Synthesis of stable W/O microemulsions of a hybrid grafted copolymer using a new inorganic cationic backbone within a unique "polyhedral cell"

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A novel graft copolymerization on an inorganic cationic backbone processing within polyhedral cell(s) (PHC) is discussed. This procedure can produce stabilized W/O (water in oil) PHC microemulsions of hybrid grafted acrylic type copolymers. Three water-soluble monomers acrylamide, sodium acrylate and dimethyldiallylammonium chloride were examined and all were proved to be successful. MgAl-LDH3 (MgAl-layered double hydroxide with Mg/Al = 3), an electropositive colloid, was first applied as an inorganic backbone for hybrid graft polymerization in this study. MgAl-LDH3 not only acted as a cationic functional backbone, but also stabilized the PHC system due to the electropositive repulsion force. The polymerization occurring within the PHC system could reduce the oil phase percentage of the emulsion, which potentially increases the stability of the final product. The polymerization was initiated by the backbone/ceric sulfate redox system and a variety of hybrid graft copolymers with MgAl-LDH3 as the backbone chain was synthesized. The influence of [monomer] and [MgAl-LDH3][Ce^{4+}] were examined based on the obtained reaction kinetic data. The percentages of PHC under different F_d were determined by microscopy and the backbone structure was characterized by X-ray diffraction (XRD).

1. Introduction

Lissant *et al.* borrowed the crystal concept "polyhedral cell" in their studies of polystyrene O/W latexes[1] to characterize a unique aggregation state, where the isolated gel droplets of the dispersed phase are compressed compactly when the fraction of dispersed phase $F_d = V_W/(V_W + V_O)$ exceeds the critical value ($F_{dc} = 0.74$). The unique state is denoted as a polyhedral cell.[1,2] It is known that the W/O emulsion polymerization of acrylamide type monomers is one of the best techniques to make water-soluble polymers.[3] Normally, polymers obtained from W/O emulsions have disadvantages such as poor stability, high oil percentages, and are difficult to store or convey,[4–6] so to develop a new protocol to produce stabilized concentrated W/O microemulsions is desirable.[7] This paper describes a new and unique *in situ* polymerization which allowed $F_d > F_{dc}$ so leading to the formation of the PHC. The polymerization was initiated by the backbone/ceric sulfate redox system,[8–9] which assured the grafting polymerization proceeded within the PHC. Furthermore, the inorganic cationic colloid MgAl-LDH3 was used as a backbone to form the hybrid graft polymer. MgAl-LDH3 is an easily accessible, nontoxic and environment friendly material.[10–13] It has a layered octahedral cubic crystal lattice and possesses a permanent positive charge.[14–15] It is our hypothesis that the repulsion force between positive charges of the MgAl-LDH3 might help to stabilize the PHC during the process of polymerization.

2. Experimental

2.1 Reagents and materials

Ethylenediaminetetraacetic acid disodium salt (EDTA2Na), ceric sulfate, Span-80, Span-60, Towen-80, Towen-85, OP-10, Isopar-M50, C_{14}–C_{16} (IPS) were obtained from local suppliers and were used directly without further purification. Acrylamide (AM) was recrystallized from acetone three times prior to use. Acrylic acid was distilled at reduced pressure. Sodium acrylate was prepared through the reaction between acrylic acid and sodium hydroxide. Diallyldimethylammonium chloride (30% aqueous solution) was purified using an ionic exchangeable membrane prior to use. MgAl-LDH3 ($[Mg_3Al(OH)_8]Cl\cdot 2H_2O$, $M = 307.38$), as a superfine powder of 200 mesh, was obtained from Dalian Fumeida New Materials Co., LTD, China.

2.2 The preparation W/O PHC of monomers

The powder of MgAl-LDH3 was placed in a glass vessel, and degassed deionized water was added. The pH value was adjusted to 9.0–9.2 by aqueous ammonia solution, and then the vessel was tightly capped, followed by ultrasonication. The resulting suspension was filtered using a membrane filter (0.2 μm, Millipore) to separate out insoluble gel, and the

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filtrate was dialyzed using a cellulose acetate bag against dilute ammonia aqueous solution (0.5% w/w) for 48 h. The dialyzed effused solution was monitored by $AgNO_3$ solution. The solution inside the bag was concentrated to generate the cationic colloid MgAl-LDH3. The MgAl-LDH3 and the monomers were mixed in water in designed ratio to form a range of 30–50% aqueous phases (W). The oil phase was prepared by mixing IPS, Span-80, Span-60, Towen-80 and -85 together in the designed ratio. The ratio of (W/O) was adjusted to achieve $F_d > F_{dc}$, when mixing the aqueous phase into the oil phase under nitrogen purging and stirring, and W/O microemulsions with a high percentage of PHC (W/O PHC) of monomers were prepared. The W/O PHC samples were frozen by liquid nitrogen and frozen sections were examined by measurement microscopy to calculate the percentage of PHC.

2.3 The polymerization process and kinetic studies

The *in situ* graft polymerizations were conducted in a four-necked flask equipped with stirrer, thermometer, condenser and a dropping funnel. The initial temperature was controlled at 25 °C. The W/O PHC (PHC% = 86%) microemulsion of monomers was added and the stirring was stopped when ceric sulfate solution was diffused into the dispersed phase. The temperature was then raised steadily at 2.5 $^\circ C\ min^{-1}$ up to 85 °C and was kept at that temperature for 30 min. The temperature was the allowed to cool to room temperature. Kinetic studies were conducted for each monomer and $M_{mixture}$. Samples were taken at set time intervals, precipitated by acetone, and extracted with a mixture of deionized water and 2-propanol (20 : 80 v/v). The conversions (%) were calculated by measuring the weight of the extracted precipitates. The polymerization rate (R_P, mol L^{-1} s^{-1}) was calculated according to $R_p = dc/dt \times [M_0]$.[16]

2.4 The characteristics of W/O PHC products

The products of each monomer and $M_{mixture}$ in W/O PHC were studied with a U-tube electrophoresis apparatus. The polymeric particles in the samples were carefully colored by a water-soluble dye methylene blue to ensure only the polymeric particles in the water phase were colored and diluted with IPS. The rheological properties of the $M_{mixture}$ products in W/O PHC were measured by a NDJ-79 model four-speed rotameter viscometer to evaluate the effect of MgAl-LDH3 amount on the degree of polymerization (DP).

2.5 The characteristics of the structure of MgAl-LDH3 and the hybrid grafted copolymers

The cationic colloid MgAl-LDH3 paste was dried under vacuum to afford a powder, which was put into an oven for 4 h at 120 °C. The obtained powder was analyzed by XRD using an X'Pert PRO diffractometer with monochromatic Cu-Kα radiation. The experiment was conducted at 25 °C and relative humidity of 45%. The electrophoretic mobility (S) and the zeta-potential (ξ) of the layered colloid of MgAl-LDH3 in deionized water were measured by DXD-II video-microelectrophoresis at room temperature. The structure of hybrid grafted copolymers with grafting chains of AM was examined by IR spectroscopy.

3. Results and discussion

3.1 The kinetic studies of the *in situ* grafting copolymerization

3.1.1 The influence of the amount of monomers on R_P. The monomer conversions *vs.* time at various $[M_{mixture}]$ are shown in Fig. 1. Using the linear regression method dealing with steady phases (conversion from 20 to 70%), dc/dt, r and R_p were calculated and the results are listed in Table 1. The slope of $\ln R_p$ *vs.* $\ln[M_{mixture}]$ is determined to be 1.56, which is significantly higher than those of regular radical polymerizations. This might be partly due to the fact that the W/O PHC polymerization took place in PHC aggregation state, where the isolated gel droplets were compressed compactly. The monomer concentration is very high and the heat generated during the polymerization was difficult to be dispersed, so the system's temperature rose along with an increase in R_P. On the other hand, the PHC is very viscous, and the rate for the termination reaction is low. These two combined factors result in the observation of high R_p in this polymerization process.

3.1.2 The influence of the amount of MgAl-LDH3 on R_P. The monomer conversion *vs.* time at various [MgAl-LDH3] is shown in Fig. 2. The relationship between R_p and MgAl-LDH3 *vs.* $[M_{mixture}]$ is $R_p \propto [\text{MgAl-LDH3}]^{1.34}$ (Table 2). The correlation between R_p and MgAl-LDH3 *vs.* [AM], [SA] and [DMDAAC] are also calculated and shown in Table 3, Table 4 and Table 5, respectively, and the results for [AM], [SA] and [DMDAAC] are $R_p \propto [\text{MgAl-LDH3}]^{1.30}$; $R_p \propto [\text{MgAl-LDH3}]^{1.48}$; $R_p \propto [\text{MgAl-LDH3}]^{1.20}$. For all the three monomers (including nonionic monomer acrylamide (AM), anionic monomer sodium acrylate (SA) and cationic monomer diallyldimethylammonium chloride (DMDAAC) examined, the influences of MgAl-LDH3 on R_P are all higher than 1.0. This is because MgAl-LDH3 possesses many hydroxyl groups, which can easily react with Ce^{4+} to form a large amount of backbone radicals, and also the positive charge on MgAl-LDH3 could accelerate the diffusion of monomers. Fig. 3 shows the acceleration effect of [MgAl-LDH3] to R_P for each monomer.

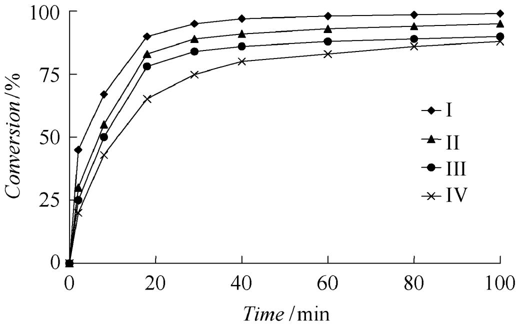

Fig. 1 Conversion–time curves at different $M_{mixture}$ concentrations: $M_{mixture}$ (AM : SA : DMDAAC = 0.7 : 0.25 : 0.05; by mol ratio); [MgAl-LDH3] = 0.5 × 10^{-2} mol L^{-1}; PHC% = 0.92; $[Ce^{4+}]$ = 0.25 × 10^{-4} mol L^{-1}; E% = 20; $[M_{mixture}]$/mol L^{-1} = (I) 4.7, (II) 3.7, (III) 2.9, (IV) 2.1.

Table 1 The effect of [M] concentration on R_p[a]

$[M_{mixture}]$/mol L^{-1}	dc/dt (DMDAAC)	r/s^{-1}	$10^4 R_p$/mol L^{-1} s^{-1}	ln R_p	ln[$M_{mixture}$]
2.1	1.50	0.4210	3.09	1.13	0.723
2.9	1.82	0.4215	5.26	1.66	1.065
3.7	2.09	0.4218	7.80	2.05	1.316
4.6	2.34	0.4212	10.70	2.37	1.520

[a] $M_{mixture}$ (AM : SA : DMDAAC = 0.7 : 0.25 : 0.05; by mol ratio); [MgAl-LDH3] = 0.5 × 10^{-2} mol L^{-1}; PHC% = 0.92; [Ce^{4+}] = 0.6 × 10^{-4} mol L^{-1}; E% = 20.

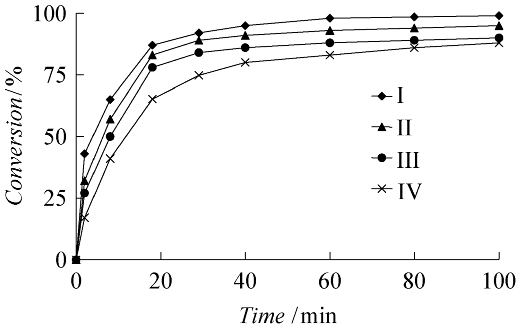

Fig. 2 Conversion–time curves at different MgAl-LDH3 concentrations [$M_{mixture}$] = 2 mol L^{-1}; PHC% = 92%; [Ce^{4+}] = 0.25 × 10^{-4} mol L^{-1}; E% = 20; 10^2[MgAl-LDH3]/mol L^{-1} = (I) 1.0, (II) 0.75, (III) 0.5, (IV) 0.25.

3.1.3 The influence of the amount of Ce^{4+} and [E] on R_P. The monomer conversion *vs.* time at various [Ce^{4+}] is shown in Fig. 4. The influence of Ce^{4+} amount on R_P was examined by keeping [E], [M] and [MgAl-LDH3] constant while varying Ce^{4+} concentration. The relationship between R_p and [Ce^{4+}] is determined to be $R_p \propto [Ce^{4+}]^{0.66}$.

3.2 The influence of F_d value, MgAl-LDH3 concentration and emulsifier (E) concentration on PHC formation

3.2.1 The influence of F_d value on the percentage of PHC. Keeping [Monomer] and [MgAl-LDH3] constant and the [emulsifier] higher than 20% (by volume), then allowing F_d to vary from 0.76 to 0.79, the percentage of PHC was observed to increase from 0.76 to 0.98. A linear correlation between PHC% and F_d value is observed as shown in Table 6.

3.2.2 The influence of MgAl-LDH3 concentration on the percentage of PHC. When F_d values are 0.76 and 0.78, the influence of the amount of MgAl-LDH3 on the percentage of PHC was studied. The data listed in the Table 7 indicates that MgAl-LDH3 can facilitate PHC formation. The higher the amount of MgAl-LDH3, the higher the PHC percentage. This observation supports our hypothesis that the positive charge between MgAl-LDH3 layers could enhance W/O PHC stability.

3.2.3 The influence of emulsifier concentration on the percentage of PHC. Increasing the amount of [E] while keeping the F_d value at 0.76 and 0.78, the percentage of PHC increased correspondingly. A linear correlation between [E] and the percentage of PHC is also observed as shown in Table 8.

3.3 The characteristics of MgAl-LDH3

3.3.1 The size and viscosity of layered cationic colloids of MgAl-LDH3 were changed when pH value decreased. This might due to the fact that aluminium–magnesium hydroxide colloids reacted with H^+ as the pH value decreased. This dissolution reaction resulted in the formation of smaller particles.[17]

3.3.2 The electrophoresis mobility (S) of the layered colloid in deionized water is 3.06 μcm V^{-1} S^{-1}, indicating positive charge. The zeta-potential (ξ) is 42.4 mV as determined by DXD-II video-microelectrophoresis at room temperature. The surface charge density of the micelle is calculated at 0.286 C m^{-2}, which also matches the reported data.[18]

3.3.3 The layered cationic colloids of MgAl-LDH3 were dried and ground into a powder for XRD analysis, and the results are shown in Fig. 5. Structural hydroxide is present according to three diffraction peaks at 2θ = 11.394, 23.022 and 34.882. The MgAl-LDH3 is indeed crystalline as observed by the strong diffractions and the crystal structure is 3-D hexagonal as indicated from the diffraction peaks (Table 9). The size of cell parameter c is related to M–O length, metal ion charge, anion radius, and electrostatic force of anion and hydroxide tablets.[19] The size of cell parameter a is only related to M–O length and metal ion charge.[20] As the ionic radius of Mg^{2+} (0.066 nm) is larger than Al^{3+} (0.055 nm),[21] the electrostatic force of $Al^{3+}$and OH^- is stronger than that of $Mg^{2+}$and OH^- in the same octahedron hydroxide layer. Increase of cell volume occurs as both parameter a and parameter c increased under the condition of the same anion in the layer.[22]

Table 2 The effect of [MgAl-LDH3] concentration on R_p *vs.* $M_{mixture}$[a]

10^2[MgAl-LDH3]/mol L^{-1}	dc/dt	r/s^{-1}	$10^4 R_p$/mol L^{-1} s^{-1}	ln R_p	ln[MgAl-LDH3]
0.25	0.60	0.4620	0.15	−11.11	−8.294
0.50	0.75	0.4648	0.38	−10.19	−7.601
0.75	0.87	0.4632	0.65	−9.64	−7.195
1.00	0.96	0.4639	0.95	−9.26	−6.908

[a] [$M_{mixture}$] = 2 mol L^{-1}; PHC% = 92%; [Ce^{4+}] = 0.6 × 10^{-4} mol L^{-1}; E% = 20.

Table 3 The effect of [MgAl-LDH3] concentration on R_p *vs.* acrylamide (AM)[a]

10^2[MgAl-LDH3]/mol L^{-1}	lg(d*c*/d*t*) (AM)	r/s^{-1}	$10^4 R_p$/mol L^{-1} s^{-1}	ln R_p	ln[MgAl-LDH3]
0.25	2.4693	0.4920	4.14	−7.79	−5.991
0.50	2.0173	0.4948	10.20	−6.88	−5.298
0.75	1.6501	0.4832	17.28	−6.36	−4.893
1.00	1.4000	0.4939	25.12	−5.99	−4.605

[a] [AM] = 2 mol L^{-1}; PHC% = 92%; $[Ce^{4+}] = 0.6 \times 10^{-4}$ mol L^{-1}; E% = 20.

Table 4 The effect of [MgAl-LDH3] concentration on R_p *vs.* sodium acrylate (SA)[a]

10^2[MgAl-LDH3]/mol L^{-1}	lg(d*c*/d*t*) (SA)	r/s^{-1}	$10^3 R_p$/mol L^{-1} s^{-1}	ln R_p	ln[MgAl-LDH3]
0.25	0.5958	0.4920	0.141	−8.87	−5.991
0.50	1.1890	0.4948	0.393	−7.84	−5.298
0.75	1.1401	0.4832	0.716	−7.24	−4.893
1.00	1.0400	0.4939	1.096	−6.82	−4.605

[a] [SA] = 2 mol L^{-1}; PHC% = 92%; $[Ce^{4+}] = 0.6 \times 10^{-4}$ mol L^{-1}; E% = 20.

Table 5 The effect of [MgAl-LDH3] concentration on R_p *vs.* diallyldimethylammonium chloride (DMDAAC)[a]

10^2[MgAl-LDH3]/mol L^{-1}	lg(d*c*/d*t*) (DMDAAC)	r/s^{-1}	$10^3 R_p$/mol L^{-1} s^{-1}	ln R_p	ln[MgAl-LDH3]
0.25	3.5101	0.4920	0.754	−7.20	−5.991
0.50	2.4775	0.4948	1.733	−6.36	−5.298
0.75	1.9334	0.4832	2.819	−5.87	−4.893
1.00	1.6000	0.4939	3.981	−5.53	−4.605

[a] [DMDAAC] = 2 mol L^{-1}; PHC% = 92%; $[Ce^{4+}] = 0.6 \times 10^{-4}$ mol L^{-1}; E% = 20.

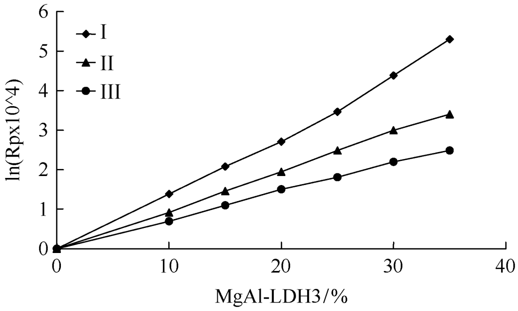

Fig. 3 The acceleration affect of MgAl-LDH3 on R_P. I: [SA] = 0.25 mol L^{-1}; II: [AM] = 0.25 mol L^{-1}; III: [DMDAAC] = 0.25 mol L^{-1}; PHC% = 92%; $[Ce^{4+}] = 0.25 \times 10^{-4}$ mol L^{-1}; E% = 20.

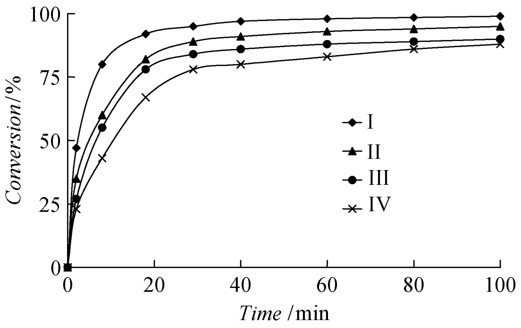

Fig. 4 Conversion–time curves at different $[Ce^{4+}]$ concentrations: $[M_{mixture}]$ = 2 mol L^{-1}; PHC% = 92%; [MgAl-LDH3] = 0.25×10^{-2} mol L^{-1}; E% = 20; $10^4[Ce^{4+}]$/mol L^{-1} = (I) 0.8, (II) 0.6, (III) 0.4, (IV) 0.2.

Table 6 The influence of F_d value on PHC%

No.	F_d	E%	PHC%
1	0.76	15	76.0
2	0.77	17	86.0
3	0.78	20	92.0
4	0.79	22	94.0

Table 7 The effect of LDH3 on PHC%

No.	LDH3%	E%	PHC%
5	2.5	18	90.0
6	2.8	20	92.0
7	3.0	22	94.0
8	3.2	26	96.0
9	3.5	30	98.0

3.4 The characteristics of the grafted polymers in form of W/O PHC

3.4.1 Stability. W/O PHC products are found to be more stable than normal W/O microemulsions, according to the tolerance storage performance of varying temperature from 4 to 40 °C for extended (16 months) storage. No oil phase separation was observed.

3.4.2 The electronic charges of the grafted copolymeric particles. The studies of electrophoresis show that the particles of the products are positively charged originating from the cationic backbone MgAl-LDH3. The grafted copolymers are cationic or zwitterionic, and all of them are amphiphilic products.

Table 8 The effect of [Ce^{4+}] concentration on R_p[a]

10^4[Ce^{4+}]/mol L^{-1}	dc/dt	r/s^{-1}	$10^4 R_p$/mol L^{-1} s^{-1}	ln R_p	ln[Ce^{4+}]
0.2	0.3960	0.4542	0.08	−7.14	−10.820
0.4	0.3128	0.4548	0.13	−6.68	−10.127
0.6	0.2725	0.4550	0.16	−6.42	−9.721
0.8	0.2471	0.4539	0.20	−6.23	−9.433

[a] [$M_{mixture}$] = 2 mol L^{-1}; PHC% = 92%; [MgAl-LDH3] = 0.25×10^{-2} mol L^{-1}; E% = 20.

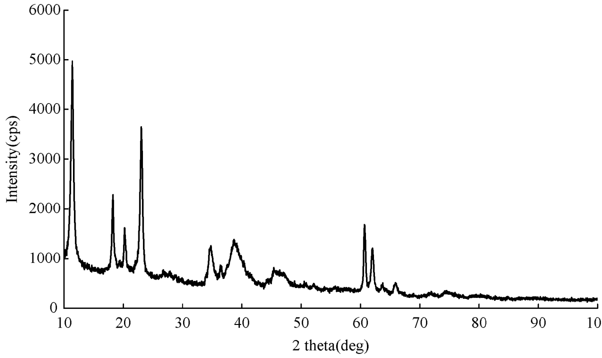

Fig. 5 XRD analysis of MgAl-LDH3.

Table 9 The cell parameters of LDH3

		Cell parameters/nm	
Sample	Crystal system	c	a
MgAl-LDH3	Hexagonal	2.421	0.3072

3.4.3 The rheological properties of the grafted copolymeric microemulsions. The rheological properties studies indicate that the microemulsion products are pseudoplastic liquids. With the enhancement of shear pressure (τ), the apparent viscosity (η) decreases. The rotational viscosity of the product is related to its viscosity-average molecular weight, which can be used to evaluate the behavior of the copolymerizations. The influence of the amount of MgAl-LDH3 on the rotational viscosity is shown in Fig. 6. A sample of acrylic acid grafted polymer was dried and ground into powder and mixed with KBr for IR analysis and the results are shown in Fig. 7. Strong carbonyl peaks were observed near 1651 cm^{-1} and the C–N stretching peak was observed at 1414 cm^{-1}. Absorption peaks of CH and CH_2 are found at 2925 and 1451, 1384 cm^{-1}, respectively; C–O absorption peaks were observed at 1171, 1119 and 1041, arising from the combination of hydroxyl from the inorganic backbone and carbon from acrylic acid, showing that acrylic acid was grafted on the inorganic backbone.

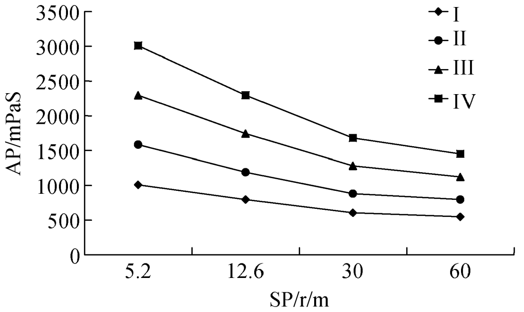

Fig. 6 The η_{iso}–τ relation of copolymer microemulsions for different MgAl-LDH3 contents. The products were obtained under the following conditions: [$M_{mixture}$] = 2 mol L^{-1}; PHC% = 92%; [Ce^{4+}] = 0.25×10^{-4} mol L^{-1}; E% = 20; 10^2[MgAl-LDH3]/mol L^{-1} = (i) 1.0, (ii) 0.75, (iii) 0.50, (iv) 0.25.

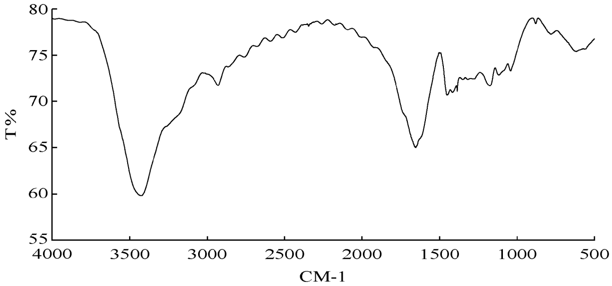

Fig. 7 IR spectrum of a grafted product having MgAl-LDH3 as backbone chain with poly-(AM).

4. Conclusion

This work describes a new hybrid grafting copolymerization within W/O polyhedral cells using the cationic colloid MgAl-LDH3 as an inorganic backbone. MgAl-LDH3 is an easy accessible, nontoxic and environment friendly material. As a carrier of positive charges, MgAl-LDH3 can facilitate the formation of PHC and stabilize PHC to conduct the polymerization successfully. This cationic backbone can be grafted with cationic, anionic and nonionic monomers to form cationic, zwitterionic and hybrid graft copolymers. The results suggest that W/O PHC is a useful polymerization medium to produce a highly concentrated W/O microemulsion, and the products are more stable than the ordinary W/O microemulsions. The W/O PHC products were pseudoplastic liquids and the pre-transformed O/W products can be diluted directly by water and potentially used as flocculants and sludge dewatering agents.

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