Functionalization of montmorillonite by methyl methacrylate polymers containing side-chain ammonium cations

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Non-extractable poly(methyl methacrylate) (PMMA)–montmorillonite adducts were prepared by two distinct processes: (a) In the first method, free-radical copolymerization of MMA with clay previously treated with 2-(*N*-methyl-*N*,*N*-diethylammonium iodide) ethyl acrylate (QD1) or 2-(*N*-butyl-*N*,*N*-diethylammonium bromide) ethyl acrylate (QD4) was performed. (b) The second method was based on the direct interaction of montmorillonite with various copolymers of MMA with QD1 or QD4. The structure of the adducts as determined by Fourier-transform infra-red spectroscopy, thermogravimetric analysis and X-ray diffraction was shown to consist of the insertion of MMA macromolecules between lamellar layers whose separation was consequently higher than in the polymer-free clay. The polymer was strongly fixed to the inorganic surfaces, probably due to cooperative formation of electrostatic bonding. The thermal stability of the organic polymers was substantially enhanced in the adducts.

(Keywords: montmorillonite; methyl methacrylate polymers; functionalization)

INTRODUCTION

Several layer silicates undergo cation-exchange reactions connected with the presence of negative charges arising from isomorphous replacement of Si^{4+} with Al^{3+} in the tetrahedral lattice and of Al^{3+} with Mg^{2+} in the octahedral arrangement[1,2]. These negative charges are balanced in general by alkaline or alkaline-earth ions disposed on the free external and internal surfaces. The easy penetration of solutions into the expandable lamellar clay structure allows a rapid exchange of these cations.

The surface of clays and inorganic mineral fillers, in general, is hydrophilic, and this impedes their dispersion in, and rapid wetting by, the organic phase. The compatibility of the mineral with the organic phase, in terms of wetting and dispersion, may be substantially increased by the prior adsorption of a monolayer of a suitable organic substance over the particle surfaces or by the covalent addition of some simple organic compounds to the reactive surface groups of the mineral.

In order to make a hydrophobic clay surface, mixing with organic compounds[3–5] or absorption of organic compounds on the surface itself[6,7] have been attempted. Physical (van der Waals) attraction plays a prominent part in the adhesion, although chemical interactions and bridging of the clay surface to the polymer network are also involved. However, these systems suffer from easy leaching of the organic component, which is very weakly fixed on the inorganic matrix; the adsorbed layer (coat) may be displaced by solvents or during compounding. Examples of these systems are the complexes produced by polymerizing methyl methacrylate (MMA) in the presence of montmorillonite[8–10] or by intercalation with ε-caprolactam, which was successively polymerized to give a nylon-6–clay hybrid[11].

A most effective method of achieving compatibility and hence strong bonding between filler and polymer matrix is to use minerals and clays onto whose surface a suitable polymeric species has previously been grafted [12,13]. Grafting normally implies that the polymer is attached to the mineral by primary (covalent) bonds. However, secondary interactions (van der Waals or hydrogen bonds) may also lead to extremely strong bonding between polymer and solid surface. For this reason and because, in many instances, some homopolymer is formed concurrently, the occurrence of 'true' grafting is often difficult to demonstrate directly.

Alternatively, stable hydrophobic clays can be prepared by replacing part or all of the exchangeable cations with small organic cations or polycations.

Accordingly in the present investigation the following two procedures were used to prepare better defined polymer–clay complexes with real chemical bonds between the two materials: (a) Functionalization of alkaline montmorillonite with monomers QD1 (2-(*N*-methyl-*N*,*N*-diethylammonium iodide) ethyl acrylate) or QD4

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(2-(*N*-butyl-*N*,*N*-diethylammonium bromide) ethyl acrylate), followed by *in situ* copolymerization of MMA initiated by free radicals (*Figure 1*). (b) Interactions of alkaline montmorillonite with cationic PMMA prepared by free-radical copolymerization of MMA with QD1 or QD4 (*Figure 2*).

Treatment of the resulting products with boiling acetonitrile in continuous extractors (Kumagawa) allowed removal of unattached organic polymer fractions. The residue was constituted of real clay–polymer complexes with up to 35.9% (*Table 2*) by weight of organic polymer, arranged in interlamellar layers of the silicate.

EXPERIMENTAL

Bentonite BP 100 (Industria C. Laviosa Chimica Mineraria) had a content of montmorillonite of 90% and a cationic (Na^+) exchange power of 100 mEq/100 g.

Quaternary ammonium salt monomers QD1 and QD4 have been synthesized respectively by reaction of methyl iodide and n-butyl bromide with 2-(*N*,*N*-diethylamino) ethyl acrylate (Fluka) as reported in the literature[14].

Preparation and copolymerization of functionalized montmorillonite

A controlled amount of Na^+ cations on the lamellar surface was exchanged by reaction of an aqueous montmorillonite suspension with an aqueous solution of the quaternary ammonium salt monomers QD1 and QD4, at 80°C for 6 h. The reaction product was filtered and dried in an oven under vacuum at 80°C. The dry product was ball milled and purified by solvent extraction with boiling acetonitrile for 8 h in a Kumagawa extractor[15]. The yield and the quaternary ammonium salt monomer content of functionalized montmorillonite were determined by t.g.a.

Functionalized montmorillonite samples were copolymerized with different amounts of MMA in the presence of α,α'-azobisisobutyronitrile (AIBN) as radical initiator, in bulk or in acetonitrile solution at 60°C for 72 h (*Tables 1* and *2*). After reaction, the polymerization product was poured into a large excess of diethyl ether, filtered, dried under vacuum and successively purified by solvent extraction with boiling acetonitrile for 8 h in a Kumagawa extractor.

Copolymerization of MMA/quaternary ammonium salt monomers

MMA and the quaternary ammonium salt monomers QD1 and QD4 were copolymerized with different feed compositions, in the presence of α,α'-azobisisobutyronitrile as radical initiator, in acetonitrile solution at 60°C for 72 h. After reaction, the polymerization product was poured into a large excess of diethyl ether, filtered and dried under vacuum. The yield and the quaternary ammonium salt monomer content in the copolymers were determined by ^1H n.m.r. (*Table 3*).

Montmorillonite interaction with copolymers of MMA/quaternary ammonium salt monomers

Suitable amounts of the copolymers of MMA/quaternary ammonium salt monomers dissolved in a water/acetonitrile mixture were added to a montmorillonite suspension in the same solvent mixture at 80°C for 6 h. The reaction products were recovered by filtration, dried under vacuum and successively purified by solvent extraction with boiling acetonitrile for 8 h in a Kumagawa extractor. The data concerning these samples are reported in *Table 4*.

MEASUREMENTS

*FT*i.r. spectra were recorded in the range of 4000–400 cm^{-1} using a Perkin–Elmer spectrophotometer (model 1760) connected with an infra-red database (model 3600). The montmorillonite–polymer complexes examined were obtained by potassium bromide pressed disc.

^1H n.m.r. spectra of the MMA/QD copolymers were obtained at 200 MHz on a Varian Gemini 200 spectrometer using 5–10 wt% chloroform polymer solutions in 5 mm tubes and in the presence of tetramethylsilane (TMS).

For X-ray analysis, a Guinier focusing camera using a quartz crystal monochromator in a Philips PW-1840 X-ray crystallographic unit, fitted with a copper target, was used (40 kV, 20 mA, entrance slit 0.2 nm) for recording X-ray data in the range of $2\theta = 2$–32° (the samples were dried in vacuum at 90°C overnight).

Molecular weights of MMA/QD copolymers were determined by g.p.c. using chloroform as solvent with a Perkin–Elmer h.p.l.c. chromatograph (model 2/2) with u.v. and r.i. detectors. The number-average molecular weights were determined also by vapour-pressure osmometry using chloroform as solvent, at 40°C, with a Gonotec Osmomat 070 osmometer.

Thermogravimetric measurements were carried out on a Mettler TG 50 thermobalance, constituted by a microbalance and a base with the furnace controlled by a TA processor TC 11, connected to an MS-DOS computer. This instrument simultaneously measured the temperature *T*, the change in weight and the rate of weight change. The samples were heated in an oven according to a predetermined programme, ensuring a linear dependence of temperature on time. The heating rate was 10 K min^{-1} and the range investigated was 323–1123 K. The substances under investigation and references were placed in alumina crucibles. The sample size was chosen in such a manner that the weight loss during experiments did not exceed 20 mg.

RESULTS AND DISCUSSION

Polymerization of MMA in the presence of montmorillonite functionalized with QD1 or QD4

Montmorillonite was functionalized by treatment with acrylate monomers having quaternary ammonium groups (QD1 or QD4). The non-bonded organic material was removed by extraction with boiling acetonitrile and the residual organic content determined by t.g.a.

The fraction of active sites reacted with the acrylic ammonium salt increased by increasing the starting amount of the latter (*Table 1*), but even with an excess of 4:1 only 58% of sites were involved. This can be in part attributed to the bulkiness of the ammonium salt and to the limited accessibility of some sites in the inorganic lamellar structure. Diffusion limitations arising from the increasing hydrophobic character of the surface should also be taken into account. However, the similar behaviour of QD1 (methyl group on $-NR_3^+$) and QD4 (butyl group on $-NR_3^+$) favours the hypothesis of very low accessibility of some sites and of kinetics that slows down with increasing functionalization.

In order to use the acrylic species attached to the montmorillonite surface as binding points, MMA was polymerized by AIBN in a suspension of the functionalized montmorillonite (*Figure 1*). Again the unattached polymer was removed by CH_3CN extraction and the organic residue weight determined by t.g.a.

The low functionalized inorganic matrix (0.5BQD1M) gave a lowest loading by the polymer formed in spite of the largest MMA/QD1 ratio; in the other cases similar amounts of PMMA formation were observed. A

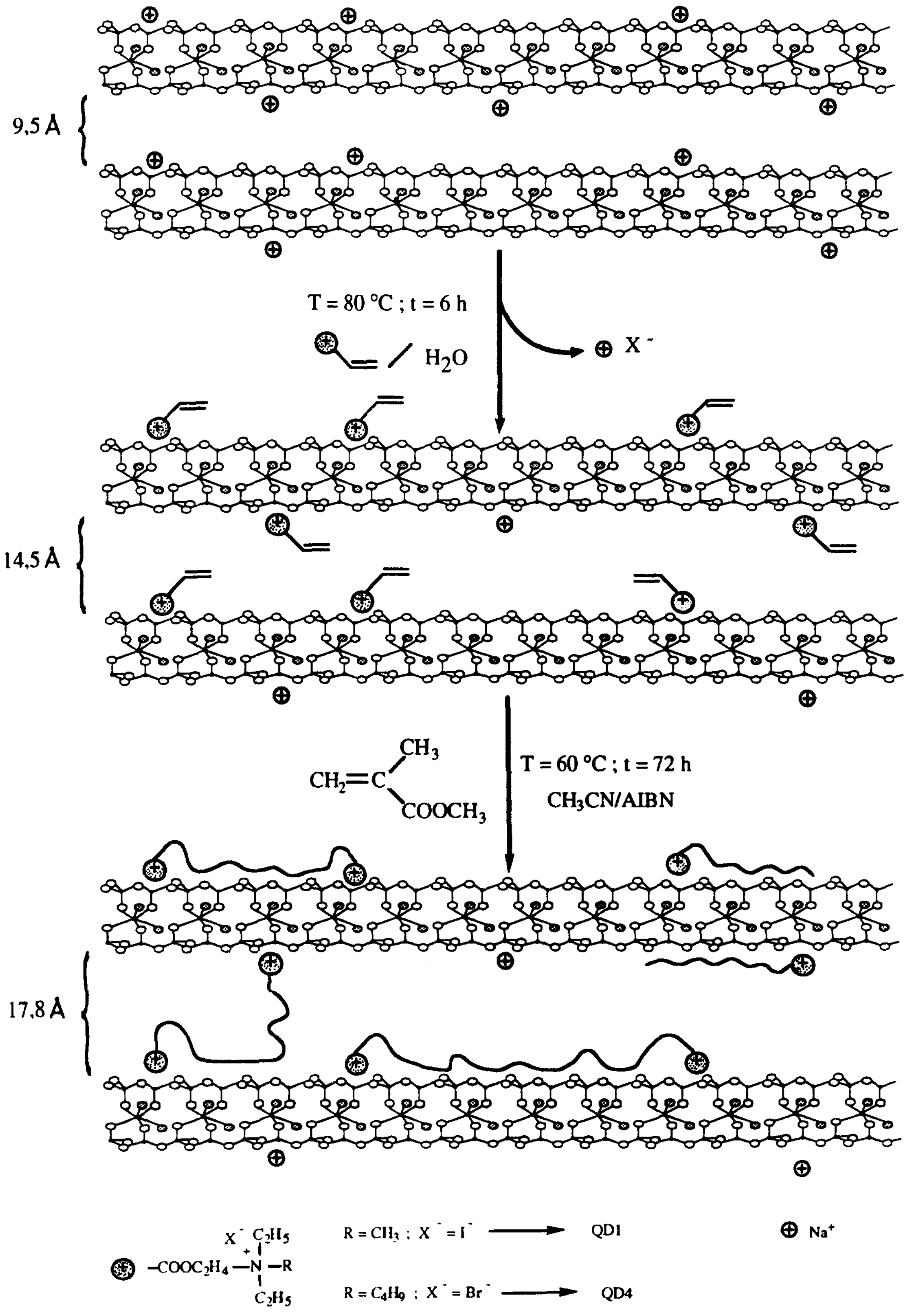

Figure 1 Schematic representation of polymerization of MMA in the presence of montmorillonite functionalized with QD1 or QD4

substantial increase of the latter was, however, observed when carrying out copolymerization experiments in bulk with neat MMA (*Table 2*). By assuming that all QD1 or QD4 units in the montmorillonite took part in the copolymerization, the average length of PMMA blocks between two binding groups was in the range 1.1–8.2, values larger than 3.5 being obtained only by bulk polymerization (*Table 2*). This result can be attributed to the high loading of QD molecules on the surface where copolymerization mainly takes place.

Table 1 Functionalization of montmorillonite by acrylic monomers with quaternary ammonium groups

			Complex	
Sample	Monomer	Reaction ratio[a]	QD1 or QD4 (wt%)	Active sites reacted (%)[b]
0.5BQD1	QD1	2	5.1	29
BQD1		1	8.4	49
2BQD1		0.5	8.4	49
4BQD1		0.25	9.7	58
BQD4	QD4	1	9.8	47
2BQD4		0.5	10.1	49

[a] Starting molar ratio between anionic active sites on the montmorillonite surface (cationic exchange capacity, 100 mEq/100 g) and ammonium groups, i.e. montmorillonite active sites/QD1 or QD4 units

[b] Fraction of active sites exchanged with QD1 or QD4

Table 2 Copolymerization of MMA with QD1- or QD4-modified montmorillonite[a]

	QD1 or QD4 reaction ratio		Complex	
				MMA[e]
Sample[b]	(wt%)	(MMA/QD)	Polymer[d] (wt%)	QD1 or QD4
0.5BQD1M	5.1	33	8.0	1.1
BQD1M	8.4	21	17.2	2.2
2BQD1M	8.4	20	17.4	2.3
4BQD1M	9.7	17	20.1	2.4
BQD1M/ms[c]	8.4	20	35.9	8.2
BQD4M	9.8	21	16.8	1.9
2BQD4M	10.1	20	22.8	3.5
BQD4M/ms[c]	9.8	21	26.9	5.0

[a] AIBN, 60°C for 72 h in CH_3CN

[b] See also *Table 1* for symbols

[c] Without CH_3CN as solvent

[d] After extraction with CH_3CN

[e] Determined by difference

Comparison with the copolymerization experiments carried out in solution with the uncomplexed ammonium salt (*Table 3*) shows that the copolymerization is controlled by the inorganic matrix in favour of the ammonium salt. Thus this preparative method seems to be unable to provide a high loading, while giving a uniform coating of the matrix surface.

Complexation of montmorillonite with preformed MMA/QD1 or QD4 copolymers

The MMA/QD copolymers with quaternary ammonium groups in the side chains from 33 to 1 mol% were reacted with Na montmorillonite at room temperature in H_2O/CH_3CN mixture (*Figure 2*). After drying, the mixture was extracted with boiling CH_3CN and the amount of organic material bonded to the matrix determined by t.g.a. (*Table 4*).

It is of interest to note that, in the case of a similar mixture prepared with PMMA not containing $-NR_3^+$ groups, practically the whole polymer could be extracted under the above conditions.

While the CH_3CN alone already allows an appreciable incorporation of MMA/QD copolymer in the inorganic matrix, addition of H_2O up to 20% gives a substantial increase and a saturation value is reached; thus additional water produces only a very modest increase (*Figure 3*). This effect can be attributed to the swelling capacity towards the montmorillonite with consequent expansion of the interlamellar distance allowing the insertion of a larger amount of organic polymer and favouring also the interchange between Na^+ cations and the quaternary ammonium groups.

The content of organic loading decreases with increasing content of $-NR_3^+$ groups in the copolymer (that is by decreasing the MMA/QD ratio); such decreasing, however, corresponds to an increase of the starting amount of copolymer (*Table 4*). This effect is particularly

Table 3 Solution copolymerization of MMA with QD1 or QD4[a]

			Copolymer		
Sample	Feed MMA/QD (molar ratio)	Conversion (%)	MMA/QD (molar ratio)[b]	$\overline{M}_n \times 10^{-3}$[c]	$\overline{M}_w/\overline{M}_n$[c]
1MQD1	99.0	97.7	99.0	13	2.0
2MQD1	32.3	98.1	32.3	12	1.9
3MQD1	19.0	96.0	19.0	10	1.9
4MQD1	9.0	97.8	8.1	10	1.4
5MQD1	4.9	95.1	5.7	9	1.6
6MQD1	2.3	94.9	2.0	–	–
1MQD4	32.3	91.3	32.3	29	1.7
2MQD4	9.0	92.4	9.0	35	2.0
3MQD4	5.7	92.3	5.3	5	2.0
4MQD4	2.3	95.7	2.1	–	–

[a] AIBN, 60°C for 72 h in CH_3CN

[b] Obtained by ^1H n.m.r. data

[c] Obtained by g.p.c. data using chloroform polymer solutions

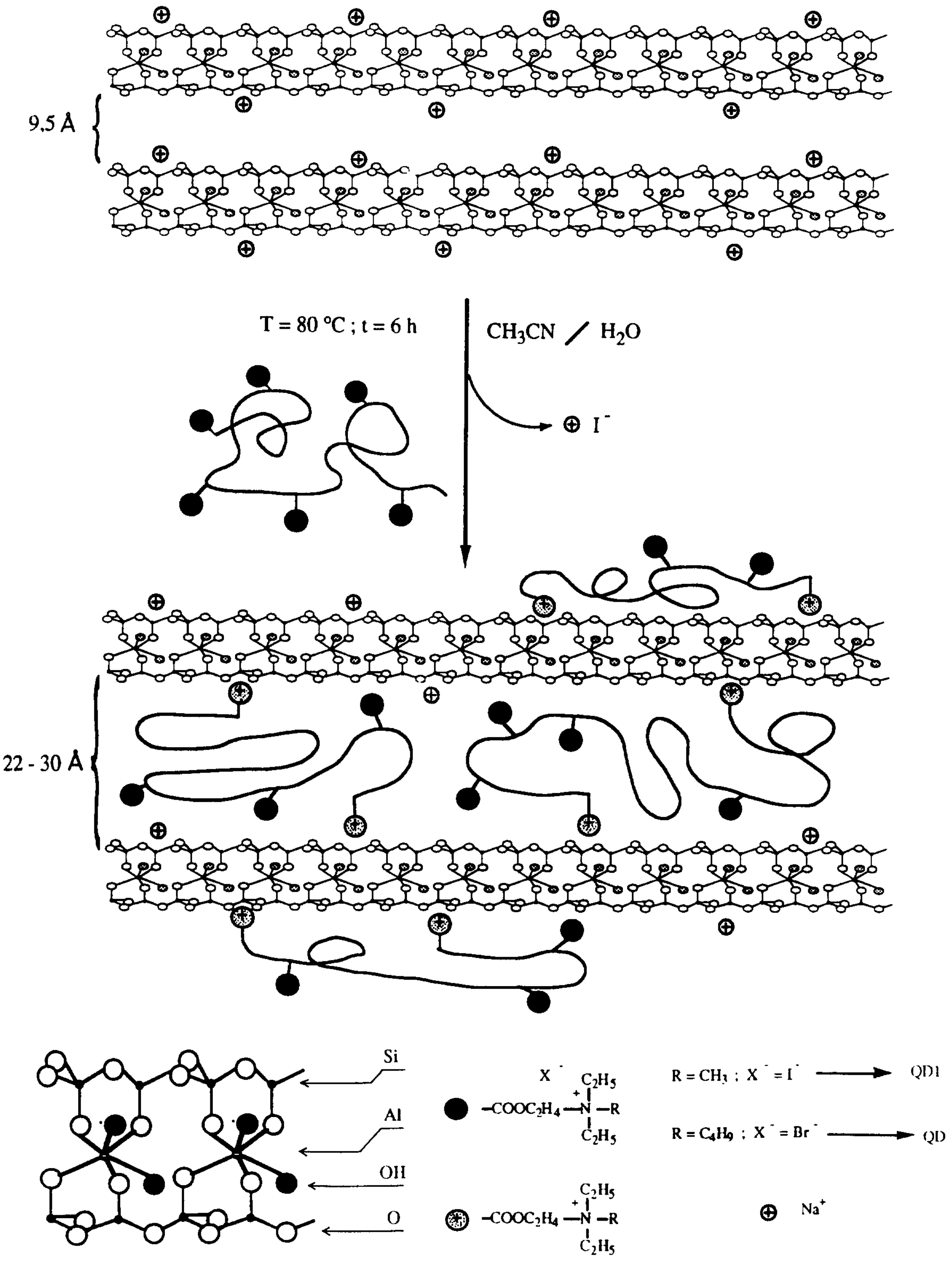

Figure 2 Schematic representation of complexation of montmorillonite with MMA/QD1 or QD4 copolymers

evident by varying MMA/QD1 ratio in the copolymer from 99 (sample 1MQD1B) to 32.3 (sample 2MQD1B), which gives a reduction of 10 wt% of complexed organic materials. Further reduction of the MMA/QD1 ratio down to 2 still has a decreasing effect, but the slope becomes less pronounced (*Figure 4* and *Table 4*). Steric effects and limited accessibilty of anionic sites on the surface of montmorillonite can be responsible for this behaviour, as well as the small number of original $-NR_3^+$ groups involved in the fixation.

A lower ratio between available anionic sites on the clay surface and $-NR_3^+$ groups in the side chain of the polymer produces for the same copolymer (samples 1MQD4B/1, 1MQD4B/2 and 1MQD4B/3 in *Table 4*) an increase of the complexed polymer weight, and a limiting value is rapidly reached.

Direct interactions between Na montmorillonite and preformed MMA polymers with quaternary ammonium species in the side chains seem to be at first sight more versatile than the copolymerization of MMA on the

Table 4 Preparation of complexes from montmorillonite and MMA/QD copolymers[a]

Sample	MMA/QD (molar ratio)[b]	Solvent CH_3CN/H_2O (vol/vol)	Montmorillonite active sites QD1 or QD4 units	Copolymer (wt%) Starting	Copolymer (wt%) Complex[c]
1MQD1B	99	80/20	2	83.8	74.3
2MQD1B	32.3	80/20	1	78.2	64.0
3MQD1B/1	19	33/67	1	69.0	62.0
3MQD1B/2	19	100/00	1	69.0	46.3
3MQD1B/3	19	90/10	1	69.0	54.6
3MQD1B/4	19	80/20	1	69.0	58.9
3MQD1B/5	19	60/40	1	69.0	61.0
4MQD1B	8.1	33/67	1	55.0	45.3
5MQD1B	5.7	33/67	1	44.6	41.9
6MQD1B	2.0	33/67	1	34.0	33.0
1MQD4B/1	32.3	33.67	4	47.6	38.0
1MQD4B/2	32.3	33/67	1	78.4	59.5
1MQD4B/3	32.3	33/67	0.5	87.9	60.0
2MQD4B	9.0	33/67	1	55.2	45.2
3MQD4B	5.3	33/67	1	42.0	41.9
4MQD4B	2.1	33/67	1	35.6	33.2
B/PMMA[b]	∞	–	–	–	3.2

[a] See *Table 3*
[b] Obtained by ^1H n.m.r. data
[c] Obtained by t.g.a. traces

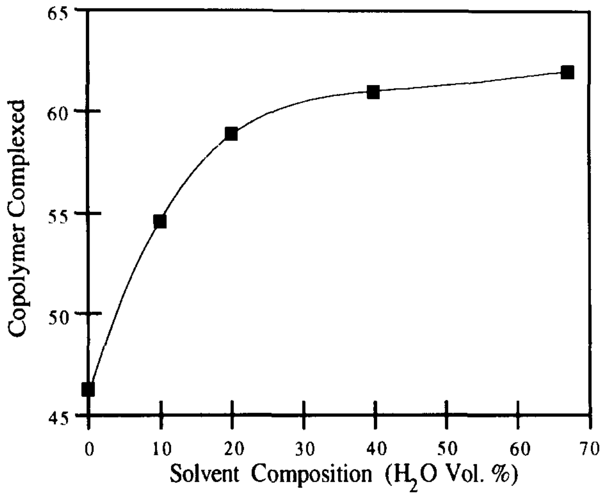

Figure 3 Dependence of montmorillonite fixed copolymer amount in complex vs. solvent composition

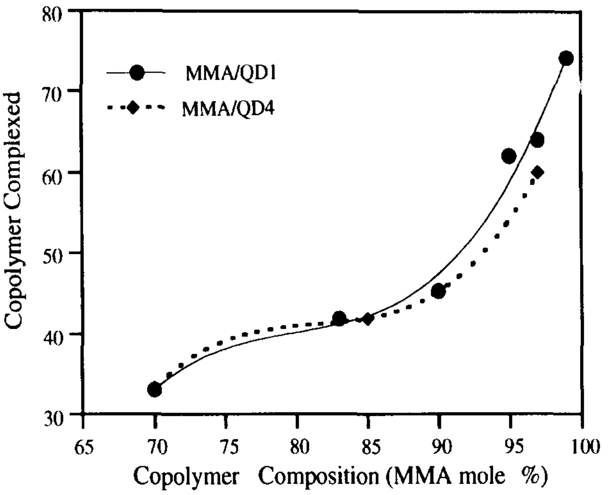

Figure 4 Dependence of montmorillonite fixed copolymer amount vs. copolymer composition

functionalized inorganic surface (*Figure 1*). Indeed, with the former method up to 75% of non-extractable organic materials with MMA/QD ratio from 2 to 99 could be introduced into the complexes. In the latter case only a smaller fraction of MMA could be copolymerized on the surface with the fixed QD monomers.

Properties of the complexes between montmorillonite and MMA/QD copolymers

The structural studies on the complexes obtained by reaction with preformed MMA/QD copolymers were carried out by *FT*i.r.[16,17] and X-ray analysis.

The *FT*i.r. spectra (*Figures 5* and *6*) of the complexes reveal the presence of characteristic absorptions of both inorganic and organic components. Indeed, the peak at 1040 cm^{-1} can be associated with Si–O stretching vibrations, and those between 600 and 400 cm^{-1} with stretching of Al–O and bending of Si–O. On the other hand, the organic polymer component shows bands at 1300–1100 cm^{-1} (C–O stretching) and 1730 cm^{-1} (C=O stretching).

No evidence of new bands that could be associated with interactions between organic and inorganic materials was observed, suggesting that fixation occurs by electrostatic bonds involving $-NR_3^+$ groups.

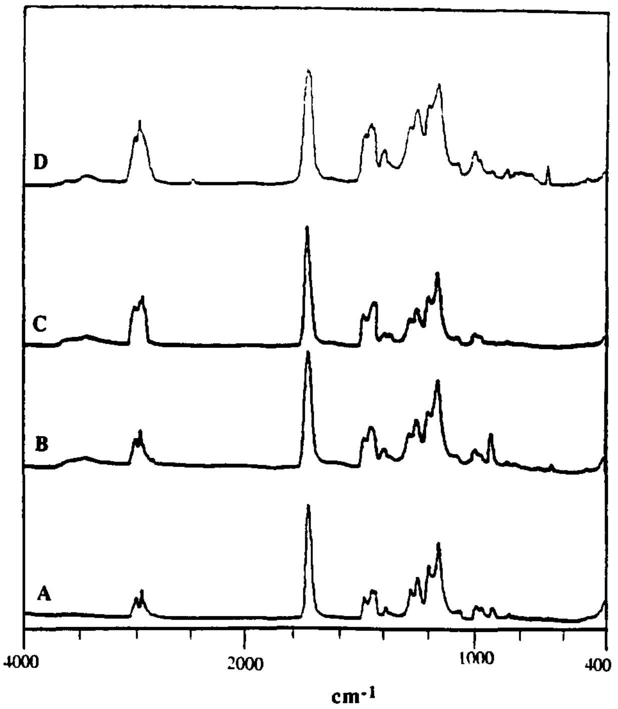

Figure 5 I.r. spectra of MMA/QD4 copolymers: 4MQD4 (A), 3MQD4 (B), 2MQD4 (C) and 1MQD4 (D) (see *Table 3*)

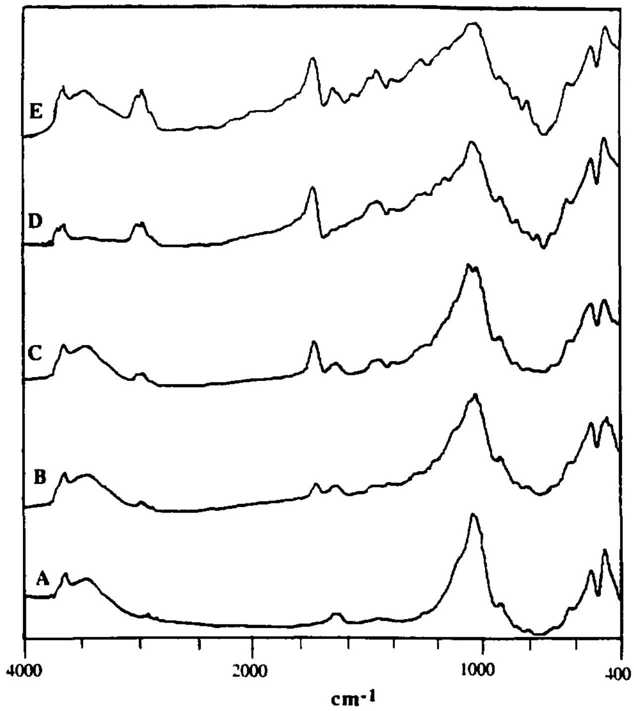

Figure 6 I.r. spectra of: 4MQD4B (A), 3MQD4B (B), BQD4M (C), BQD4 (D) and montmorillonite (E) (see *Tables 1, 2* and *4*)

The lack of variation in the bulk spectroscopic features of the inorganic matrix is consistent with the disposition of the PMMA macromolecules in the space between lamellae without distortion of the symmetry of the crystalline lattice. On the other hand, the organic macromolecule is fixed on the surface through the side-chain quaternary ammonium groups, while the ester

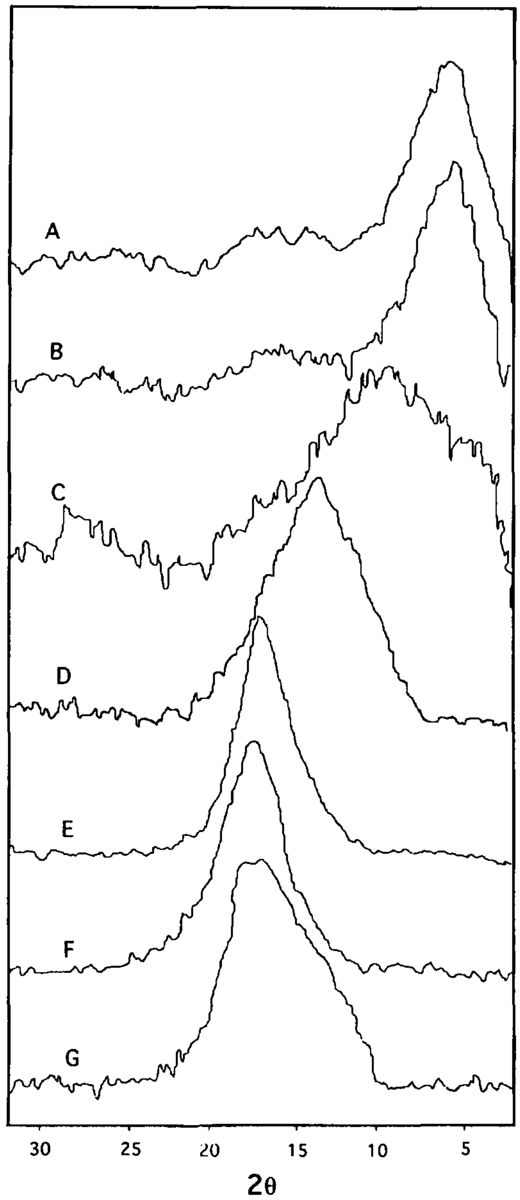

Figure 7 X-ray diffraction patterns of: montmorillonite (A), BQD1 (B), BQD4 (C), BQD1M (D), 2MQD1B (E), 3MQD1B (F) and 4MQD4B (G) (see *Tables 1, 2* and *4*)

Table 5 X-ray diffraction data of montmorillonite functionalized by QD1 or QD4 and of complexes from montmorillonite and MMA/QD preformed copolymers

	Organic loading			Interlamellar distance	
Sample	(wt%)	MMA/QD (molar ratio)	Mont/QD (weight ratio)	*d*(Å)	Δ(Å)[a]
Montmorillonite	0	–	∞	9.5	0
BQD1	8.4	0	11	14.2	4.7
BQD4	9.8	0	9	14.6	5.1
2MQD1B	64.0	32	19	21.4	11.9
3MQD1B	62.0	19	12	24.0	14.5
5MQD1B	41.2	5.7	8.5	29.6	20.1
2MQD4B	45.2	9	12.0	22.8	12.5
BQD1M	31.0	2.3	15.7	17.8	8.3

[a] Δ = variation of interlamellar distance of the montmorillonite induced by organic loading

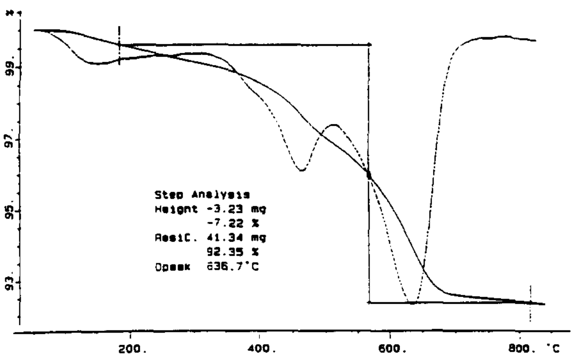

Figure 8 T.g.a. and d.t.g.a. curves of bentonite (Laviosa BP 100)

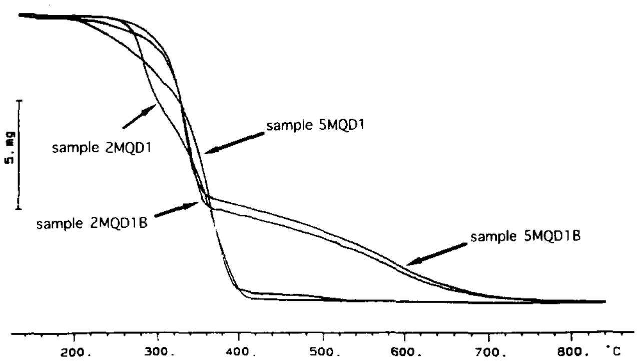

Figure 9 T.g.a. curves of the copolymers 2MQD1 and 5MQD1 (see *Table 3*) and of the composites 2MQD1B and 5MQD1B (see *Table 4*)

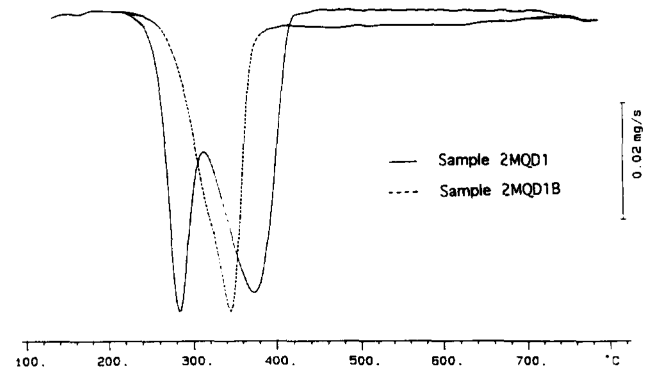

Figure 10 D.t.g.a. curves of the copolymer 2MQD1 (see *Table 3*) and of the composite 2MQD1B (see *Table 4*)

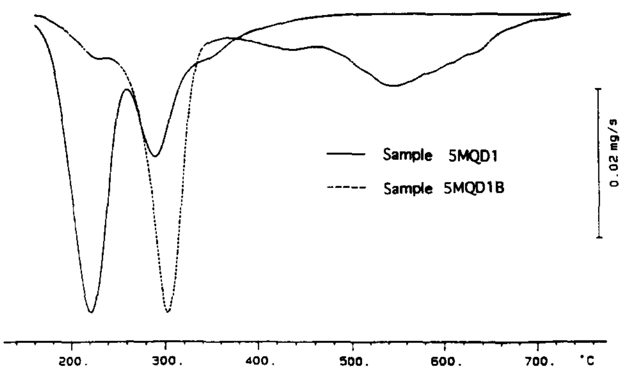

Figure 11 D.t.g.a. curves of the copolymer 5MQD1 (see *Table 3*) and of the composite 5MQD1B (see *Table 4*)

groups probably give rise only to limited interactions, by intensity and/or number, with the inorganic surface.

Accordingly X-ray analysis[18,19] shows (*Figure 7*) that the interlamellar distance increases with polymer loading, the major effect being connected to the content of ammonium ion with respect to the montmorillonite (that is, decrease of the ratio of montmorillonite to $-NR_3^+$) (*Table 5*). Indeed, already the treatment with QD1 or QD4 determines the increase of the basal distance from 9.5 to 14.5 Å, and successive copolymerization with MMA gives a further increase to 17.8 Å in spite of the higher montmorillonite to $-NR_3^+$ ratio.

The contribution of MMA units to the increase of the interlamellar distance is particularly evident in the composites prepared by interactions of montmorillonite with the preformed copolymers. However, even in these systems the highest values are obtained with copolymers containing the most $-NR_3^+$ groups. Thus 5MQD1B has a basal distance of 29.6 Å in spite of only 41.2% organic content but with a MMA/QD ratio of 5.7 (*Table 5*).

Additional information about the interactions between montmorillonite and organic polymers is obtained by thermal analysis of the sample. The t.g.a. curve of bentonite (*Figure 8*) resembles the usual t.g.a. run for montmorillonite. Decomposition took place in two ranges. The adsorbed water remained in the interlayer space at 110°C. No further water removal was observed up to 200°C. From 400 to 700°C water was released in two steps, the first peak was detected at 455°C and the second at 635°C. In the latter temperature interval the clay mineral loses the OH groups and the crystallographic structure collapsed.

T.g.a. traces of MMA/QD1 polymers and of composites prepared by their interaction with montmorillonite are reported in *Figure 9*. In *Figures 10* and *11* are compared the d.t.g.a. traces of the composites prepared from preformed copolymers with a low QD1 content (sample 2MQD1B in *Table 4*) and high QD1 content (sample 5MQD1B in *Table 4*). These last show two different degradation steps, the former at lower temperature being associated with the decomposition of the ammonium groups; indeed, their intensity markedly increases from the sample with 3% (sample 2MQD1) to that with 15% (sample 5MQD1). By complexation with montmorillonite the two peaks merge into one peak, thus indicating that the $-NR_3^+$ groups are strongly involved with the inorganic matrix, their decomposition not being easily detectable because it has moved to higher temperature.

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