Controlled Structure Methacrylic Copolymers as Dispersants for Ceramics Processing

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Group-transfer polymerization was used to make block and random copolymers of methacrylates with a small fraction of methacrylic acid units. These polymers bind strongly to aluminum oxide surfaces through the acid groups and act as efficient dispersants for alumina particles in polar organic solvents such as esters and ketones. The dispersion efficiency was measured by the sediment density method as a function of chain length and composition. Ceramic green tapes and sintered ceramic sheets were made using these dispersants and poly(butyl methacrylate) as a binder.

Introduction

The production of high-density ceramics by sintering of powders depends on forming a ceramic "green body" with closely packed particles, preferably with a particle size of much less than 1 mm. Production of such fine powders tends to give aggregates, bound together by covalent or hydrogen bonds at the points of contact. Typical ceramics production involves breaking up these aggregates by milling the powder into a suitable liquid to form a slip. The slip solvent usually also contains a polymer, which acts as a binder to give mechanical strength to the green body. This slip is converted into the appropriate form by processes such as centrifugal casting or doctor-blade coating, and the suspending liquid removed by drying. To achieve close packing, it is believed that the individual particles must be allowed to come together under conditions where the interparticle forces are repulsive, so that the particles pack into the green body as individuals rather than agglomerating into loosely packed clumps. The extent of dispersion of the powder into the slip liquid is crucial in determining the microstructure and sinterability of the green body.

The dispersion force between two particles in a medium of different polarizability is always attractive.[2] In aqueous media this attractive force can be overcome by the electrostatic repulsion of excess charge on the particle surface, which can readily be controlled by the pH and ionic strength of the liquid. This combination of a dispersive attraction and a Coulombic repulsion is described by DLVO theory.[3]

In nonaqueous media and in aqueous suspensions at high ionic strength or particle concentration, electrostatic repulsion is easily overcome. Most successful dispersants for these cases are believed to act by steric repulsion.[4] Part of the dispersant (the "head") is attached to the particle surface, while a "tail" is solubilized by the surrounding liquid. Each particle is then surrounded by a cloud of tails. Osmotic interactions oppose overlap of tails on different particles and so make a barrier to close approach of particles. Numerous steric dispersants for oxide particles have been described, including fish oil,[5] titanates,[6] silanes,[7] aromatic carboxylic acids,[8] and styrene–methyl methacrylate block copolymers.[9]

In principle, polymers of controlled structure are interesting dispersants, but they have been relatively little studied in the context of ceramics processing. Any dispersant has to be compatible with the binder polymer, and the choice of binder is limited by the condition that it must burn out of the green body during firing, without leaving any carbonaceous or ion-containing residues.

Since methacrylate polymers degrade very cleanly, they are attractive candidates as binders and dispersants. In previous work,[10,11] a novel system was described for forming thin ceramic sheets by casting a slip of alumina or barium titanate in a methacrylate monomer and polymerizing this. One disadvantage of this system was that few dispersants were effective for alumina in methacrylates. The use of methacrylate polymers as dispersants has also been limited by the synthetic problems of making them with controlled structures; methacrylates are sufficiently reactive toward nucleophilic attack at the ester group to cause severe problems in anionic polymerization.

A recent development in synthesis of methacrylic polymers was the introduction by Webster et al.[12,13] of group-transfer polymerization (GTP). This involves a catalyzed Michael-type addition, initiated by a silyl ketene acetal with appropriate catalysis. It is a living polymerization which can be carried out under relatively simple conditions with either acrylates or methacrylates as monomers, yielding monodisperse polymers with a high degree of structure control.[14] Simms and Spinelli[15] have described the use of GTP for making acrylic block copolymers which were used as dispersants for pigments in high-solids coatings. They claimed that the narrow molecular weight distribution alloys higher solids content, better pigment dispersion, and better color development than do conventional dispersants.

There are clear advantages in using GTP to produce copolymers with potential as dispersing agents for ceramics powders. Among the questions of interest which could be addressed with controlled polymer structures are the

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length of the tails necessary for good dispersion, the effect of different dispersing solvents, the comparison between block and random copolymers, and the effect of different tail compositions. In addition it may be preferable for safety and environmental reasons to use ester and ketone solvents rather than hydrocarbons in ceramics processing. Methacrylic polymers are good candidates for use as dispersants with these solvents.

In this paper we discuss the effect of molecular architecture on the action of dispersants based on methacrylic acid–methacrylate copolymers with well-defined compositions and sequence distributions, prepared by GTP.

Experimental Section

Polymer Synthesis. All of the monomers were obtained from commercial sources. They were freed of inhibitors by washing with aqueous NaOH then dried and fractionally distilled. Before being used in polymerizations, they were further dried over calcium hydride. For GTP, the acid group of methacrylic acid must be masked, since active hydrogens interfere. This was done by reaction with hexamethyldisilazane, according to the procedure of Chapman and Jenkins.[16] The initiator for all polymerizations was 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (methyl trimethylsilyl dimethyl ketene acetal, MTS), prepared by the method of Ainsworth et al.,[17] modified as described by Eastmond and Grigor.[18] Polymerizations were catalyzed by bifluoride ions derived from the in situ hydrolysis of tris(dimethylamino)sulfonium difluorotrimethyl silicate, purchased from Aldrich and used as a 1M solution in acetonitrile. Polymerizations were performed in glass apparatus under nitrogen, using standard syringe-pumping methods. All glassware was oven dried at 175 °C and flamed out under vacuum before use. In a typical experiment, a solution of 1.9 ml (9.3×10^{-3} mol) MTS in 100 mL of THF was prepared under nitrogen. To this solution was added 1 mL of a 1 M solution of the catalyst followed by slow addition of 50 mL (0.47 mol) of freshly distilled methyl methacrylate. The exothermic reaction was controlled by the rate of monomer addition, to maintain gentle reflux of the solvent. When the temperature had returned to ambient, the living chains were extended by addition of freshly prepared trimethylsilyl methacrylate (7.5 mL, 0.047 mol), giving a second exotherm. After the reaction was completed, the active centers were destroyed, and the protecting silyl groups removed, by addition of 10 mL of methanol and stirring for 1 h. The polymer was finally recovered by precipitation into cold, acidic methanol. It was reprecipitated from chloroform solution into cold methanol and dried in vacuo. Similar procedures were used to prepare statistical copolymers, except that the mixed monomers were added simultaneously.

Polymer Characterization. Polymers were characterized by the IR (Perkin-Elmer 1720 FTIR) spectra of thin films cast from dichloromethane solution and by ^{1}H and ^{13}C NMR (Bruker WM 360) spectra in $CDCl_3$ or CD_3OD solutions. Acid group concentrations were estimated by titration of a solution of the copolymer in acetone with NaOH solution in methanol to the phenolphthalein endpoint. In some cases we attempted to measure low concentrations of acid groups using the colorimetric method of Palit and Chosh,[19] which depends on the color change of rhodamine 6G from yellow to pink in the presence of low concentrations of acid. The color change was determined spectrophotometrically at 514 nm, and the analysis was calibrated using dilute solutions of formic acid in benzene.

Molecular weight characterization was carried out by GPC, using the SERC service at RAPRA. All chromatograms were obtained using THF solutions at room temperature with calibration by polystyrene standards. Since Mark–Houwink parameters were not available for most of the polymers and light-scattering detection is unreliable for copolymers, all molecular weights are reported as polystyrene equivalents.

Assessment of Dispersants. The ceramic powder used in all experiments was Reynolds R172 DPM alumina. Scanning electron microscopy showed near-spherical particles with diameters around 0.2–0.3 mm. The specific surface area was determined by a chromatographic BET method, calibrated with NPL standard alumina and found to be 7.2 ± 0.1 m^2 g^{-1}. For most experiments the alumina was dried at 150 °C in a circulating-air oven for 24 h before use.

Solvents used in dispersion testing were obtained commercially and were dried by normal laboratory methods. Dispersions were prepared by mixing the desired quantity of alumina with a solution of the dispersing agent and agitating manually and ultrasonically for at least 1 h. For larger scale preparations of green bodies, the dispersion of alumina in solvent, containing dispersing agent and binder polymer, was prepared by ball milling the components together for 24 h.

Concentrations of adsorbed polymer on the alumina surface were estimated from the intensity of the 1729-cm^{-1} IR vibration of the ester carbonyl group, using diffuse-reflectance FTIR spectroscopy, calibrated with samples prepared from a standard solution of poly(*n*-butyl methacrylate) in CH_2Cl_2. Samples were examined as 10 wt % dispersions in dried KBr, using a polymer-free sample as a reference for spectral subtraction.

For gravitational settling experiments, the dispersion was prepared in a stoppered 25-mL graduated cylinder and allowed to stand at room temperature until settling was complete (up to 1 month). The height of the top surface of the solid bed, measured as the main front of particles above which the suspension is only thinly cloudy, was monitored as a function of time and the final bed volume used to calculate a packing density. All experiments were carried out in duplicate.

For centrifugal settling each dispersion was centrifuged at approximately 2000G for 1 h. The clear supernatant liquid was removed carefully, and its volume determined. Since the original volume of solvent was known, the packing density could be calculated. All experiments were performed in duplicate.

Results

Polymer Synthesis. Using the standard GTP method, we prepared copolymers with methyl methacrylate (MMA), *n*-butyl methacrylate (BuMA), or 2-ethylhexyl methacrylate (HMA) as the major component. Trimethylsilyl methacrylate blocks were incorporated into each of these polymers. These blocks hydrolyzed to methacrylic acid (MAA) during precipitation of the polymer in cold acidic methanol. Polymerizations were carried out in THF solution with MTS as initiator and a bifluoride catalyst. For all polymerizations the molar ratio of ester and acid monomers was maintained at 1:10, but the MTS concentration was varied to give molecular weights in the range 4×10^3–4×10^4.

Block copolymerizations were performed by sequential monomer addition. In the case of MMA and BuMA, copolymers were typically obtained in very close to 100% yield, and there was little effect of the sequence of monomer addition, implying that either type of chain end can initiate the polymerization of the other monomer. Polymerizations of the silylated acid were typically slower than those of the ester monomers, presumably due to competing coordination of the bifluoride catalyst with the silicon atoms of the monomer and of the active center. We have found that copolymerizations involving high concentrations of the silylated monomer are inefficient, again suggesting that competing coordination of the nucleophile by the various silyl groups has a deleterious effect on polymerization.[20] The polymerization of HMA initiated by MTS was found to be slow and gave low (<60%) conversions to polymers which could not be chain extended with

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Table I. Characterization of Copolymers Prepared by GTP

polymer	$M_n/10^4$ theor	$M_n/10^4$ GPC	D	conv %	acid content (wt %) spectrophotometry	acid content (wt %) titration
poly(BuMA)	0.43	0.60	1.23	98	0	0
poly(BuMA-*co*-MAA)						
1	0.43	0.59	1.18	99	4.5	5.6
2	1.14	2.46	1.12	98	4.20	5.63
3	2.27	3.22	1.22	98	4.28	5.63
4	4.54	28.9	3.13	40	4.76	5.98
poly(BuMA-*b*-MAA)						
1	0.43	0.62	1.29	95	3.25	5.08
2	1.14	2.37	1.26	96	3.46	5.58
3	2.27	3.4	1.58	96	3.52	5.16
4	4.45	24.20	3.09	45	2.94	4.86

MAA or with MMA, implying loss of the active centers. Surprisingly, initiation of HMA by preformed MAA polymer gave near-quantitative conversions to block copolymer. Statistical copolymerizations of HMA and MAA also gave high (>95%) yields.

Table I shows some typical analytical data for the copolymers. For molecular weights below 10^4, the products are of narrow molecular weight distribution (D) with M_n close to the value calculated from the molar ratio of initiator and monomer, bearing in mind that the GPC data give PS-equivalent molecular weights. The polydispersity index increases and the yield falls as the desired molecular weight increases. Increased polydispersity could be due to inherent termination or to termination by adventitious impurities. In the present case the latter seems more probable. As the desired molecular weight increases the required concentration of catalyst and initiator decrease and it becomes much more difficult to maintain purity. Farnham and Sogah[21] reported a polydispersity of 4.3, when they attempted to prepare PMMA with $M_n = 2.5 \times 10^4$. The acid contents of all copolymers were reasonably close to the expected values, when measured by titration. Values measured by the colorimetric method were much less reliable. In particular, the values were lower for block copolymers than for statistical copolymers of the same nominal composition. It appears that the protonation of the rhodamine G to give the analyte species depends on the strength of the acid. The acid groups on the polymer are less effective than those of the calibrant (formic acid) in inducing the color change, and the effect is sensitive to the sequence distribution of the acid groups. We feel that the colorimetric method should be regarded as unreliable.

In principle, polymerization of a mixture of monomers could lead to a blocky copolymer, depending on the relative reactivity ratios of the two monomers. Very few data are available for reactivity ratios in GTP copolymerization, although Jenkins et al.[22] found $r_1 = 0.44 \pm 0.03$ and $r_2 = 0.26 \pm 0.04$ for GTP copolymerization of MMA (M1) and BuMA (M2).

For all of our low-molecular-weight copolymers, the GPC elution curves were single sharp peaks, with no shoulders, implying that the products were true copolymers. IR spectroscopy showed broadening under the O–H stretching vibration between 3700 and 3400 cm^{-1}, characteristic of the hydrogen-bonded –OH groups. In statistical copolymers, where the MAA groups should be relatively isolated, the carbonyl stretching absorption at 1729 cm^{-1} showed a sharp shoulder at 1700 cm^{-1}. In block copolymers the effect was smaller and the carbonyl band was typically featureless but significantly broader compared to polymers containing no MAA. We were unable to resolve the two monomer units in either block or statistical copolymers by either ^{1}H or ^{13}C NMR at the highest field (360 MHz) available to us.

Table II. Effect of Drying Alumina Powder on Dispersion

drying condition	% packing density homopolymer[a]	% packing density block copolymer[b]	% packing density random copolymer[c]
as received	37.9	55.0	57.9
air dried at 150 °C	50.1	55.8	59.7
vacuum dried at 0.1 mmHg/150 °C	52.5	55.5	58.6

[a] $M_n = 0.59 \times 10^4$, $D = 1.30$. [b] $M_n = 2.37 \times 10^4$, $D = 1.26$, acid content (wt %) = 5.58. [c] $M_n = 2.46 \times 10^4$, $D = 1.12$, acid content (wt %) = 5.63.

Further evidence that the statistical copolymers were different from the block copolymers was that the solubility properties of the two polymers were very different. For example, statistical copolymers could easily be precipitated from chloroform solution into methanol; block copolymers produced swollen gels unless the methanol was acidified with HCl. None of the copolymers had any water extractable (MAA) fraction.

We conclude that GTP is a very satisfactory method for preparing the low-molecular-weight block and statistical copolymers of methacrylic monomers required for dispersion studies.

Dispersion Testing. The main test of dispersant efficiency that we use is the sediment volume.[23] Alumina powder is ultrasonically agitated into a solution of the dispersant. The resulting dispersion is either allowed to settle under gravity or is centrifuged. The packing density of the final particle bed is measured and expressed as a fraction of the theoretical density of a fully dense ceramic. Perfect packing of spheres would yield a density of 74%; random close packing of spheres gives 69% density. Agglomerated particles typically settle rapidly to packing densities of the order of 20%. Dispersants giving packing densities in the range from 30% to 60% are currently regarded as good. A ceramic green body will sinter reasonably successfully if the packing density exceeds about 30%, but the final density after firing continues to improve with improved green density.

Effect of Powder Hydration, Time, and Dispersant Concentration. Centrifuge sediment density tests were run with BuMA homopolymer and its block and statistical copolymers with MAA, using as-received alumina and the same material after it had been dried to remove physisorbed and chemisorbed water. As can be seen in Table II there is little effect on packing density for the copolymers with methacrylic acid binding groups, but residual water does interefere with dispersion by methacrylate homopolymers. This presumably reflects the strong binding of the acid groups to the particle surface, as compared with the methacrylate ester groups which bind weakly and can be displaced by water. In all other tests the alumina was dried for 24 h at 150 °C before use.

Sediment density was unaffected if the powder was left to react with the dispersant for 3 days before testing. The dispersant–surface interaction must be complete within

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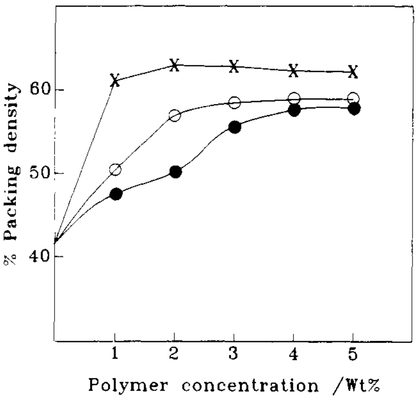

Figure 1. Effect of polymer concentration on centrifuged sediment density of alumina in toluene: (×) poly(BuMA-*co*-MAA), $\bar{M}_n = 5.9 \times 10^3$; (○) poly(BuMA-*b*-MAA), $\bar{M}_n = 6.2 \times 10^3$; (●) poly(BuMA) homopolymer $\bar{M}_n = 5.9 \times 10^3$.

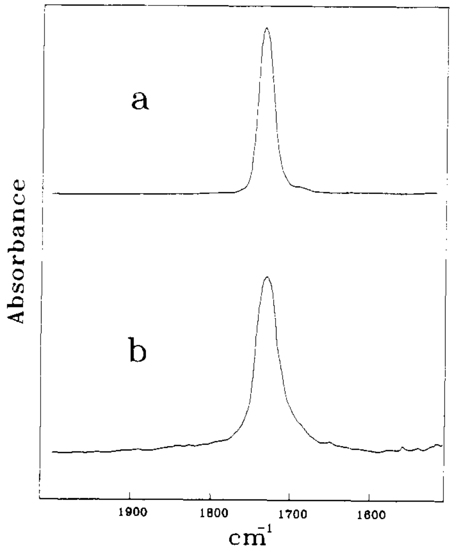

Figure 2. (a) IR (film) spectrum of poly(BuMA) homopolymer before adsorption; (b) DRIFT spectrum of adsorbed polymer onto alumina: >C=O stretching region only.

the hour it takes to set up a normal test.

In principle, the dispersant will be fully effective only if sufficient is added to cover the powder surface. If too little is present, any "bare spots" will allow particle–particle contact. With the copolymers one might expect that sufficient must be added to cover all the surface sites with methacrylic acid groups. As can be seen in Figure 1, saturation occurs in the range 2–3% dispersant in solvent. In subsequent experiments 2% copolymer in solvent was taken as the standard concentration.

Surface Adsorption of Polymers. Diffuse reflection infrared spectroscopy (DRIFTS) was used to examine adsorbed polymer on the alumina surface and to estimate its concentration.

In the case of the homopolymers, the sharp peak at 1729 cm^{-1}, due to the ester carbonyl group, broadens on adsorption and shows a shoulder at about 1680 cm^{-1}, as shown in Figure 2, due to hydrogen-bonding interactions with the surface. Since this change appears as a shoulder, only a small fraction of the carbonyls are directly interacting with the surface and there may be a range of such interactions. Work by Sun et al.[24] has shown that, at least

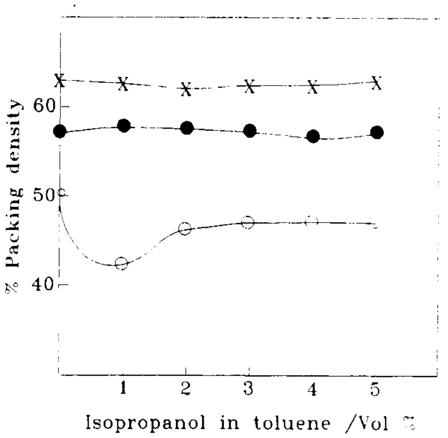

Figure 3. Effect of small additions of isopropyl alcohol on centrifuged sediment density of alumina powder in toluene: (×) poly(BuMA-*co*-MAA) $\bar{M}_n = 5.9 \times 10^3$; (●) poly(BuMA-*b*-MAA) $\bar{M}_n = 6.2 \times 10^3$; (○) poly(BuMA) homopolymer $\bar{M}_n = 5.9 \times 10^3$.

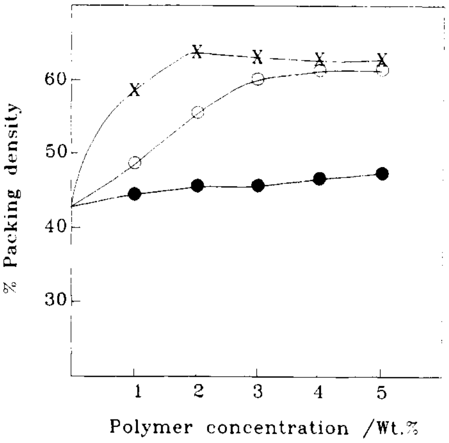

Figure 4. Effect of polymers on centrifuged sediment density of alumina powder in acetone: (×) poly(BuMA-*co*-MAA), $\bar{M}_n = 5.9 \times 10^3$; (○) poly(BuMA-*b*-MAA), $\bar{M}_n = 6.2 \times 10^3$; (●) poly(BuMA) homopolymer, $\bar{M}_n = 5.9 \times 10^3$.

after heating, some ionic carboxylate can form when commercial PMMA is in contact with an alumina surface; under our conditions there was no detectable peak at 1565 cm^{-1}, characteristic of carboxylate anions. All of the homopolymers were easily removed from the particle surface by simple washing.

For copolymers, the alumina powder was sedimented from a 2% solution of dispersant in the normal way, then the concentration of adsorbed copolymer was determined on the dried powder and on powder which was successively washed with fresh solvent, washed with boiling solvent in a Soxhlet extractor for 10 h, and refluxed with ethyl acetate for 72 h. Table III shows the data for BuMA–MAA copolymers. The copolymer is adsorbed at a level of 1.5–2 mg m^{-2} and is very resistant to loss by the washing treatments. This adsorption is apparently due to chemical reaction of the carboxylic acid group with the surface, as evidenced by the disappearance of the acid shoulder at 1700 cm^{-1} on the carbonyl peak at 1729 cm^{-1}. A peak at 1565 cm^{-1} appears on adsorption, due to the formation of carboxylate anions at the surface.[22]

Effect of Binding Groups and Solvent. While Figure 1 shows that the BuMA homopolymer and the copolymers with MAA are effective dispersants in toluene, we can see in Figure 3 that addition of a small amount of isopropyl alcohol displaces the homopolymer from the surface. Likewise, (Figure 4) the homopolymer is not a good dispersant in acetone because the ester function does not bind to the surface in strong preference to the ketone carbonyl.

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Table III. Quantitative Determination of the Amount and Area Occupied by Adsorbed *n*-BuMA/MAA Copolymers onto Alumina Powder Surface

solvent	method of washing	block copolymer[a]		random copolymer[b]	
		amt of polym adsorbed/mg m^{-2}	area occupied by polym/$Å^2$	amt of polym adsorbed/mg m^{-2}	area occupied by polym/$Å^2$
toluene	UWS[c]	2.082	423	2.091	403
	3 TW[d]	1.906	462	1.968	427
	Soxhlet[e]	1.662	530	1.823	462
	reflux[f]	1.696	520	0.998	843
isopropyl alcohol	UWS[c]	1.869	471	1.761	477
	3 TW[d]	1.670	527	1.675	502
	Soxhlet[e]	1.410	625	1.306	643
	reflux[f]	1.471	598	1.122	750

[a] $\bar{M}_n = 6.20 \times 10^3$, $D = 1.29$, acid content (wt %) = 5.08. [b] $\bar{M}_n = 5.92\ 10^3$, $d = 1.18$, acid content (wt %) = 5.60. [c] UWS = unwashed samples. [d] 3 TW = three times washing with fresh solvent. [e] Soxhlet = continuous Soxhlet extraction for 10 h. [f] Reflux = refluxing in ethyl acetate for 72 h.

Table IV. Effect of Different Organic Solvents on Dispersion Properties of MMA/MAA Copolymers on Alumina Suspensions

solvt	ΔSP	% packing density					
		centrifuge settling			gravity settling		
		no polym	block[a]	random[b]	no polym	block[a]	random[b]
MMA	0.33	45.6	46.5	53.6	26.3	33.9	48.6
acetone	0.40	42.8	44.2	59.3	24.2	32.0	53.2
ethyl acetate	0.40	40.6	42.6	55.3	24.5	30.9	52.1
toluene	0.60	41.6	45.7	44.6	24.3	37.2	27.1

[a] Block copolymer, $\bar{M}_n = 1.08 \times 10^4$, $D = 1.28$. [b] Random copolymer, $\bar{M}_n = 1.03 \times 10^4$, $D = 1.33$.

Table V. Packing Density of Alumina Dispersed in Different Organic Solvents, Using 2% of Block and Random Copolymers of *n*-BuMA/MAA

solvt	ΔSP	% packing density					
		centrifuge settling			gravity settling		
		no polym	block[a]	random[b]	no polym	block[a]	random[b]
toluene	0.15	41.6	56.9	61.6	24.3	53.0	59.9
ethyl acetate	0.35	40.6	52.8	58.9	24.5	43.5	57.5
n-BuMA	0.55	41.0	54.1	58.7	24.8	48.6	57.6
acetone	1.55	42.8	55.9	59.2	24.2	48.1	53.5
isopropyl alcohol	2.75	46.9	49.6	59.0	31.9	32.2	34.3

[a] Block copolymer, $\bar{M}_n = 2.37 \times 10^4$, $D = 1.26$. [b] Random copolymer, $\bar{M}_n = 2.46 \times 10^4$, $D = 1.12$.

Table VI. Packing Density Obtained from Dispersion of 2% of 2-HMA/MAA Copolymers in Alumina Using Different Organic Solvents

solvt	ΔSP	% packing density					
		centrifuge settling			gravity settling		
		no polym	block[a]	random[b]	no polym	block[a]	random[b]
2-EHMA	0.17	38.1	56.3	56.5	25.7	57.8	58.1
toluene	1.20	41.6	56.0	58.1	24.3	53.8	55.4
ethyl acetate	1.40	40.6	57.6	59.2	24.5	56.9	57.0
acetone	2.20	42.8		53.3	24.2		27.9
isopropyl alcohol	3.50	46.9		54.6	31.9		26.6

[a] Block copolymer, $\bar{M}_n = 1.40 \times 10^4$, $D = 1.20$. [b] Random copolymer, $\bar{M}_n = 1.98 \times 10^4$, $D = 1.23$.

Table VII. Effect of 2% of BuMA/γMPS Copolymers on the Dispersion of Alumina in Different Organic Media

solvt	ΔSP	% packing density					
		centrifuge settling			gravity settling		
		no polym	block[a]	random[b]	no polym	block[a]	random[b]
toluene	0.15	41.6	50.6	53.6	24.3	41.1	42.7
ethyl acetate	0.35	40.6	52.9	54.0	24.5	46.0	48.4
n-BuMA	0.55	41.0	49.1	54.3	24.8	40.2	44.2
acetone	1.15	42.8	50.4	50.0	24.2	42.4	43.2
isopropyl alcohol	2.75	46.9	48.2	49.4	31.9	24.1	24.2

[a] Block copolymer, $\bar{M}_n = 1.91 \times 10^4$, $D = 1.71$. [b] Random copolymer, $\bar{M}_n = 1.70 \times 10^4$, $D = 1.81$.

Similar experiments were carried out with MAA copolymers of BuMA, MMA, and HMA. As shown in Tables IV–VII, the MMA polymers are poorer dispersants than the polymers with longer side chains. Also shown in Tables IV–VII is the difference in solubility parameter between the polymer and solvent, ΔSP; solubility parameters are literature values or were estimated by the group additivity method.[25] It might be expected that a lower solubility of

Table VIII. Amount and Area Occupied by Adsorbed *n*-BuMA/γ-MPS Copolymers onto Alumina Powder Surface

		block copolymer[a]		random copolymer[b]	
solvt	method of washing	amt of polym adsorbed/mg m^{-2}	area occupied by polym/Å^2	amt of polym adsorbed/mg m^{-2}	area occupied by polym/Å^2
toluene	UWS	2.025	1339	1.967	1228
	3 TW[d]	1.865	1455	1.892	1276
	Soxhlet[e]	1.733	1566	1.821	1326
	reflux[f]	1.699	1596	1.715	1408
isopropyl alcohol	UWS[c]	1.731	1567	1.691	1428
	3 TW[d]	1.434	1892	1.611	1499
	Soxhlet[e]	1.351	2007	1.453	1662
	reflux[f]	1.147	2364	1.530	1578

[a] $\bar{M}_n = 1.70 \times 10^4$, $D = 1.81$. [b] $\bar{M}_n = 1.81 \times 10^4$, $D = 1.78$. [c] UWS = unwashed samples. [d] 3 TW = three times washing with fresh solvent. [e] Soxhlet = continuous Soxhlet extraction for 10 h. [f] Reflux = refluxing in ethyl acetate for 72 h.

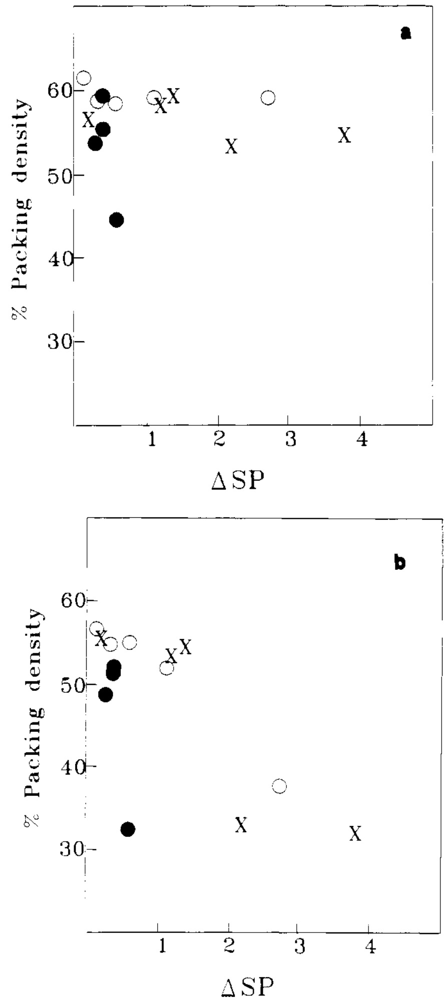

Figure 5. Relationship between solubility parameter difference and sediment density for alumina dispersed with random copolymers in various solvents: (●) MMA-*co*-MAA; (○) BuMa-*co*-MAA; (×) 2-EHMA-*co*-MAA. (a) Centrifugal settling; (b) gravity settling.

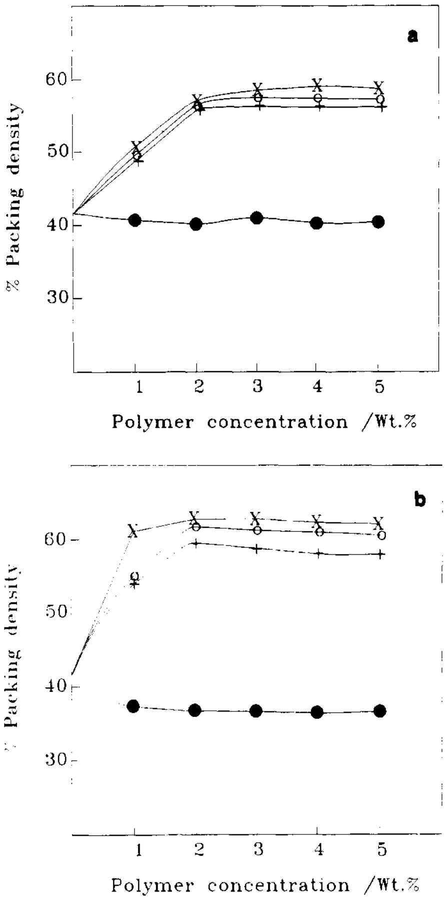

Figure 6. (a) Effect of poly(BuMA-*b*-MAA) concentration on centrifuged sediment density of alumina in toluene: (×) $\bar{M}_n = 6.2 \times 10^3$; (○) $\bar{M}_n = 2.4 \times 10^4$; (+) $\bar{M}_n = 3.4 \times 10^4$; (●) $\bar{M}_n = 2.4 \times 10^5$. (b) Effect of poly(BuMA-*co*-MAA) concentration on centrifuged sediment density of alumina in toluene: (×) $\bar{M}_n = 5.9 \times 10^3$; (○) $\bar{M}_n = 2.5 \times 10^4$; (+) $\bar{M}_n = 3.2 \times 10^4$; (●) $\bar{M}_n = 2.9 \times 10^5$.

the polymer chain in the solvent, or a larger Flory–Huggins interaction parameter, χ, might lead to more polymer–polymer interactions when the adsorbed layers on two particles overlap. These attractive interactions between chains on separate particles could lead to loose agglomeration. In Figure 5 the packing density is plotted against the solubility parameter difference for gravity and centrifugal settling. Although the data are scattered, it can be seen that a larger solubility parameter difference seems to lead to poorer dispersion under gravity settling, whereas there is little effect on centrifugal settling. MMA polymers give worse packing for the same ΔSP.

A similar series of studies was done with copolymers of BuMA with (methacryloxypropyl)trimethoxysilane. This silylated polymer is capable of reacting with the hydroxylated alumina surface to form covalent Si–O–Al bonds. It can be seen from Table IV that the dispersion results were rather worse than for the equivalent MAA copolymer. Infrared spectroscopy showed similar coverage of the surface by this polymer, as shown in Table VIII.

Effect of Molecular Weight. Figure 6 shows the sediment density for BuMA block and random copolymer dispersants with molecular weights from 6000 to 300 000. It can be seen that there is small but consistent drop in density with molecular weight up to 30 000 and then a large drop to 300 000, at which level the packing is slightly worse

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(25) Small, P. A. *J. Appl. Chem.* **1953**, *3*, 71.

with the copolymer present. Random and block copolymers behave similarly, with the random copolymer showing consistently higher packing densities, except at the highest molecular weight.

Discussion

The results of DRIFTS analysis and washing experiments show that the methacrylic copolymers are strongly bound to the particle surfaces by formation of aluminum carboxylates. The limiting adsorption is about 1 molecule/5 nm^2 for a molecular weight of 6000. This corresponds to 3.7 acid groups/5 nm^2. Measurements of hydroxyl concentration on alumina surfaces[5] put this at about 1 acid group/0.1–0.5 nm^2, so that the adsorption must be limited by the polymer size rather than by the surface. The absence of a shift in the main carbonyl peak suggests that most of the ester groups are not bound to the surface but remain in the solvent phase. Even with the homopolymer it seems clear that the majority of the ester groups are not on the surface.

Under the conditions of the sedimentation experiments (8 g of powder to 8 mL of solvent) the amount of polymer remaining adsorbed after washing corresponds to about 70% of the polymer originally present in the solution. Thus the sedimentation curves shown in Figure 1 level off at a dispersant concentration which corresponds to saturation of the surface with the copolymer. Sedimentation experiments were also carried out by redispersing polymer-treated and washed powder into pure solvent. The powder dispersed as well as in the original polymer solution. This implies that these surface treatments are effectively irreversible.

The steps to achieve a well-packed sediment must include (1) deagglomeration and dispersion of the dry powder into the solvent, (2) settling of the powder without agglomeration due to interparticle attractive forces, and (3) high mobility and low friction within the sediment to allow optimum packing.

It is unlikely that the alumina which we use is totally free of large aggregates, but we believe that these are sufficiently few in number that they fall rapidly and occupy a small fraction of the volume at the base of the sediment. This small zone of aggregates has been observed in microscopic studies of our sediments.

In previous discussions of powder packing the emphasis has been placed on this second stage as being the key to achieving good packing by the elimination of the attraction between pairs of particles. The best measure of this second effect is the sedimentation rate of the powder. Soft agglomerates, which form due to interparticle attractions, will act as large particles and will sediment rapidly. Figure 7 shows the initial settling rate under gravity of alumina suspensions in toluene. We can identify this initial rate with the settling of those particles of radius roughly equal to the average, which is calculated as 0.1 μm from the surface area of 7.2 m^2 g^{-1}. Stokes law gives the velocity of sedimentation as $V = 2\pi r^2(\rho - \rho_0)g/9\eta$, where r is the particle radius, ρ and ρ_0 are the densities of particle and solution and η is the solution viscosity. Using this equation we predict a settling rate of 0.9 cm day^{-1}, which corresponds to that observed for dilute suspensions with a BuMA copolymer dispersant. The MMA copolymers show more rapid settling, implying significant agglomeration. More concentrated dispersions are expected to settle more slowly because both the effective viscosity and the density of the suspension are increased.[26]

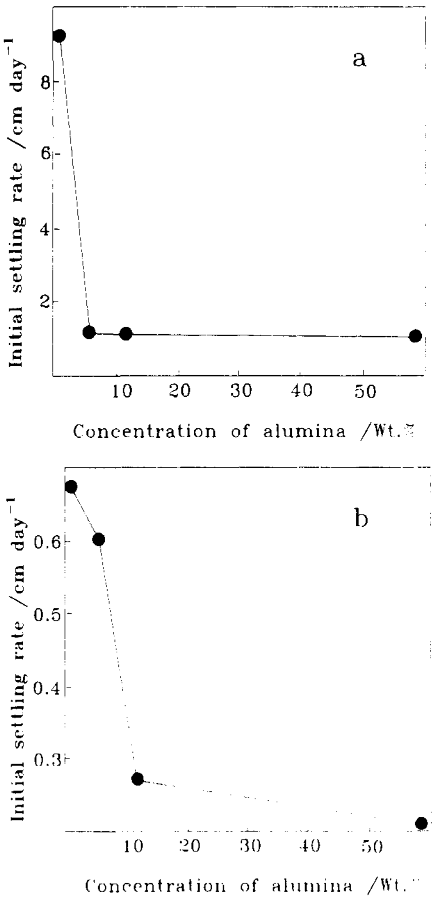

Figure 7. Effect of alumina concentration on initial settling rate of particles in toluene with (a) poly(MMA-*co*-MAA) and (b) poly(BuMA-*co*-MAA).

In the third stage, as the particles come together in the sediment, they will settle initially at the equilibrium center–center distance for the combination of attractive and repulsive forces acting, but with a low coordination number. Particles will slide into lower positions and the packing will improve until bridges form or until the effective shear yield stress of the interparticle gel opposes the gravitational force acting on the particle. It can be seen from Tables IV–VII that the greater settling forces of centrifugation lead to much closer packing, especially in the partly agglomerated MMA system.

The expected decrease in packing density with increasing molecular weight can be based on calculations of the increased equilibrium particle separation due to the attached polymer layer. For terminally bonded chains the layer thickness is expected to depend on molecular weight, the adsorption density and the quality of the solvent.[27] The layer thickness is typically a few times the random coil end–end distance of the polymer. These calculations are in agreement with measurements of layer thickness of terminally anchored 2-vinylpyridine–styrene block copolymers on mica.[28] Shown in Figure 8 is the expected change in packing density if the particles are separated by a distance equal to n times the calculated RMS end–end distance of the polymer in ideal solution. The effect of layer size is large. It is expected to be smaller for the random copolymer than the block copolymer since the former consists of a series of loops attached to the surface

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[26] Tadros, Th.F. In *Solid/liquid dispersions*; Tadros, T. F., Ed., Academic Press: London, 1987.

[27] Russell, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal dispersions*; Cambridge U.P., 1989.

[28] Hadziioannou, G.; Patel, S.; Granick, S.; Tirrell, M. *J. Am. Chem. Soc.* **1986**, *108*, 2869.

Table IX. Properties of Some Ceramic Green Tapes

dispersant	binder % (vol)	flexural strength, δ_f/MPa	modulus of elasticity, E_b/GPa	bending strain, ϵ%	bulk density/g mL^{-1} green tape	bulk density/g mL^{-1} fired tape	% theoretical density in fired tape
oleic[a]	60	7.63	4.97	0.82	2.441	3.754	94.6
block[b]	60	34.14	10.16	0.62	2.506	3.821	96.3
random[c]	60	36.84	10.75	0.56	2.551	3.849	96.9
oleic[a]	50	4.80	2.75	0.62	2.390	3.735	94.0
block[b]	50	21.60	7.57	0.58	2.398	3.774	95.1
random[c]	50	29.90	9.26	0.47	2.414	3.785	95.3
oleic[a]	40	4.21	2.45	0.46	2.301	3.660	92.2
block[b]	40	12.80	4.24	0.43	2.340	3.709	93.4
random[c]	40	22.00	8.15	0.35	2.369	3.728	93.9

[a] Oleic = oleic acid (mol wt equal to 282.47). [b] Block = block copolymer of BuMA/MAA having $\bar{M}_n = 2.37 \times 10^4$, $D = 1.26$, acid content (wt %) = 5.58. [c] Random = random copolymer of BuMA/MAA having $\bar{M}_n = 2.46 \times 10^4$, $D = 1.12$, acid content (wt %) = 5.63.

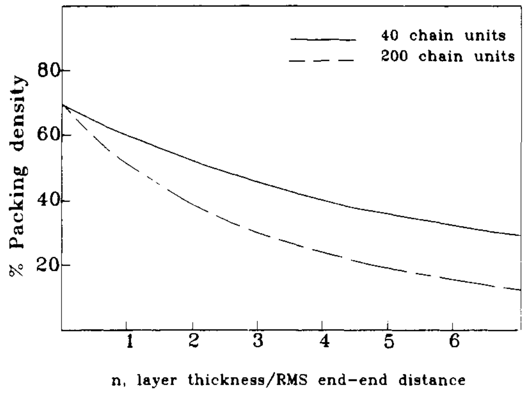

Figure 8. Theoretical packing density for alumina spheres covered with a *n*-BuMA homopolymer layer of thickness equal to *n* times the RMS end–end distance.

at both ends while the latter is a single tail extending into the solution.

According to simple steric stabilization theories,[3] agglomeration of particles with attached chains occurs at the critical flocculation point, which is closely correlated with the θ temperature for the polymer-solvent combination. Thus if packing were controlled by critical flocculation we would expect sediments to be either well-packed or very poorly packed. It is clear that our solvents are all fair-to-good and our sediments are all moderately well-packed. Nonetheless, we see some agglomeration of the MMA-treated particles. If packing density were governed by chain extension, we would expect poorer packing as the solvent quality improved and the surface layers became more extended. The opposite is true. Under our conditions of dense particles the final packing density may be strongly affected by the viscous forces between coated particles in sediments. Aksay and co-workers have discussed this as a "lubrication" effect for particles dispersed with homopolymers of methacrylates with long hydrocarbon side chains.[29]

Particles are expected to remain well-dispersed in a better-than-θ solvent. In fact, for any polymer, we find that the packing does improve with improving polymer–solvent compatibility as measured by the solubility parameters. In addition, the MMA polymer is clearly a poor dispersant relative to the two other methacrylates, despite being in a good solvent. Weak agglomeration of the particles, is shown by the settling rate data but some samples dispersed with MMA copolymers show fast sedimentation to high packing density. This suggests that interchain forces are stronger in the MMA polymers than in the BuMA for a given ΔSP. This appears to be reasonable in terms of a higher polarity and lower steric hinderance in MMA.

Random copolymers gives consistently tighter packing than the equivalent block copolymers. This reflects the distribution of surface binding sites along the chain with short loops between, giving at higher chain density near the surface for the random polymer. At very high molecular weights the random chains are capable of bridging flocculation between particles, which is not possible with the block copolymer.

Sheets of alumina were tape cast with a binder of polybutylmethacrylate (40–60 vol %) from suspension in 2-butanone. Table IX compares the properties of green tapes and final ceramic made with copolymer dispersants and with oleic acid. It can be seen that the copolymers give denser and stronger tapes, reflecting better packing and less entrapped porosity. The final ceramic is also more dense. Lower fractions of binder gave less dense tapes, presumably due to porosity, but similar property enhancements by the copolymers over oleic acid. Modulus and strength were determined in three-point bend of 50 × 10 × 0.5 mm sheets.

Conclusions

Methacrylic acid–methacrylate copolymers are efficient dispersants for alumina in polar solvents such as ketones and esters. Group-transfer polymerization allows us to prepare block and random copolymers with closely defined molecular weight distributions. Highest packing density sediments were obtained with low molecular weight butyl methacrylate–methacrylic acid random copolymers. The packing density is sensitive to dispersing solvent, polymer composition, molecular weight, and microstructure. Ceramic sheets could be cast successfully with these dispersants using a ketone solvent and poly(butyl methacrylate) as a binder.

Registry No. Al_2O_3, 1344-28-1; (methyl methacrylate)(trimethylsilyl methacrylate) (copolymer), 35561-08-1; (butyl methacrylate)(trimethylsilyl methacrylate) (copolymer), 35561-10-5; (2-ethylhexyl methacrylate)(trimethylsilyl methacrylate) (copolymer), 114615-96-2.

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