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Structure determination of clay/methyl methacrylate copolymer interlayer complexes by means of ^{13}C solid state n.m.r.

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The interlayer complexes of several methyl methacrylate (MMA)/2-(*N*-methyl-*N*,*N*-diethylammonium iodide) ethyl acrylate (MDEA) copolymers with two smectite clays (bentonite and hectorite), synthesized in two different ways, were studied by means of solid state ^{13}C n.m.r. techniques. Given the relatively high content of paramagnetic centres in bentonite, which is approximately 50 times more paramagnetic than hectorite, the s.p.e./m.a.s. and c.p./m.a.s. spectra of the different complexes with bentonite show differences according to the proximity of the different copolymer moieties to the clay surface. The dynamics of the organic macromolecules in the inorganic interlayers has been investigated by measuring various relaxation times (^{13}C T_1, ^{13}C $T_{1\rho}$ and ^{1}H $T_{1\rho}$). The paramagnetism of the clay, where relevant, strongly influences the relaxation times measured, whereas in the other cases the different relaxation times allow one to discern differences in the structural organization and mobility of the organic macromolecules depending on the complex preparation. Useful indications on the structure of the different complexes have been obtained by combining the above results with X-ray measurements of the interlayer distance for all the samples investigated. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The good potential of solid state n.m.r. in the analysis of both polymers[1] and clays[2] prompted us to use this technique for investigating the new complexes of side-chain cationic polymers and sodium-exchanged bentonite[3], recently prepared in our laboratory[4]. These materials are of great interest because they provide unique systems where the effect of the inorganic materials on the complex structure and related macromolecular dynamics can be investigated making reference to a rather simple supramolecular model structure. Moreover, this type of molecular complexation can help to develop improved hybrid materials with modulated inorganic/organic content for applications as speciality filler, selective absorbants and heterogeneous catalysts.

In this work we have undertaken a ^{13}C n.m.r. study of complexes between Na-bentonite and various free radical copolymers of methyl methacrylate (MMA) with 2-(*N*-methyl-*N*,*N*-diethylammonium iodide) ethyl acrylate (MDEA) (*Figure 1*), synthesized following two different procedures: one consisted in the copolymerization within the clay previously functionalized with MDEA, the other in the direct interaction of the preformed MMA/MDEA copolymers with clay swollen in a water/acetonitrile mixture.

In both cases, the MDEA cation replaces the exchangeable Na cations present on the external as well as on the internal surfaces of the clay, which balance the negative charges arising from isomorphous replacement of Si^{4+} with Al^{3+} in the tetrahedral sites and Al^{3+} with Mg^{2+} in the octahedral ones.

Bentonite is known to contain non-negligible quantities of paramagnetic impurities as well as a certain amount of Al-substituting iron. Effects of these paramagnetic centres both on the spectral features and on relaxation times were found; these effects served to monitor the proximity of the different copolymer moieties to the clay surface, and also strongly influenced the relaxation times, thus masking information on the dynamics. In order to discriminate between dynamic and paramagnetic effects on relaxation, we prepared analogous complexes of MMA/MDEA copolymers with hectorite, which shows a considerably lower content of paramagnetic centres than bentonite; therefore the measured relaxation times allowed us to investigate the copolymer dynamics within the layers.

The information on structure and dynamics obtained from the n.m.r. spectra and relaxation time measurements, together with the interlayer spacings determined from X-ray diffraction experiments and the glass transition temperatures obtained from differential scanning calorimetry (d.s.c.), allowed us to determine the structural differences between the various complexes and to correlate

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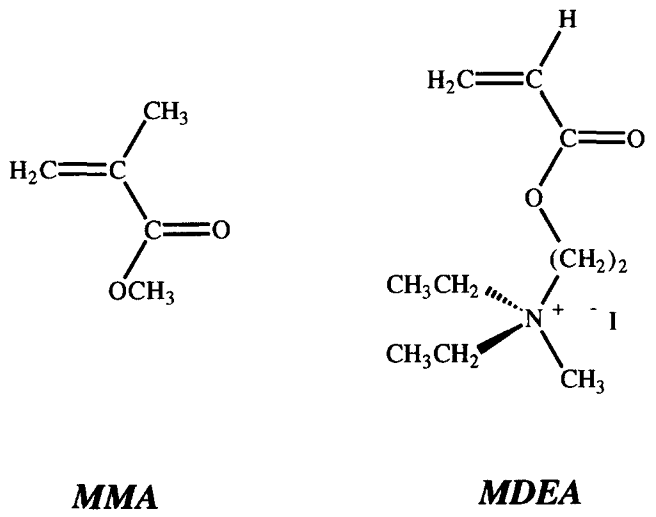

Figure 1 Monomers MMA and MDEA

such differences with the synthetic procedure employed and with the copolymer composition.

EXPERIMENTAL

The complexes of Na-exchanged clay (bentonite and hectorite) and MMA/MDEA copolymers were prepared by following two distinct routes[4,5]. In the first case, the clay was previously functionalized by direct interaction of MDEA with the clay swollen in water for 2 h at 80°C. The products of this reaction will be denoted as MDEAB and MDEAH when the clay is bentonite and hectorite, respectively. MMA was then allowed to copolymerize with the pre-functionalized clay by using α-α'-azobisisobutyronitrile (AIBN) as initiator at 60°C. Extraction with acetonitrile removed the organic material not bound to the inorganic matrix, i.e. the homopolymer MMA, whereas the MMA/MDEA copolymer was not extractable, being bound to the clay surface through electrostatic bonds involving the R_4N^+ moiety (MDEA) and $-SiO^-$ anions. The resulting complex was around 30–40% by weight of copolymer with an MMA/MDEA molar ratio of approximately 8:1 both for bentonite and hectorite (samples 8polB and 8polH respectively).

The second type of complex was prepared by direct interaction of a preformed MMA/MDEA copolymer with the clay swollen in a water CH_3CN mixture for 6 h at 80°C. Copolymers with different MMA/MDEA molar ratios were used: the complexes thus obtained are referred to as *n*insB and *n*insH for bentonite and hectorite respectively, with *n* indicating the approximate MMA/MDEA molar ratio. The syntheses were performed to obtain complexes with similar copolymer content. The MMA/MDEA copolymers were synthesized with the free radical initiator AIBN at 60°C in acetonitrile solution (samples *n*MMDEA); their molar ratio was determined by means of ^1H n.m.r. in $CDCl_3$.

Thermogravimetric analyses were performed in order to determine the quantity of copolymer within the different samples. Glass transition temperatures were measured from d.s.c. experiments. The layer spacings of the clay in the different systems were determined by means of X-ray diffraction measurements. The data are reported in *Table 1*.

The ^{13}C n.m.r. experiments were performed at 75.47 MHz on a Bruker AMX-300 WB spectrometer using 4 mm rotors. The 90° proton pulse was 3 μs. In all the cross-polarization magic angle spinning (c.p./m.a.s.) experiments we used a contact time of 1 ms and a recycle time of 4 s. In the single pulse excitation (s.p.e./m.a.s.) experiments the recycle time used was 30 s except for the *n*insB complexes where a relaxation delay of 4 s could be used. The ^{13}C spin–lattice relaxation times in the laboratory frame ($T_1(^{13}C)$) were determined by means of Torchia's sequence[6] or, when cross polarization was poor, the inversion–recovery experiment[7]. ^{13}C spin–lattice relaxation times in the rotating frame ($T_{1\rho}(^{13}C)$) were measured using a variable spin lock pulse after the c.p. pulse sequence[8]. ^1H spin–lattice relaxation times in the rotating frame ($T_{1\rho}(^1H)$) were determined, through ^{13}C observation, using variable contact pulse c.p. experiments[9].

The m.a.s. rate was always 6 kHz; all experiments were performed at room temperature.

Table 1 Composition, glass transition temperatures (T_g) and average layer spacing of the copolymers and complexes studied

Sample	Molar ratio MMA/MDEA[a]	Weight % organic fraction[b]	T_g^c (°C)	Average layer spacing[d] (Å)
6MMDEA	6.0		109	
5MMDEA	5.0		111	
2MMDEA	2.2		111	
MDEAB		8.4		14.2[e]
MDEAH		11.6		14.4
8polB	8.2	30.0	127, 159	17.8
8polH	8.4	42.7	119, 151	18.5
7insB	7.2	38.8		48.0
6insB	6.0	33.2	130	34.7
6insH	6.0	27.7	120	33.0
5insH	5.0	42.0	127	32.6
2insB	2.2	30.3	150	23.6
2insH	2.2	36.6	148	24.6

[a] From ^1H n.m.r. spectra in $CDCl_3$

[b] From t.g.a.

[c] From d.s.c. measurements

[d] From X-ray powder diffraction spectra. The layer spacing was 14.0 Å for bentonite and 14.2 Å for hectorite

[e] From ref. 4

RESULTS AND DISCUSSION

The ^{13}C c.p./m.a.s. n.m.r. spectra of two uncomplexed copolymers (samples 6MMDEA and 2MMDEA) are shown in *Figure 2*. Good signal-to-noise ratio could be obtained with a low number of accumulations (200 scans). The six distinguishable groups of resonances observed could be assigned to specific groups present in the two monomer units (*Table 2*)[10]. The broad asymmetric peak centred around 15 ppm, assigned to the α-methyl of MMA, arises

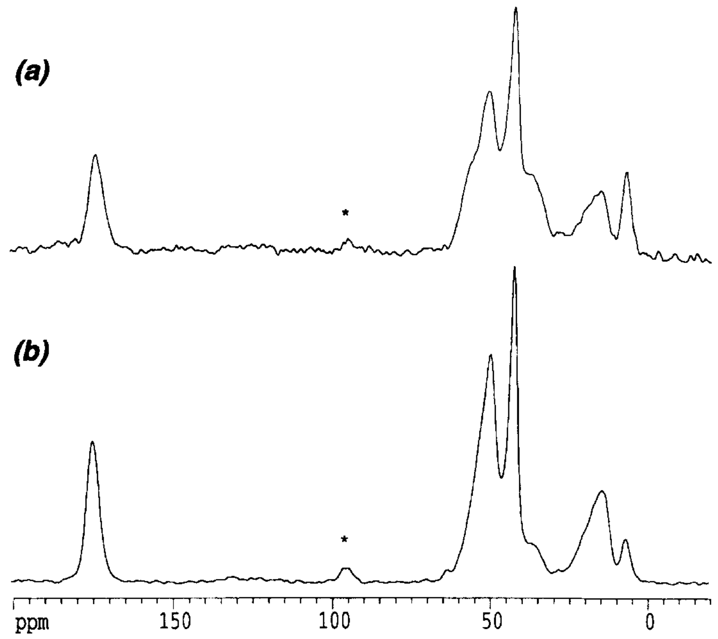

Figure 2 ^{13}C c.p./m.a.s. spectrum of (a) 2MMDEA and (b) 6MMDEA. Asterisks denote spinning sidebands

Table 2 Peak assignment of ^{13}C n.m.r. spectra

176 ppm	50,58 ppm	43 ppm	38 ppm	15 ppm	8 ppm
C=O MMA **C=O** MDEA	$\mathrm{CH_3}$-$\mathbf{CH_2}$-N MDEA O-$\mathbf{CH_2}$-$\mathbf{CH_2}$-N MDEA $\mathbf{CH_3}$-O MMA $\mathbf{CH_2}$ β MMA	**CH** α MDEA $\mathbf{CH_3}$-N MDEA **C** α MMA	$\mathbf{CH_2}$ β MDEA	$\mathbf{CH_3}$ α MMA	$\mathbf{CH_3}$-$\mathrm{CH_2}$-N MDEA

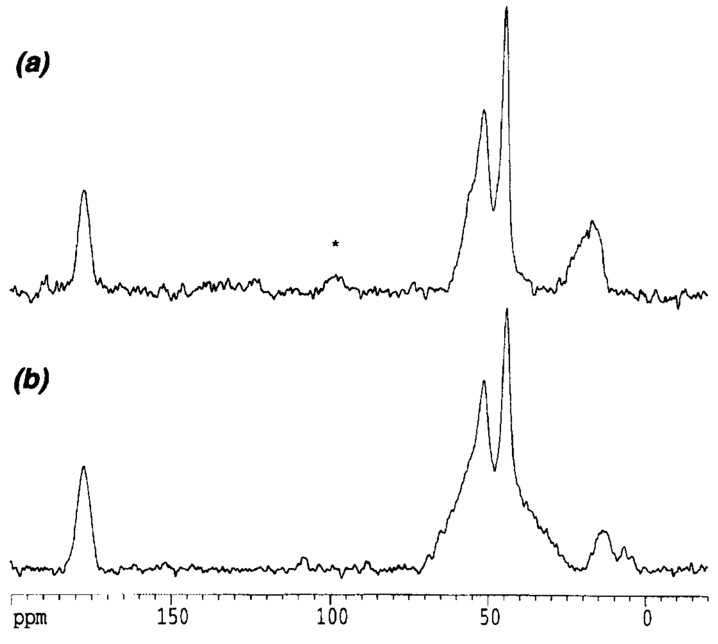

Figure 3 (a) ^{13}C c.p./m.a.s. spectrum of 8polB; (b) ^{13}C s.p.e./m.a.s. spectrum of 8polB

from the overlap of peaks corresponding to different tacticities in the polymer[11].

The ^{13}C c.p./m.a.s. n.m.r. spectrum of 8polB, shown in *Figure 3a*, was obtained with 600 scans. Comparison with the spectrum of the pure copolymers indicates that only the MMA signals are present; this is particularly evident from the absence of the peak relative to the methyl carbon of the ethyl group in MDEA. The inefficiency of cross polarization for the MDEA ^{13}C nuclei was confirmed by the ^{13}C c.p./m.a.s. n.m.r. spectrum of a sample of bentonite functionalized with MDEA monomers (sample MDEAB), which did not show any signal, even with different experimental parameters, i.e. contact pulse and recycle time. On the other hand, in the ^{13}C s.p.e./m.a.s. n.m.r. spectra for both 8polB (*Figure 3b*) and MDEAB, the expected peaks for the MDEA moieties are present. The comparison of the s.p.e./m.a.s. spectrum of 8polB with that of the free copolymer 6MMDEA shows small shifts for the MDEA peaks, which are expected as a consequence of the electrostatic bonding of the ammonium groups to the silicate anions on the layer surface of the clay, and a pronounced broadening probably due to interaction with paramagnetic centres.

Analogous observations can be made for the complexes 6insB and 7insB, prepared by interaction of the preformed copolymers with bentonite, whose spectra are quite similar.

Sample 2insB showed an even more remarkable cross-polarization inefficiency, which in this case was not only observed for the MDEA carbons, but also for the MMA signals: hardly any signal was observed in the ^{13}C c.p./m.a.s. experiment, while the ^{13}C s.p.e./m.a.s. spectrum, reported in *Figure 4*, shows all the expected peaks. The small peak around 0 ppm is ascribed to residual acetonitrile fixed to the clay during the synthesis.

The complete cross-polarization inefficiency for the MDEA moieties in samples 2insB, 7insB, 6insB and 8polB is indicative of the complexation to the bentonite through the R_4N^+ groups and can be ascribed to the presence in the clay of paramagnetic centres[12,13] such as iron and manganese, which could dramatically reduce the $T_{1\rho}$ values of the protons and carbons in proximity to the bentonite surface. The very poor cross-polarisation efficiency for all the ^{13}C nuclei in sample 2insB could be due either to a dynamic effect or to a particular organization of the copolymer macromolecules within the interlamellar space which allows interaction of all the moieties with the surface.

In order to have further insight into the structure of these complexes, it was thus necessary to distinguish the effects of paramagnetism from possible dynamic effects; it therefore seemed useful to perform the same experiments on samples prepared in the same way but using another smectite clay, hectorite, with much less paramagnetic ion content. E.p.r. spectra of both bentonite and hectorite indicated that bentonite indeed has a high concentration of paramagnetic centres, 5.3×10^{19} spins mg^{-1}, which is 50 times higher than that of hectorite, 1.1×10^{18} spins mg^{-1}.

Because of the lower paramagnetism, the spectra of the complexes with hectorite do not show evidence either of missing peaks in the c.p./m.a.s. or of line broadening in the s.p.e./m.a.s. experiments, and, moreover, there are no striking differences between the two experiments. As an example the ^{13}C s.p.e./m.a.s. spectrum of 2insH is reported in *Figure 5*.

For a better understanding of the dynamics of these polymeric systems within the layers, we measured the ^{13}C spin–lattice relaxation times in the laboratory frame, $T_1(^{13}C)$, reported in *Table 3*, which are sensible to motions in the MHz frequency range. Given the different response of the samples to cross-polarization, two different methods were used: on one hand, Torchia's technique,

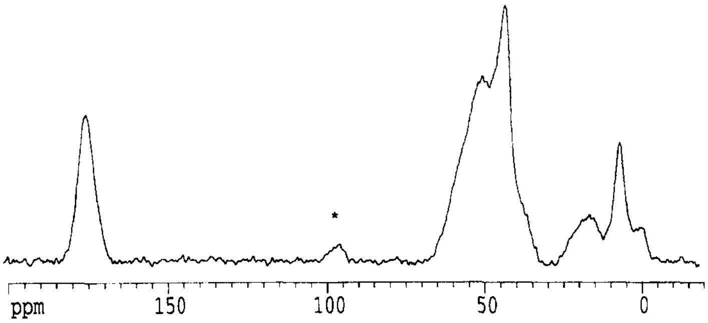

Figure 4 ^{13}C s.p.e./m.a.s. spectrum of 2insB

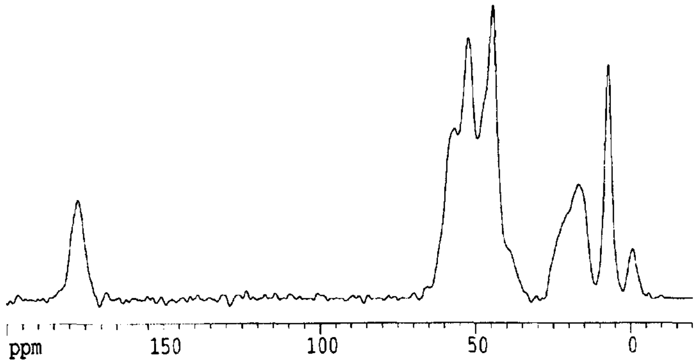

Figure 5 ^{13}C s.p.e./m.a.s. spectrum of 2insH

Table 3 ^{13}C spin–lattice relaxation times (s) determined using the Torchia sequence, unless stated otherwise. The T_1 values are obtained with a maximum error of 10%

Sample	176 ppm	50,58 ppm	38,43 ppm	15 ppm	8 ppm
6MMDEA	14.7	7.8	8.3	0.24	1.2
2MMDEA	16.9	6.2	9.5	0.17	1.1
8polB	4.4	4.6	3.0	0.084	
	2.8[a]	1.7[a]	1.4[a]	0.065[a]	0.040[a]
8polH	11.5	8.9	7.2	0.13	0.36[a]
6insB	0.96	1.02	0.87	0.098	
				0.057[a]	
6insH	13.2	8.1	8.0	0.13	1.4
2insB	0.066[a]	0.058[a]	0.058[a]	0.042[a]	0.047[a]
2insH	13.4	6.5	8.0	0.16	1.4

[a] Measured using the inversion–recovery experiment

less time-consuming in the case of high cross-polarization efficiency and, on the other hand, the inversion–recovery technique. It must be pointed out that, due to the high degree of overlap of peaks, the relaxation times measured result from a combination of different relaxation times and the single contributions cannot be extracted. In samples where the cross-polarization is effective for MMA only, however, the combined use of the two techniques allows to have a rough estimate of the contribution of the two separate monomers.

Within each sample, the values for the different alkyl ^{13}C resonances are all of the same order of magnitude, the only diverging values being those relative to the α-methyl carbon of MMA and the low-frequency methyl carbon of MDEA. The comparison between the data of the pure copolymers and the hectorite complexed ones shows only minor differences and no dependence from the preparation route of the sample as well as from the MMA/MDEA ratio. The only exception is represented by the $\mathbf{CH}_3$–CH_2–N in 8polH, which shows a lower value than those found for the other samples. Variable temperature measurements indicate that the $T_1({}^{13}C)$ minimum for this carbon occurs below room temperature; therefore the low T_1 observed in 8polH suggests a reduced mobility for this methyl group. Sensibly lower values are found for all the resonances in the bentonite complexes (6insB, 2insB and 8polB), which appear strongly affected by paramagnetism: all $T_1({}^{13}C)$ values decrease by a factor which increases with decreasing MMA/MDEA ratio. In 8polB, the inversion recovery measurements yield lower values with respect to those obtained using Torchia's sequence where only the contribution of MMA is measured, thus indicating that the MDEA carbons have shorter relaxation times. The very low values measured in the case of 2insB, where all the carbons have approximately the same relaxation time, together with a generalized cross-polarization inefficiency, suggest that in this sample the whole copolymer lies very near the layer surface thus being strongly influenced by the paramagnetic centres of the clay. This is presumably due to the fact that the MMA/MDEA ratio is low and, therefore, being the MDEA moieties bound to the surface, the MMA units are also constrained in the proximity of the clay surface.

In the hectorite complexes, where the paramagnetic effect is not relevant, measurements of $T_{1\rho}({}^{13}C)$ and of $T_{1\rho}({}^{1}H)$ were also performed.

While the $T_{1\rho}({}^{1}H)$ decay could be well fitted with a single exponential function, a biexponential curve had to be used for the $T_{1\rho}({}^{13}C)$ decay; thus, in the latter case, two relaxation time values and the relative weights were obtained. In the case of multi-exponential decays the comparison between the weighted average values, instead of the single components, is often more significant. The experimental $T_{1\rho}({}^{1}H)$ and the calculated weighted $T_{1\rho}({}^{13}C)$ average values are given in *Tables 4* and *5*, respectively.

Within each sample different $T_{1\rho}({}^{13}C)$ values are found for the different resonances, whereas reasonably uniform $T_{1\rho}({}^{1}H)$ values are obtained because of spin diffusion. Nevertheless both the relaxation times exhibit the same trend throughout the different samples: 6MMDEA and 6insH show nearly equal $T_{1\rho}({}^{1}H)$ and average $T_{1\rho}({}^{13}C)$ values, whereas lower and higher values are found in 2insH and 8polH, respectively. The similar results obtained for 6MMDEA and 6insH indicate that no relevant variations to the dynamics in the kHz range are induced by the insertion of the copolymer within the clay. The differences in 2insH can be ascribed to either a fair influence of the few paramagnetic centres present in the proximity of the hectorite surface or a reduced mobility of the copolymer chains induced by the high number of links to the clay. 8polH appears substantially different from the other samples, possibly indicating a different structure of the copolymer in this complex.

The peculiarity of the samples obtained by polymerization on the prefunctionalized clay (8polB and 8polH) is also evident from the interlayer distance in the complexed and uncomplexed clays obtained from X-ray measurements

Table 4 ^{1}H $T_{1\rho}$ spin lattice relaxation times (ms) in the rotating frame. Errors are within 15%

Sample	176 ppm	50,58 ppm	38,43 ppm	15 ppm
6MMDEA	7.5	8.0	6.8	7.6
8polH	18	19	16	17
6insH	8.1	9.2	6.9	10.1
2insH	4.6	5.5	5.4	5.2

Table 5 ^{13}C $T_{1\rho}$ population averaged relaxation times (ms). Errors are within 15%

Sample	176 ppm	50,58 ppm	38,43 ppm	15 ppm
6MMDEA	32.6	16.4	34.2	25.4
8polH	72.5	35.7	39.1	26.9
6insH	37.0	18.9	43.3	16.0
2insH	24.8	9.4	19.8	18.2

reported in *Table 1*, as well as glass transition temperatures determined by d.s.c., reported in the same table. The basal spacing between layers is not sensibly influenced by small differences in organic content, but rather by the MMA/MDEA molar ratio and the way the complex is formed. In fact, when the preformed copolymer is inserted in the clay, the layer spacing increases with increasing MMA/MDEA molar ratio, but does not change sensibly with respect to the value found for the sole clay when MMA is copolymerized on the clay previously functionalized with MDEA. The former behaviour can well be rationalized considering the amount of non-bonded MMA moieties present, which increases with increasing MMA/MDEA molar ratio. The glass transition temperatures (*Table 1*) show an increase with decreasing MMA/MDEA molar ratio in the case of the inserted copolymers; samples 8polB and 8polH, on the contrary, show two transition temperatures, instead of the one shown by the other samples: one close to that of PMMA ($T_g = 120°C$)[14], the other similar to that of the copolymer in the inserted complexes with lower MMA/MDEA molar ratio. All this seems to indicate that in the copolymerization of the preformed MDEA/clay complexes with MMA, only a small percentage of MMA copolymerizes with MDEA thus forming a low MMA/MDEA molar ratio copolymer, while the larger part of MMA forms essentially polymer chains with long MMA unit sequences which are attached to the clay through a MDEA moiety but essentially remain out of the layers.

CONCLUSIONS

Although copolymer–clay complexes are not simple systems and a complete and detailed picture of all the molecular aspects is difficult to obtain, some features emerge from the experiments performed in the present work.

The spectra and the dynamics of the MMA/MDEA copolymer complexed with bentonite are dominated by paramagnetism of the ions isomorphically substituting Al^{III} (mostly Fe^{III}). Accordingly, it is not surprising that, since all the ammonium ions of MDEA result in being bonded when the molar ratio MMA/MDEA is low, as in the case of 2insB, the MMA moieties also lie close to the bentonite surface so that all the nuclei in the polymer are strongly relaxed by surface paramagnetism.

The copolymer complexes obtained starting from MDEA prefunctionalized clays behave quite differently from the complexes obtained by inserting the preformed copolymer. This can be observed both from the spectra and the relaxation behaviour but also very clearly from the basal distances. In particular, ^{13}C T_1 measurements indicate that the influence of paramagnetism is substantially less in the 8polB sample than in the inserted copolymer having the most similar monomer ratio, 6insB; moreover, the $T_{1\rho}(^1H)$ values observed in 8polB are substantially larger than those of the pure copolymer. These results, together with the low interlayer spacing found in these complexes, seem to suggest that this copolymer is formed either completely or mostly outside the layers, possibly attached to the ammonium ions of the MDEA moieties complexed to edge sites.

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