Anal. calcd for $[(C_{10}H_{10})_{0.20}(C_8H_8)_{0.70}(C_{15}H_{19}O_2N)_{0.10}]$: N, 1.2 found N, 1.6; loading: 1.14 mmol/g.

4.5. General polymerization procedure to obtain polymers 9a–d

Azobisisobutyronitrile (1 wt% relative to the monomers) was dissolved in 4 wt parts of a mixture consisting of 4-cloromethylbenzene and DVB (using the molar ratios shown in Table 2). The porogenic solvents, a mixture of toluene/1-dodecanol (1:5), were admixed slowly to the monomers. The total weight of the porogenic mixture was 6 parts. A glass mould was filled with the polymerization mixture, purged with nitrogen in order to remove the oxygen and placed in a vertical position into a water bath. The polymerization was allowed to proceed for 24 h at 80°C. The resulting polymeric monolith was washed with THF in a soxhlet to remove the porogenic solvents and any other soluble compounds that remained into the polymer to obtain **9a–d** in almost quantitative yields.

4.6. General procedure for FT-Raman measurements

FT-Raman spectra were obtained using a FT-IR, NIR-FT-Raman Perkin–Elmer Spectrum 2000 instrument equipped with a diode pumped Nd:YAG laser PSU and using the standard Spectrum v2.0 software. The samples of the polymers were analyzed with no previous treatment using different Raman holders according to the physical nature of the resins. The localization of the sample was manually adjusted, for each case, in order to obtain the maximum intensity for a laser power of 710 mW. In all cases the resolution was adjusted to 0.1 cm^{-1} and four scans were accumulated for organic polymers.

For quantitative measurements several bands characteristic for the group being studied were analyzed, if possible, in each case, being selected the one giving more reproducible results. In general, for reference purposes, the absorbance of a given region was always used instead of individual bands, as, in this way, much better correlations were obtained. Best results were achieved when the absorbance of the region from 1240 to 1135 cm^{-1} was used as the reference for PS–DVB polymers.

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