Reactions of Functional Polymethacrylates Grafted on Phosphate-Modified Calcium Carbonate

TAKUO NAKATSUKA, *Industrial Technology Center of Okayama Prefecture 3-18, Ifuku-cho 4 chome, Okayama 700, Japan* and SHINZO YAMASHITA, *Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan*

Synopsis

Five methacrylate monomers of methyl (MMA), dimethylaminoethyl (AEMA), 2-chloroethyl (CEMA), 2,3-epoxypropyl (GMA), and 2-hydroxyethyl (HEMA) were graft-polymerized in fine yields onto the calcium carbonate, which surface had been modified with 2,2'-dimethyl-2,2'-azobisbutyronitrile-4,4'-dicarboxyethyl bisdihydrogenphosphate (AZDP). For the GMA and HEMA, styrene (St) was used as a hydrophobic comonomer for convenience to make homopolymers easily removed. The resulting grafted polymers were treated with such reagents: methyl iodide for the poly-AEMA (pAEMA), sodium diethyldithiocarbamate (NaETC) for the poly-CEMA (pCEMA), 2,2'-iminodiethanol for the poly-co-GMA–St (pGMA–St), and *m*-trifluoromethylphenyl isocyanate for the poly-co-HEMA–St (pHEMA–St). Diffusive reflectance infrared spectroscopy indicated that these reactions resulted in excellent yields, whereas the detection of the product from NaETC and 6-chlorohexyl dihydrogenphosphate (CHP)-modified calcium carbonate failed. The results of thermal analyses (DSC–TG), gel permeation chromatography (GPC), and changes of their surface wettabilities toward water are also discussed.

INTRODUCTION

We have already reported that some dihydrogenphosphates of reactive alcohols such as 6-chlorohexanol (CHP) introduce the organic functional groups onto the surface of calcium carbonate powder.[1] The functional groups available in the phosphate should be stable under acidic conditions, because the phosphate itself is a strong acid. Moreover, a basic group as amine is unavailable for the phosphate, for the formation of zwitter ion and subsequent increasing of the calcium salt solubility in water. Therefore, alternative methods should be developed to introduce these functional groups.

In the preceding paper,[2] the modification of calcium carbonate powder with AZDP has been found to be an excellent method for graft polymerization of styrene. Hence, the graft polymerization of functional monomers and the resulting polymer reactions have been of our interest.

Functional groups in the graft polymers on the calcium carbonate will be shown to have such reactivities as those of the homopolymers in an appropriate solvent. In contrast, the chloride group in CHP on the calcium carbonate was found to be negligibly reactive in the chloride substitution. The difference in the reactivities of the chlorides in CHP and graft pCEMA seems to stem from the solvation and activation of the reaction sites in the polymer.

CCC 0021-8995/83/113549-10$02.00

EXPERIMENTAL

Materials

The CEMA was prepared by transesterification of MMA with 2-chloroethanol and purified by distillation. Other methacrylate monomers were obtained commercially and purified by distillation in the usual manner. The AZDP and CHP were synthesized as shown in the previous works,[1,2] and the purities were confirmed by tlc. The calcium carbonate powder has been characterized as described before.[1]

Procedure

Instrumentations about infrared spectroscopy, thermal analyses, and gas chromatography were referred to elsewhere.[1] The GPC analysis was carried out with a Yanagimoto Liquidchromatograph L-1100 using a RI monitor R-202. The mobile phase was tetrahydrofuran (THF) of chromatography grade.

Graft Polymerization of Methacrylates on CaCO$_3$

The methods of the surface modification of the calcium carbonate with CHP or AZDP and of the graft polymerization were described previously.[1,2] The polymerized products were precipitated using solvent systems of benzene/methanol for pMMA, pCEMA, and pGMA–St, acetone/hexane for pAEMA, and acetone/ether–petroleum ether for pHEMA–St. To remove free polymers from the precipitated products, Soxhlet extraction was conducted for 12 h by use of benzene for pMMA, pCEMA, pGMA–St, and acetone for pAEMA and pHEMA–St.

Reactions of Grafted Polymethacrylates on CaCO$_3$

Reaction of Grafted pAEMA with Methyl Iodide. After about 0.07 g of the pAEMA-graft calcium carbonate was suspended in 5 mL toluene, 2 mL of methyl iodide was added into the suspension, followed by heating the mixture at 50°C for 1 h. The powder allowed to react was filtered, washed successively with benzene and acetone, and dried *in vacuo*.

Reaction of Grafted pGMA–St with 2,2′-Iminodiethanol. To 0.12 g of pGMA–St-graft calcium carbonate suspended in 4 mL acetone, 1 mL of 2,2′-iminodiethanol, and 0.01 mL of pyridine were added. The mixture was maintained at 60°C for 6 h under stirring and the product was filtered out, washed with acetone, and dried *in vacuo*.

Reaction of Grafted pHEMA–St with *m*-Trifluoromethylphenyl Isocyanate. About 0.053 g of pHEMA–St-graft calcium carbonate was suspended in 3 mL of *N,N*-dimethylformamide (DMF) and added 0.50 mL of *m*-trifluoromethylphenyl isocyanate. The suspension was stirred at room temperature for 1 h, the powder was filtered out, washed successively with DMF and acetone, and dried *in vacuo*.

Reaction of Grafted pCEMA or CHP-Modified Calcium Carbonate with NaETC. The pCEMA-grafted calcium carbonate or CHP-modified calcium

carbonate (0.04 g) was suspended in 3 mL of DMF, and 0.11 g of NaETC was added. The mixture was kept at room temperature for 17 h, and then discharged into methanol. The product was filtered, washed with methanol, and dried *in vacuo*.

RESULTS AND DISCUSSION

Graft Polymerization of MMA, AEMA, and CEMA

The results of the graft polymerization of MMA, AEMA, and CEMA are collected in Table I, showing that the AZDP-initiating system is generally superior to AIBN-initiating system in a sense of effective polymer grafting method. No products in this table were gelled.

Graft polymerization of styrene by AZDP on calcium carbonate has been reported in the previous paper,[2] where the parameters of graftivity and graft efficiency have been referred to. Compared with the graft efficiencies of the styrene grafting, the efficiency of MMA is found to be smaller. This may be ascribable to the increased solubility of AZDP in MMA.

The graft pMMA was obtained by decomposing the polymer grafted on calcium carbonate by a hydrochloric acid–THF solution, followed by precipitation from methanol. GPC analyses on the pMMA revealed that the weight average molecular weights were 7.5×10^5 and 9.2×10^5 for the polymer of run nos. 3 and 4, in Table I, respectively. Such high molecular weights of the grafted polymers are presumably due to a gel effect on calcium carbonate surface, that is, the grafted polymer radicals restricted on their freedom in movements to result in the reduction of recombination of the polymer radicals.

The graftivity for AEMA is relatively large even in the AIBN-initiation system. The value came up to more than 10-fold larger than the values for MMA or CEMA. Such increased amount of the polymer adsorbed is explicable by the polar group of dimethylaminoethyl attached to the polymer.

For the graft polymerization of CEMA, the same tendency about graftivity and graft efficiency may be recognized as those of MMA; both the parameters exhibit high values in the AZDP-initiating system rather than the AIBN-initiating system. In the AZDP system, the graftivity increases with an increase of polymerization time, whereas the efficiency still remains almost unchanged.

Graft Copolymerization of GMA–St and HEMA–St

Homopolymers of pGMA and pHEMA were easily gelled during polymerization and showed limited solubilities in organic solvents. This is unfavorable for the separation of free polymer from graft polymer by Soxhlet extraction. To avoid this difficulty, the GMA and HEMA monomers were graft-copolymerized with styrene monomer as a hydrophobic comonomer.

In Table II, it is shown that the conversions and graftivities of copolymer GMA–St increase with increasing of the reaction time and GMA mole fraction. However, in determining the mole fraction of the graft copolymer by pyrolysis glpc, it should be noticed that the monomer yields by pyrolysis may vary with the monomer compositions. Shibazaki[3] reported that the yield of MMA under

TABLE I
Graft Polymerization of MMA, AEMA, and CEMA on AZDP-Modified CaCO$_3$[a]

Run no.	Monomer	AZDP (mg)	AIBN (mg)	Time (min)	Polymerized monomer (mg)	Conv (%)	Graftivity (%)	Grafted[b] polymer (mg)	Graft efficiency (%)
1	MMA		15.0	15	0.185	6.5	0.02	0.08	0.04
2	MMA		15.0	30	0.275	10	0.02	0.10	0.04
3	MMA	21.6		15	0.060	2.1	4.4	23.0	38
4	MMA	21.6		30	0.173	6.1	14	82.8	48
5	AEMA		15.0	60	1.126	40	0.6	2.9	0.3
6	AEMA	21.5		30	0.131	4.7	2.7	14.1	11
7	AEMA	21.0		60	0.385	14	7.9	38.5	10
8	CEMA		15.0	60	0.183	5.5	0.02	0.1	0.05
9	CEMA		15.0	90	0.755	23	0.08	0.4	0.05
10	CEMA	36.8		60	0.245	7.4	14	78.0	32
11	CEMA	37.6		90	0.610	18	29	202.4	33

[a] Polymerization conditions: CaCO$_3$ 0.50 g, temp 60 ± 0.2°C (run nos. 1–9), and 80 ± 0.2°C (run nos. 10 and 11).
[b] Grafted polymer was calculated by: grafted polymer = graftivity (%)/(100 − graftivity (%)) × CaCO$_3$.

TABLE II
Graft Copolymerization of GMA–St on AZDP-Modified CaCO₃[a]

Run no.	Mole fraction of GMA in monomer	AZDP (mg)	AIBN (mg)	Time (min)	Conv (%)	Graftivity (%) GMA	St	Mole fraction of GMA in graft polymer
21	0.33		15.0	30	4.0	0.005	0.002	0.6
22	0.33		15.0	60	7.2	0.021	0.016	0.5
23	0.67		15.0	30	7.2	0.023	0.012	0.6
24	0.67		15.0	60	15	1.9	0.34	0.8
25	1.00		15.0	30	64	nd[b]	nd[b]	nd[b]
26	0.33	36.0		30	0.2	0.90	0.45	0.60
27	0.33	36.2		90	2.3	3.5	2.3	0.52
28	0.67	36.1		30	1.4	3.4	1.0	0.71
29	0.67	36.6		90	6.0	15.3	5.3	0.68
30	1.00	36.8		30	8.4	nd	nd	nd

[a] Polymerization conditions: CaCO₃ 0.50 g, temperature $60 \pm 0.2°C$.
[b] nd = not determined because of product gelation.

pyrolysis of MMA–St copolymer at 450°C, decreased with an increase of MMA fraction. Thus, a GMA–St copolymer without calcium carbonate was prepared and analyzed (Table III). The results in Table III show that the mole fractions of GMA determined by the pyrolysis glpc are smaller than those by elemental analysis. Therefore, the real values of GMA mole fraction in Table II should be slightly enlarged.

In the graft copolymerization of HEMA–St, the styrene monomer was fed by 0.33 mole fraction, the product with run number 32 in Table IV, was gelled. In this graft copolymerization, the graftivity as well as monomer conversion is increased with increasing reaction time and HEMA fraction. The HEMA fractions in polymer are generally larger than the HEMA feed fractions. These findings are in agreement with homogeneous copolymerization.[4]

Relative graftivity of the two monomers of GMA–St or of HEMA–St are easily estimated by diffusive reflectance infrared spectroscopy. Characteristic peaks

TABLE III
Determination of Mole Fraction of GMA–St Copolymer[a]

Run no.	41	42	43
In monomer			
Mole fraction of GMA	0.67	0.59	0.33
Conv of monomers (%)	13.6	11.3	3.6
In Polymer			
By pyrolysis glpc			
Content of GMA[b] (wt %)	74	68	57
Content of St[b] (wt %)	32	35	48
Mole fraction of GMA	0.63	0.59	0.46
By elemental analysis			
Content of carbon (%)	68.48	70.04	75.01
Mole fraction of GMA	0.72	0.67	0.52

[a] Polymerization conditions: GMA + St 3.0 mL, AIBN 3.7×10^{-2} mol/L, temperature $60 \pm 0.2°C$, time 30 min.
[b] Contents of GMA and St were determined by calibrating homopolymers.

TABLE IV
Graft Copolymerization of HEMA–St on AZDP-Modified $CaCO_3$[a]

Run no.	Mole fraction of HEMA in monomer	AZDP (mg)	AIBN (mg)	Time (min)	Conv (%)	Graftivity (%)		Mole fraction of HEMA in graft polymer
						HEMA	St	
31	0.33		15.0	60	12	0.15	0.16	0.4
32	0.67		15.0	30	12	nd[b]	nd[b]	nd[b]
33	0.33	37.5		30	2.6	7.7	3.9	0.61
34	0.33	37.0		60	5.7	12.6	8.3	0.55
35	0.67	37.2		15	1.5	8.5	1.8	0.79
36	0.67	38.1		30	4.9	19.4	6.3	0.71

[a] Polymerization conditions: $CaCO_3$ 0.50 g, temperature 60 ± 0.2°C.
[b] nd = not determined because of product gelation.

TABLE V
Analyses of Graft Copolymer on $CaCO_3$

Run no.	Monomer	Peak height ratio on diffusive reflectance IR	Mole fraction of GMA or HEMA determined by pyrolysis glpc
37	GMA–St	$I_{907}/I_{760} = 0.25$	0.68
38	GMA–St	$I_{907}/I_{760} = 0.15$	0.52
39	HEMA–St	$I_{3500}/I_{760} = 1.92$	0.71
40	HEMA–St	$I_{3500}/I_{760} = 1.73$	0.55

of the three monomers were compared; 3500, 907, and 760 for HEMA, GMA, and St, respectively. The results are shown in Table V, where the data on pyrolysis glpc are also reproduced. The relative infrared peak intensities are demonstrated to reflect well their corresponding monomer graftivities.

Reactions of Graft Polymethacrylates

In order to evaluate the reactivities of the graft polymers, we treated the functional groups with reactive agents: Dimethylaminoethyl group in the graft pAEMA was quaternarized with methyl iodide. A similar reaction of homogeneous poly(diethylaminoethyl methacrylate) with methyl iodide has been reported to proceed quantitatively.[5]

Comparison of the infrared spectra of the pre- and post-treated powder with methyl iodide shows that the quaternarization seems to change completely (Fig. 1): A peak at 2762 cm^{-1}, ascribable to the N-methyl group, disappeared after the reaction.

The pAEMA-grafted calcium carbonate powder was hydrophobic and floated on water for several hours. In contrast, the quaternarized pAEMA grafted powder exhibited hydrophilicity and the surface wettability toward water was dramatically altered. The quaternarized powder sank into water in a few seconds, and swelling of the graft polymer was observed after a few minutes.

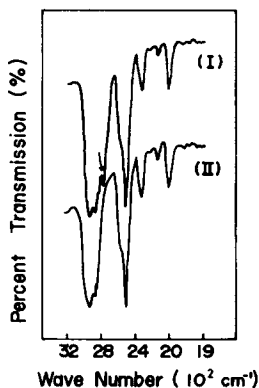Differential scanning calorimetry and thermogravimetric analyses (DSC–TG)

Fig. 1. Diffusive reflectance IR spectra of (I) pAEMA graft $CaCO_3$ and (II) MeI-treated pAEMA graft $CaCO_3$ (KBr 10%).
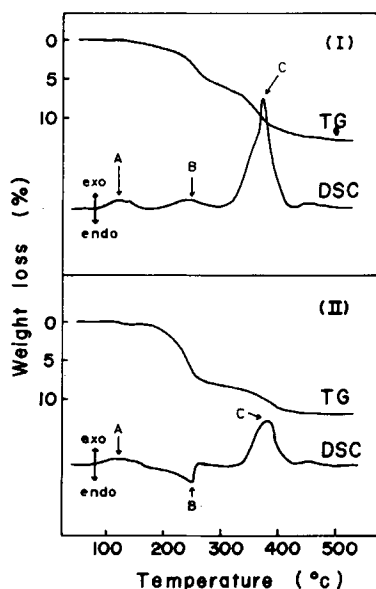
Fig. 2. DSC-TG curves for (I) pAEMA graft $CaCO_3$ and (II) MeI-treated pAEMA graft $CaCO_3$ measured in air flow of 50 mL/min and at a heating rate of 10 deg/min.

in air also presented some information about the ammonium salt formation (Fig. 2). The three peaks A–C may be assigned: A is due to the thermal decomposition of AZDP survived after polymerization; B and C are partial and complete decomposition of the graft polymer, respectively. Comparison of (I) and (II) in Figure 2 makes it clear that, after treating with methyl iodide, the peak B has become endothermic and the peak C has been reduced. These phenomena were also observed when the thermal analyses were carried out under nitrogen atmosphere. Therefore, the quaternarization should lead the graft polymer to suffer oxidation to lesser extent in air at above 250°C (peak B).

   2,2′-Iminodiethanol has been reported to react with a copolymer of GMA–acrylonitrile in a good yield.[6] Hence the epoxy group in the graft pGMA–St was
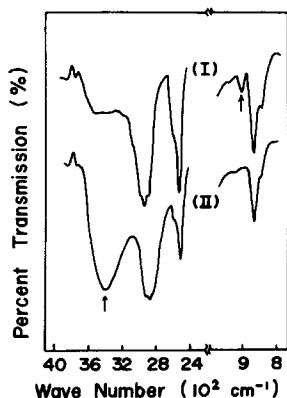

Fig. 3. Diffusive reflectance IR spectra of (I) pGMA–St graft $CaCO_3$ and (II) $NH(CH_2CH_2OH)_2$-treated pGMA–St graft $CaCO_3$ (KBr 10%).

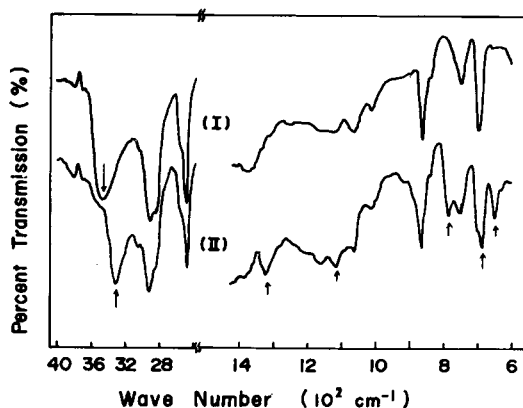Fig. 4. Diffusive reflectance IR spectra of (I) pHEMA–St graft $CaCO_3$ and (II) m-$CF_3C_6H_4NCO$-treated pHEMA–St graft $CaCO_3$ (KBr 10%).

treated with the imino alcohol. The infrared spectra of Figure 3 give a spectral support for the amination of the graft polymer: a broad peak at 3400 cm^{-1} may be assigned to the introduced and produced hydroxy group. The epoxy group at 907 cm^{-1} has disappeared. The aminated GMA–St-grafted calcium carbonate powder was found to get some more hydrophilicity.

A treatment of pHEMA–St-grafted calcium carbonate with m-trifluo-romethylphenyl isocyanate has caused a complete change in their surface nature. The original pHEMA–St-grafted powder was gradually wetted with water; however, the isocyanate-treated powder would not sink after vigorous stirring. The following spectral changes accompanied the treatment: a broad hydroxy peak at about 3500 cm^{-1} disappeared and a new peak appeared at 3330 cm^{-1},
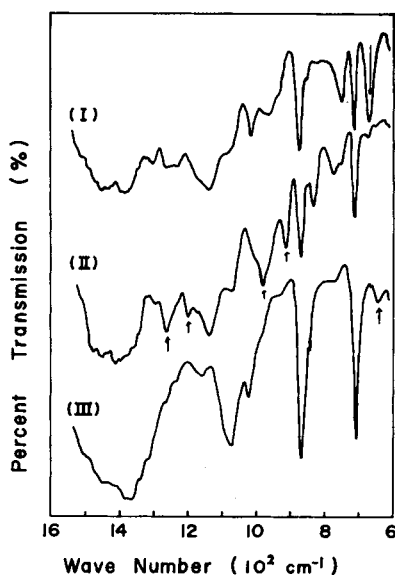

Fig. 5. Diffusive reflectance IR spectra of (I) pCEMA graft $CaCO_3$, (II) NaETC-treated pCEMA graft $CaCO_3$, and (III) NaETC-treated CHP-modified $CaCO_3$ (KBr 10%).

which is ascribable to N—H stretching in the urethane structure. Other peaks due to the m-trifluoromethylphenyl group were found at 1327, 1123, 789, 693, and 655 cm^{-1}.

A substitution of primary alkyl halide in a polymer with NaETC is known to undergo an excellent yield in a polar solvent.[7] The pCEMA-grafted calcium carbonate powder was confirmed to react with NaETC in DMF by infrared spectroscopy (Fig. 5): the peak of C—Cl at 665 cm^{-1} is almost unrecognizable and the peaks of the carbamate resulted in appearances at 1260, 1195, 975, and 910 cm^{-1}.

In contrast to the graft pCEMA, the CHP on the calcium carbonate surface has not exhibited such a high reactivity toward NaETC in DMF. The peak due to C—Cl in the CHP did not decrease in height. Spectrum III in Figure 5 was obtained for the NaETC-treated, CHP-modified powder and was the same as that of original CHP-modified calcium carbonate powder. The high reactivity of the graft pCEMA is convincingly thought to stem from the solvation and activation of the reaction sites in the graft polymer.

References

1. T. Nakatsuka, H. Kawasaki, K. Itadani, and S. Yamashita, *J. Appl. Polym. Sci.*, **27**, 259 (1982).

2. T. Nakatsuka, H. Kawasaki, S. Yamashita, and S. Kohjiya, *J. Colloid Interface Sci.*, **93**, 277 (1983).

3. Y. Shibazaki, *Kohbunshi Kagaku*, **21**, 125 (1964).

4. T. Okano, J. Aoyagi, and I. Shinohara, Nippon Kagaku Zasshi, **1976**, 161 (1976).

5. T. Shimomura, Y. Kuwabara, E. Tsuchida, and I. Shinohara, *Kogyo Kagaku Zasshi*, **71**, 283 (1968).

6. Y. Iwakura, T. Kurosaki, and N. Nakabayashi, *Makromol. Chem.*, **44**, 570 (1961).

7. S. Kohjiya, S. Ohta, and S. Yamashita, *Polym. Bull.*, **5**, 463 (1981).