Nanosize Lipophilic Polyacrylate Particles and Their Photoinduced Flocculation in Hydrocarbon Solvents†

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The synthesis, characterization, and properties of colloidal nanostructures in hydrocarbon media are reported. These sterically stabilized structures are unusual in that the stabilizing arms are attached to the particle by photoactive groups, and the arms can be cleaved through irradiation, leading to photoinduced flocculation. In the first step of the synthesis, cross-linked poly(butyl methacrylate) (PBMA) latex particles with controlled functionality (−COOH and −OH groups) were prepared by emulsion polymerization. The purified PBMA latex was neutralized with Cs_2CO_3 and then transferred to an organic medium (dimethylformamide), where it was converted to lipophilic nanoparticles through chemical modification with 2-bromo derivatives of long-chain 1-phenylalkyl ketones or nitrobenzyl ether derivatives of polyisobutylene. The particles can be dispersed in hydrocarbon solvents. Irradiation leads to flocculation, except that in the presence of hydrocarbon-soluble polymers bearing amino groups, the unprotected particles can be intercepted and flocculation inhibited. These particles serve as an interesting model for precursors to sludge formation in motor oil.

Introduction

In this paper we consider models for the formation of sludge in gasoline-engine motor oil.[1] Sludge is an unwanted precipitate that interferes with oil circulation in engines and forms deposits and varnishes on engine parts.[2] Its formation is most severe under the low-to-moderate temperature engine conditions that occur when the engine is run in stop-and-go traffic. These problems can eventually lead to engine failure. Sludge originates from incomplete combustion of fuel.[3] The partially oxidized byproducts find their way into the crankcase and degrade via so-called "nitration−oxidation" processes into products containing polar functional groups, which ultimately react to form substances that are insoluble in oil.[4] Although investigators in the lubrication field have invested considerable effort trying to understand the sludge-formation mechanism, the sludge-formation process remains largely a mystery.[5] Nevertheless, considerable progress has been made in the development of additives for motor oil that retard the formation of sludge. Some of these additives (dispersants) are designed to intercept hypothetical intermediates that are precursors to sludge.[6] Many of these additives are very effective, and modern formulations greatly slow down sludge buildup.

The lack of understanding of the sludge-formation process, and our limited knowledge of the function of these additives, hinders the development of new products. Here, we attempt to create a model system to provide insights into the mechanism of the process in which small particles form and then aggregate to form sludge. It has been suggested that the initially formed aggregates are cross-linked resin particles bearing carboxylic acid, alcohol, and carbonyl functional groups[5b] and that the resin is formed via aldol-type condensation of aldehyde and ketone groups in the molecules present in the partially oxidized fuel.[7] We consider the possibility that one could prepare and characterize substances that would serve as model intermediates in the sludge-formation process. Under the right circumstances, one could study the flocculation and precipitation of this material and also use these model sludge precursors as a test platform to assess the effectiveness and the mechanism of action of the functional polymers used as dispersants. Dispersants are designed to capture sludge precursors while they are of colloidal dimensions, hopefully less than 100 nm in size, by binding to the surface of the aggregates and providing steric stabilization.

Our model is built on the idea that the partial-oxidation products of fuel create molecules that contain aldehydes, ketones, and carboxylic acid groups. Through a series of condensation reactions, these molecules become larger in size until their solubility limit is exceeded. The entities formed at this point are the colloidal precursors to sludge formation that we wish to model. These species aggregate, and these associated structures become larger in size until a macroscopic precipitate forms. Our model intermediate must then be a particle of colloidal size (target diameter of 50 nm) with polar functional groups at its surface. Since the active functional groups at the aggregate surface are unknown, the synthetic strategy for preparing the model nanoparticles must have enough versatility to allow control of functionality within a reasonable

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† This paper is dedicated, with our best wishes, to the 60th birthday of Bob Liu, Doug Neckers, Jack Saltiel, Nick Turro, Pete Wagner, and Dave Whitten.

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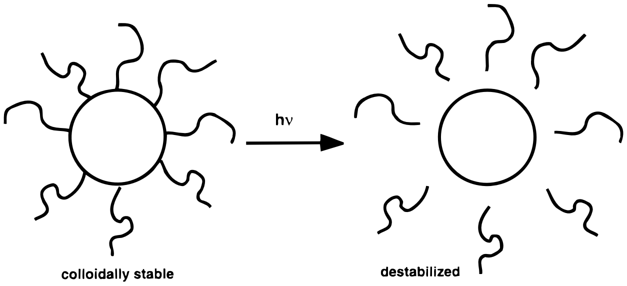
range. Finally, we must be able to control the colloidal stability of the particles so that we can induce flocculation at will.

Dispersion stability is the central issue in all technologies in which colloids play a role. In applications ranging from the synthesis of commodity polymers, such as styrene−butadiene by emulsion polymerization, to paints and inks, to medical diagnostics, the system must meet the seemingly contradictory demands of remaining colloidally stable during transport and storage, and flocculating or otherwise separating from the fluid medium during some key step during its application or processing. Here, we consider the novel idea of photoinduced flocculation of sterically stabilized colloidal dispersions. To achieve this goal, the flexible chains that provide colloidal stability are anchored by groups that are susceptible to photofragmentation. Since these types of particles are often referred to as "hairy" latex, we can think of the flocculation-inducing step as a "photochemical haircut". We conceptualize the problem in the following:



Experimental Section

Instrumentation. ^{1}H NMR spectra were recorded on a Gemini 200-MHz spectrometer at room temperature, and chemical shifts are quoted in ppm. UV−vis spectra were recorded on a Hewlett-Packard 8452A diode-array UV−vis spectrophotometer. FTIR spectra were obtained on a Perkin-Elmer Spectrum 1000 spectrometer. High-resolution mass spectra were recorded on a VG 70-250S double-focusing high-resolution mass spectrometer at 70 eV. Measurements of the particle size and size distribution were performed on a Brookhaven model 90 dynamic light-scattering particle sizer. Photolysis was carried out in a Rayonet photochemical reactor equipped with 3000 Å 12 RPR lamps (Southern New England Ultraviolet Co.). Gel permeation chromatography (GPC) was performed on a Varian 5000 liquid chromatograph equipped with a Waters 480 tunable UV−vis absorbance detector and Waters differential refractometer R401 detector. Two microstyragel columns (500 and 10 000 Å, American Polymer Standards Corporation) in series were used with THF as solvent. Molecular weight was calibrated with PMMA standards (Polymer Laboratories Ltd.).

Materials. Methyl methacrylate (MMA), butyl methacrylate, ethylene glycol dimethacrylate (EGDMA), 2-hydroxyethyl methacrylate (HEMA) and methacrylic acid (MAA), purchased from Aldrich, were distilled under nitrogen and stored at −10 °C. Spectral grade solvents were used for spectroscopic and photochemical studies. All other chemicals were obtained from Aldrich and used without further purification.

Preparation of 1-Phenyl-2-bromooctadecanone (1). To a stirring solution of 1-phenyloctadecanone (Aldrich, 3.450 g, 10.00 mmol) in 15 mL of glacial acid, bromine (1.7 g, 10.63 mmol) in 5 mL of glacial acid was added dropwise over 1 h. The final mixture was poured over water, and the excess of bromine was eliminated by adding Na_2SO_3 until a colorless solution was observed. The product was extracted with dichloromethane (3 × 100 mL) from the aqueous phase. The combined organic phases were dried over Na_2SO_4 and evaporated to yield an oil, which was recrystallized from hexane. Yield = 3.25 g (74%); mp = 51.5−52 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.08−7.24 (5H, m, Ar-*H*), 5.14 (1H, m, α-*H*), 2.15 (2H, m, *β-H*), 1.32 (28H, br. s, $(-CH_{2-})_n$), 0.90 (3H, t, *J* = 7 Hz, CH_3). FTIR (ν_{max}): 2818, 2847, 1682 (C═O), 1466, 1258, 700, 521 cm^{-1}. MS *m*/*e* (relative intensity): 424 (5.6, M$^+$), 422 (5.9, M$^+$), 343 (14.0), 200 (8.4), 198 (8.7), 120 (27.1), 105 (100), 77 (19.1). Calculated mass for $C_{24}H_{39}BrO$: 422.2184. Found: 422.2165. UV−vis (THF, 6.0 × 10^{-5} M) λ_{max} ($\epsilon \times 10^{-3}$): 286 (0.31, sh), 254 (10.0) nm.

Preparation of 1-Phenyl-2-bromododecanone (2). This was prepared in the same way as 1-phenyl-2-bromooctadecanone. The crude product was chromatographed on silica gel. The pure product was eluted from the column with 10% diethyl ether in hexanes after a small amount of impurities was washed out by hexanes. The solid product, which would be liquefied upon warming the flask in one's hands, was obtained after vacuum-drying. Yield = 85%; mp = 24−25 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.08−7.63 (2H, m, Ar−*H*), 7.60−7.38 (2H, m, Ar−*H*), 5.12 (1H, t, *J* = 7 Hz, α-*H*), 2.15 (2H, m, *β-H*), 1.32 (14H, s, $(-CH_{2-})_n$), 0.86 (3H, t, *J* = 7 Hz, CH_3). MS *m*/*e* (relative intensity): 340 (0.7, M$^+$), 338 (0.7, M$^+$), 259 (17.9), 200 (15.4), 198 (15.6), 133 (9.4), 120 (7.9), 106 (16.0), 105 (100), 77 (23.5). Calculated mass for $C_{18}H_{27}BrO$: 338.1245. Found: 338.1235. IR (KBr) ν_{max}: 2933, 2867, 1691 (C═O), 1455, 1356, 1258, 705 cm^{-1}. UV−vis (45:55 THF/cyclohexane) λ_{max} ($\epsilon \times 10^{-3}$): 254 (8.91), 286 (3.14, sh) nm.

Preparation of (1′-Phenylcarbonyl)heptadecanyl Isobutyrate (4). Isobutyric acid (3.8211 g, 43.37 mmol) was mixed with Cs_2CO_3 (7.0648 g, 21.68 mmol) in 10 mL of water. The final solution was freeze-dried to yield a solid, which was subsequently dried in a vacuum oven for 2 h at 80 °C. The dried cesium isobutyrate (**3**, 0.1105 g, 0.50 mmol) and 1-phenyl-2-bromooctadecanone (0.2111 g, 0.50 mmol) were mixed in 5 mL of DMF. The mixture was stirred overnight. By TLC (silica gel, 1:10 diethyl ether/hexane), no 2-bromooctadecanophenone was left after an overnight reaction. The final mixture was diluted with water and extracted with ether (3 × 10 mL). The combined organic phase was dried over Na_2SO_4 and evaporated to yield a white solid. The solid was further purified by silica-gel chromatography. The product was eluted with 1:10 diethyl ether/hexane. Yield = 0.18 g (83%); mp = 39−40 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.90−7.40 (5H, m, Ar−*H*), 5.82 (1H, dd, *J* = 8.2, 6.3 Hz, α′-*H*), 2.65 (1H, sept., *J* = 6.5 Hz, $(CH_3)_2CHC(O)O-$), 1.90−1.75 (2H, m, *β′-H*), 1.60−1.20 (34H, m, $(CH_3)_2CHC(O)O-$ and $-CHCH_2(CH_2)_{14}CH_3$), 0.87 (3H, t, *J* = 7.0 Hz, $-CHCH_2(CH_2)_{14}CH_3$). FTIR ν_{max} (cm^{-1}): 2919, 2850, 1744 (C═O), 1691 (C═O), 1471, 1190, 1159, 699 cm^{-1}. MS *m*/*e* (relative intensity): 431 (2, M$^+$), 408 (2), 342 (5), 206 (6.5), 176 (12.0), 105 (100), 77 (15.7), 71 (85.2). Calculated mass for $C_{28}H_{46}O_3$: 430.3447. Found: 430.3439. UV−vis (THF, 7.0 × 10^{-5} M) λ ($\epsilon \times 10^{-3}$): 270 (0.36), 244 (10.7) nm.

Preparation of Particles. The latex particles were prepared by batch emulsion polymerization in deionized water. Typical recipes are shown in Table 1. The monomers, surfactant, and Na_2CO_3 were mixed with water. The mixture was degassed by nitrogen bubbling for at least 30 min. The mixture was heated to 75 °C while being stirred mechanically, and then the initiator ($K_2S_2O_8$) solution (1−2 mL) was added. Stirring was continued for another 2−3 h under nitrogen. The final latex was cleaned by ion exchange three times by stirring the resin (5−10 g, Bio-Rad, AG-501-X8, washed subsequently with hot

TABLE 1: Recipe for the Preparation of Polyacrylate Latex Particles

	PBMA/CO_2H/OH	PMMA/CO_2H/OH
water (mL)	150	50
acrylate (g)	6.04 (BMA)	7.0 (MMA)
SDS (g)	0.46	0.448
$NaHCO_3$ (g)	0.50	0.229
KPS (g)	0.10	0.0906
EGDMA (g)	0.30	0.448
MAA (g)	0.39	0.406
latex size[a] (nm)	43	61

[a] Measured by dynamic light scattering.

deionized water at 80 °C, methanol, and water) for every 100 mL of latex each time. The cleaned latex was neutralized to pH 7.2 with Cs_2CO_3 and freeze-dried to yield the dry particles.

Modification of the Particles by 1-Phenyl-2-bromoalkanone. The same procedure was employed for the modification of the PMMA and PBMA particles in the Cs^+ salt form (polymer/OH/COOCs) with 1-phenyl-2-bromooctadecanone and 1-phenyl-2-bromodecanone. As an example, a freeze-dried sample of particles (PBMA/OH/COOCs, 2.4 g) was suspended in 20 mL of DMF and stirred with 1-phenyl-2-bromooctadecanone (0.48 g) for 4 days at room temperature. The reaction mixture was concentrated to 10 mL at 40 °C under vacuum and diluted to 30 mL with THF. CsBr was removed by stirring the diluted mixture with an ion-exchange resin (Bio-Rad, AG-501-X8, previously washed sequentially with hot deionized water at 80 °C, THF, and DMF). The ion-exchange treatment was repeated three times. The cleaned dispersion was almost transparent. The particles, which were in a mixture of THF and DMF, can be air-dried to yield a glassy material that can be redispersed in THF or cyclohexane. The same material can be obtained as a white powder by freeze-drying the dispersion in cyclohexane. GPC showed 70% of the chromophore absorption was retained on the particles. The purification of PMMA particles was carried out by precipitating the particles from THF by adding excess hexane, and the procedure was repeated at least three times.

Modification of Particles by PIB−NH_2. This transformation begins with functionalization of amino-end-capped polyisobutylene (PIB−NH_2) with a photoremovable chromophore and then attachment of the polymer to the particles. Step 1 is the reaction of PIB−NH_2 with 4-bromomethyl-3-nitrobenzoic acid. PIB−NH_2 (1.045 g of 50% in tetradecane, MW = 1100, 0.642 mmol NH_2/g PIB−NH_2, a gift from Dr. Rösch at BASF, Ludwigshafen) was mixed with 4-bromomethyl-3-nitrobenzoic acid[14] (0.1497 g, 0.576 mmol) and dicyclohexylcarbodiimide (0.1100 g, 0.582 mmol) in 10 mL of dry CH_2Cl_2. The mixture was warmed slightly to give a clear solution and then allowed to stand for 2 days. Needle crystals of dicyclohexylurea formed and were removed by filtration. The filtrate was evaporated to give an oil. Step 2 is the attachment of (PIB−NH−C(O))−C_6H_3(4-bromomethyl)(3-nitro) to PMMA particles. The above-obtained oil was redissolved in 15 mL of 1:2 THF/DMF together with PMMA/OH/CO_2Cs (1 g, 0.62 mmol CO_2Cs(H)/g). The PMMA particles were stirred in this solution for 2 days at room temperature. Cesium bromide was removed by stirring with an ion-exchange resin. The filtrate was dried under vacuum and redispersed in THF. A pure solid sample was obtained by precipitating the particles from THF dispersions using hexane. UV−vis (THF, 0.488 mg/mL) λ ($\epsilon \times 10^3$): 286 (0.46), 240 (1.78). On the basis of the maximum molar absorbance of 4-bromomethyl-3-nitrobenzoic acid at 292 nm in THF ($\epsilon = 1.81 \times 10^3$), the chromophore content of the particles was estimated as 518 μmol/g polymer.

Photoinduced Flocculation. Samples with concentrations of 0.1−10 mg/mL of polymer particles were prepared as dispersions. If required, other additives such as PIB−NH_2 were added to the solution before irradiation. The final dispersions were transparent, and size measurements by DLS indicated no aggregation or coalescence of particles. Each sample was sealed in a Pyrex cell, irradiated in a Rayonet photochemical reactor, and monitored by dynamic light scattering and/or visible absorption at 600 or 650 nm as a function of irradiation time. Note that in the case of PBMA particles, the dispersion contains a certain amount (ca. 5%) of unreacted 1-phenyl-2-bromooctadecanone.

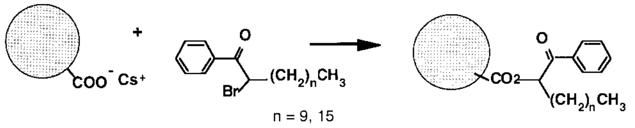
Results and Discussion

We describe a methodology to prepare nanometer-sized particles, bearing functional groups near or at the surface, that form stable dispersions in aliphatic-hydrocarbon media. Steric stabilization is provided by relatively short aliphatic chains (n-C_9H_{19}−, n-$C_{15}H_{31}$−) or by longer polymer chains (polyisobutylene, PIB, MW = 1100). These are connected to the particles by means of photoactive groups in such a way that irradiation cleaves the chains from the particles. In this way, flocculation can be induced photochemically. The particles are first prepared in water by emulsion polymerization. Because they are cross-linked, the particles prepared in water can be dried and transferred to an organic solvent like tetrahydrofuran (THF) or dimethyl formamide, where the particles disperse in the form of solvent-swollen microgels.[8]

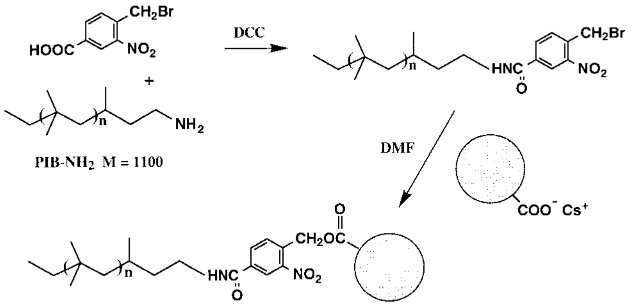
One of the interesting features of the systems we have prepared is that their colloidal stability is not dependent only on the presence of the aliphatic or PIB chains. Colloidal stability also depends on the interaction between the polymers in the particle and the solvent. These effects can be quite subtle but turn out to be useful in the purification of the particles. The materials we have prepared do not disperse well in hexane or pentane. They precipitate in these solvents and can be recovered by filtering or centrifugation. Some of the particles disperse well in cyclohexane and in cyclohexane/hexadecane mixtures. Other particles can be dispersed in mixtures of cyclohexane with more polar solvents such as THF. These represent conditions where useful photochemical experiments can be carried out.

Preparation and Properties of the Functional Nanoparticles. *Particle Synthesis*. Dispersions of nanometer-sized polymer particles can be prepared either in aqueous media by emulsion polymerization[9] or in organic media by dispersion polymerization.[10] Alternative approaches involve polymerization in microemulsions, by which one can prepare dispersions of nanosize particles in aqueous[11] and nonaqueous[12] phases. The microemulsion approach is effective for producing very small particles (i.e., 10 nm in diameter), but the method requires large amounts of surfactant. Here, we take an indirect method to the synthesis of nanometer-sized particles for dispersion in aliphatic-hydrocarbon media. We prepare the base particle by emulsion polymerization in water, with sufficient bismethacrylate in the monomer component to yield fully cross-linked particles. In emulsion polymerization, the size of the particles can be controlled through the amount of surfactant added. If anionic surfactant is employed, the particles can be purified, and the surfactant removed, by stirring the dispersion with an ion-exchange resin. This strategy offers considerable flexibility, since it is possible to control the location of functional groups in the system through seeded, multistage emulsion polymerization. Here, we find that batch polymerization, in which all the monomers are introduced into the initial reaction mixture,

SCHEME 1



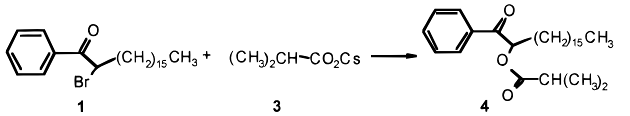
SCHEME 2



provides particles in which almost all of the functional groups are accessible and presumed to be near the surface of the particles.

We prepared both PMMA and PBMA particles by batch emulsion polymerization, using ethylene glycol dimethacrylate as a cross-linking agent and methacrylic acid and 2-hydroxyethyl methacrylate as comonomers. In this way, the particles prepared contained both carboxylic acid and primary-alcohol functional groups. We refer to these materials as PMMA/OH/CO_2H and PBMA/OH/CO_2H, respectively. Two typical recipes for the emulsion polymerization reactions are given in Table 1. The latex particles obtained had diameters ranging from 40 to 60 nm with narrow polydispersity as measured by dynamic light scattering (DLS). The dispersions of cross-linked latex were purified by ion exchange, neutralized to pH 7.2 with Cs_2CO_3, and freeze-dried for further chemical modification. The Cs^+ salt of latex particles can be dispersed homogeneously in DMF but not in THF. Attempts to disperse these powders as individual particles in CH_2Cl_2, benzene, toluene, and aliphatic-hydrocarbon solvents also failed. In contrast, freeze-dried latex particles in the acid form (freeze-dried after purification by ion exchange) can be redispersed in organic solvents such as DMF and THF. The particles are swollen by these solvents, and their diameters increase by approximately 30−40% as determined by DLS over their dimensions in water.

Particle Modification. Chemical modifications were carried out to obtain particles that have enhanced dispersibility in hydrocarbon solvents and that can be flocculated upon UV irradiation. The synthesis procedures are based upon the following reaction



1 3 4

in which the cesium salt of a carboxylic acid reacts with an α-bromoketone to form an α-ketoester. S_N2 reactions of cesium carboxylate salts with aliphatic bromides often take place with nearly quantitative yield and are relatively fast ($k \approx 10^3$ L mol^{-1} s^{-1}).[13] For example, the model compound **4**, the reaction product of 1-phenyl-2-bromooctadecanone (**1**) with cesium isobutyrate, was obtained in 83% isolated yield after reaction in DMF at room temperature overnight.

In this way, the cesium carboxylate salts of the particles were converted to esters by nucleophilic reaction with 1-phenyl-2-bromododecanone and with 1-phenyl-2-bromooctadecanone (Scheme 1). The phenyldodecane derivatives ($n = 9$ in Scheme 1) gave particles that could not be dispersed in aliphatic-hydrocarbon media but could be dispersed if a polar solvent like THF was added to the solvent. Better and more robust dispersions of both types of particles were obtained by reaction with 1-phenyl-2-bromooctadecanone ($n = 15$, Scheme 1). We took a similar approach in preparing particles stabilized with polyisobutylene chains (Scheme 2). Here, PIB−NH_2 was first reacted with 4-bromomethyl-2-nitrobenzoic acid[14] to form an ester containing the reactive bromomethyl group, which subsequently was reacted with dispersed polymer/OH/CO_2Cs in the same way as with the bromoalkanones. In each case, the dangling aliphatic chains were attached to the particles by photocleavable groups, either an α-carboxy phenyl ketone or a nitrobenzyl ester group. The particles were analyzed by UV and ^1H NMR spectroscopy in order to determine the chromophore content. The microgels formed in THF could also be analyzed by gel permeation chromatography (GPC) to determine whether all UV-absorbing entities were attached to the polymer. As shown in Table 2, not all carboxylic acid groups on the particles react. We assume that the unreactive acid groups are buried inside the particle cores and are less reactive because of steric factors.

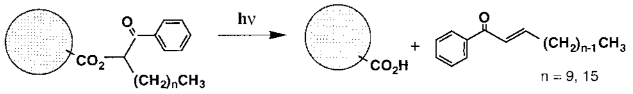
Dispersibility of Modified Particles in Hydrocarbon Solvents. The properties of the modified particle are listed in Table 2. If the pendant aliphatic chains were solely responsible for particle stabilization, we would anticipate that the particles would form stable dispersions in any solvent that is a good solvent for these aliphatic chains. Under these circumstances, the dispersibility of the particles would not depend on the core material, whether

TABLE 2: Typical Properties of Cross-Linked Polymeric Particles

	PMMA/OH/CO_2H		PBMA/OH/CO_2H	
original latex (nm)[a]	61	61	60	43
cross-linker[b] (wt %)	7.6	7.6	4.4	4.2
total CO_2H (μmol/g)[b]	620	620	564	959
total OH (μmol/g)[b]	216	216	300	315
chromophore type	PC_{12}[c]	PIB−NH_2[c]	PC_{12}[c]	PC_{18}[c]
chromophore (μmol/g)	473[d]	518[e]	274[f]	329[f]
modified particle size[a] (nm)	79 (THF)[c]	71(1:2 THF/cy)[c]	92 (THF)[c]	62 (cy)[c]
CPC[g]	45:55 THF/cy[c]	1:2 THF/cy[c]	1:10 THF/cy[c]	1:3 C_{16}/cy[c]

[a] Particle sizes were measured by dynamic light scattering. [b] Calculated based on the emulsion polymerization recipe. [c] PC_{12}, 1-phenyldodecanone derivative; PC_{18}, 1-phenyloctadecanone derivative; PIB−NH_2, polyisobutylene derivative; THF, tetrahydrofuran; cy, cyclohexane; C_{16}, hexadecane. [d] Estimated by UV spectroscopy on a purified sample based on $\epsilon_{max} = 10\,700$ at 244 nm of (1′-phenylcarbonyl)heptadecanyl isobutyrate (**4**) in THF. [e] Estimated by UV spectroscopy based on $\epsilon_{max} = 1810$ at 292 nm of 4-bromomethyl-2-nitrobenzoic acid. [f] Estimated by GPC according to UV absorption at 241 nm, eluent THF with microstyrogel columns. [g] Limiting solvent composition yielding stable dispersions, the cloud-point composition.

SCHEME 3



it was PMMA, PBMA, or even silica. Here, we find significant differences between PMMA and PBMA particles, consistent with the idea that solvent swelling of the core plays a role in the stabilization process. Particles swollen by solvent have smaller Hamaker constants (weaker attractive dispersive interactions) and smaller surface tensions than dense particles.[15] We also note differences due to the length and type of aliphatic substituent attached to the carboxyl groups. For example, the longer PIB chains are more effective steric stabilizers than the dangling ends of the octadecanol derivatives.

For all of these dispersions, during addition of nonsolvent, one reaches a critical solvent composition (cloud-point composition, CPC) at which flocculation occurs.[5] For example, PBMA particles modified with 1-phenyl-2-bromododecanone (PBMA/OH/CO_2PC_{12}) can be dispersed in 1:10 THF/cyclohexane while PMMA with the same modification can only be dispersed in 45:55 THF/cyclohexane. In Table 2 we list these limiting solvent compositions. For the same PMMA particles at roughly equal chromophore content, those stabilized with PIB are more easily dispersed in hydrocarbon-rich solvents than those with the 1-phenyldodecanone chromophore. The CPC of the PIB-stabilized PMMA particles is 1:2 THF/cyclohexane, whereas for the 1-phenyldodecanone derivative, the limiting dispersibility is 45:55 THF/cyclohexane. This behavior is consistent with the greater chain length of the PIB (MW = 1100) compared with that of the alkyl ketone derivative.

PBMA particles functionalized with 1-phenyloctadecanone (PBMA/OH/CO_2PC_{18}) can be completely dispersed in cyclohexane, in methylcyclohexane, and in mixtures of these with linear aliphatic-hydrocarbon solvents, while those modified with 1-phenyldodecanone (PBMA/OH/CO_2PC_{12}) can only be dispersed in cyclohexane by adding a small amount of THF (Table 2).

Photochemistry. α-Carboxyphenyl ketones are very photoreactive. The phenylalkyl ketone function has been used in the synthesis as a photoremovable protective group for carboxylic acids.[16] The reaction is thought to proceed through homolytic cleavage of the COO−CH bond followed by hydrogen-atom transfer to regenerate the original carboxylic acid. The reaction occurs with a high quantum yield so that the formation of carboxylic acid is the major reaction pathway.[16] However, other types of reactions occur that do not form the COOH group. For example, the Norrish type II reaction may occur before the bond to the ester group is broken.[17] Even in this case, the long aliphatic chains are cleaved, and this reaction should also be effective for our purposes. In the photoreaction as shown in Scheme 3, the particles lose their steric-stabilizing chains and develop hydrophilic surfaces. This should lead to particle flocculation.

The *o*-nitrobenzyl group has been used as a photoremovable protective group for carboxylic acids, alcohols, and other functional groups.[16] The reaction follows the path shown in Scheme 4 for the example of PMMA/OH/CO_2PIB. Hydrogen abstraction of a benzylic hydrogen by the nitro group occurs upon photoexcitation. Subsequent rearrangement of the intermediate diradical leads to cleavage of the benzylic-oxygen bond and the formation of an orthonitrosoaldehyde. In our system, the course of the photoreaction can be followed by loss of UV absorption by the PMMA particles.

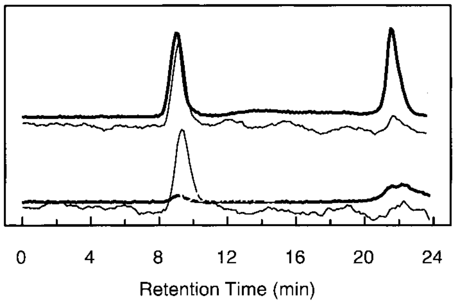
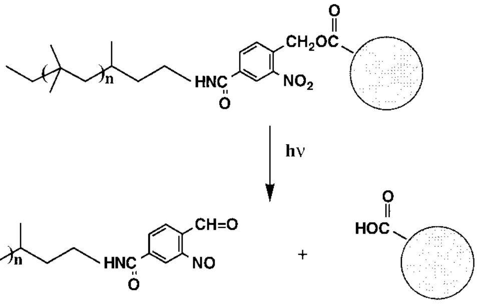


Figure 1. Gel permeation chromatograms of PBMA/OH/CO_2PC18 before (upper pair of curves) and after (lower pair of curves) 10-min photolysis (UV, >300 nm) in THF: GPC column, 500 and 10 000 Å; solvent, THF; UV detector at 249 nm (thick curves); refractive index (thin curves).

SCHEME 4



When carrying out these reactions, we were able to follow the effectiveness of the photoreaction by gel permeation chromatography (GPC). It is not widely appreciated that one can often analyze or even purify colloidal dispersions by column chromatography. Here, we use GPC to monitor the change in chromophore content of the particles after the irradiation. Consider the example of PBMA/OH/CO_2H modified with 1-phenyl-2-bromooctadecanone (PBMA/OH/CO_2PC_{18}) irradiated in THF in order to prevent the flocculation during irradiation. In Figure 1, we show the GPC chromatogram of the sample before irradiation, using dual detectors. The swollen particles elute at a retention volume corresponding to a molecular weight (based upon linear PMMA standards) of 1.1×10^7 ($M_w/M_n = 1.1$), as detected by UV absorption at 249 nm and refractive index (RI). After irradiation for about 10 min in THF, the position of the particles in the GPC trace remains unchanged as monitored by the RI detector, but the UV absorption for the particle peak is reduced almost to zero. The loss of UV absorption from the particles indicates that the photodissociation has occurred. The chromophore-containing entity has been severed from the particles, and the reaction has gone nearly to completion.

Photoinduced Flocculation of Dispersions. PMMA and PBMA particles, derivatized with either 1-phenyldodecanone or 1-phenyloctadecanone, flocculate when dispersions in media close to the CPC are irradiated with UV light. There are several ways to monitor the photoinduced flocculation. One approach uses dynamic light scattering, which provides a measure of the effective size of the aggregates formed as the photolysis proceeds. We do not have equipment to monitor light scattering during the irradiation, so the measurements involved removing the sample from the photoreactor and quickly carrying out a dynamic light-scattering measurement. A typical result is shown in Figure 2. Flocculation of the PBMA/OH/CO_2PC_{18} at its CPC (1:3 hexadecane/cyclohexane) occurred after about 3 min of irradiation. The polymer particles eventually precipitated out

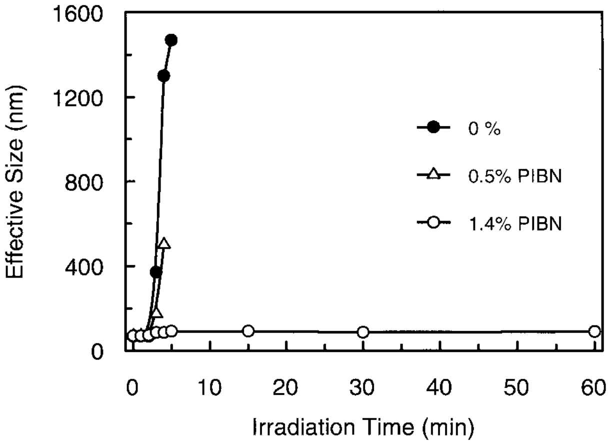


Figure 2. Effective size of the particles measured by dynamic light scattering as a function of irradiation time. Samples were irradiated in a Rayonet reactor ($\lambda > 300$ nm). The sample was PBMA/OH/PC18 (4 mg/mL) in 25:75 hexadecane/cyclohexane. PIB−NH$_2$ is polyisobutylene (MW ≈ 1000) with a primary amino terminal group. The flocculation can also be detected visually.

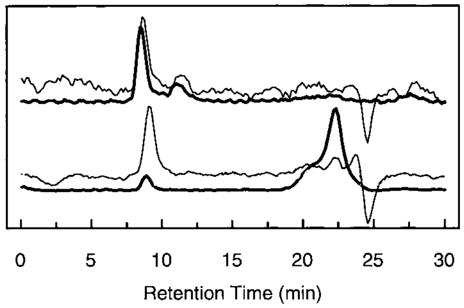


Figure 3. Gel permeation chromatogram of PMMA/OH/CO$_2$PIB−NH$_2$ before (upper pair of curves) and after (lower pair of curves) 30-min photolysis (UV, >300 nm) in 2:1 cyclohexane/THF: GPC column, 500 and 10,000 Å; solvent, THF; UV detector at 249 nm (thick curves); refractive index (thin curves).

of the solution, either upon further irradiation or if the sample was allowed to stand. Increasing the cyclohexane content of the continuous medium increased the irradiation time necessary to flocculate the dispersion. More than 1 h of irradiation was required to flocculate the particles in cyclohexane under the same irradiation conditions.

Surprisingly, PMMA particles modified with PIB−NH$_2$ did not show any indication of flocculation upon UV irradiation. When the PMMA particles modified with PIB (PMMA/OH/CO$_2$−PIB) were irradiated in THF dispersion, they showed a behavior similar to that described above for the PBMA/OH/CO$_2$PC$_{18}$ particles. When the reaction was followed by GPC, as is shown in Figure 3, the UV absorption of the particles decreased dramatically after UV irradiation. We emphasize the point, however, that no photoinduced flocculation occurred even in a solvent mixture at the CPC (1:2 THF/cyclohexane), whereas the GPC analysis showed that the photochemical reaction of the chromophore did occur in this system.

This observation is very important because it provides the first indication that a free polymer in solution can act to stabilize the carboxyl-bearing particles. For flocculation to occur, not only must the chromophore-bearing chains be cleaved from the particles but the "free" chains must not reassociate with the particles. According the reaction shown in Scheme 4, the detached PIB moiety has both nitroso and aldehyde groups. Both are reactive species and are also hydrogen-bond acceptors. One can imagine that the polymer might reassociate with particles through, for example, reaction of the aldehyde to form an acetal or hemiacetal with the hydroxyl groups of the PMMA particles, or that the nitroso and aldehyde groups might form hydrogen bonds with the COOH groups on the particle surface.

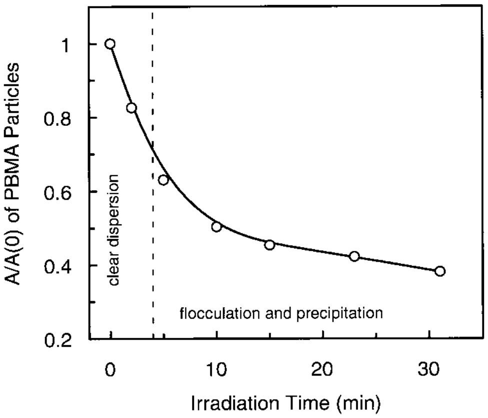


Figure 4. Photochemical bleaching of the chromophore from PBMA/OH/CO$_2$PC18 (3.7 mg/mL) in 80:20 cyclohexane/hexadecane in the presence of 15 mg/mL of PIB−NH$_2$ as stabilizer. The UV absorbance was monitored at 249 nm. The vertical dashed line at ca. 8 min indicates where flocculation would be visible to the eye in the absence of PIB−NH$_2$.

Polymeric Dispersants. Polymeric dispersants are hydrocarbon-soluble polymers introduced into a system with the express intent of preventing flocculation of any colloidal material that may form. One of the long-range goals of this research is to develop the particle and particle-surface chemistry so that photoinduced flocculation can be used as a test for the effectiveness of commercial dispersants. A convenient model dispersant, based on ideas described in the previous paragraph, might be PIB−NH$_2$. This polymer can interact with the COOH groups formed through irradiation at the particle surface.

We saw above that dispersions of PBMA/OH/CO$_2$PC$_{18}$ in cyclohexane and in cyclohexane/hexadecane mixtures flocculate when irradiated with UV light. Here, we examine the effectiveness of PIB−NH$_2$ as a model dispersant in suppressing the flocculation. Figure 2 shows the effective size of the aggregates formed, as detected by dynamic light scattering, for irradiation of a PBMA/OH/CO$_2$PC$_{18}$ dispersion (4 mg/mL in 25:75 cyclohexane/hexadecane) in the absence and presence of PIB−NH$_2$. In the absence of PIB−NH$_2$, flocculation occurs after only about 3 min of irradiation. In the presence of very small amounts (0.5 wt %) of this polymer, flocculation is somewhat retarded. If a larger amount (e.g., 1.4 wt %) of PIB−NH$_2$ is present, no flocculation occurs. Other short-chain aliphatic amines such as butylamine do not suppress flocculation, even at higher concentrations. In the presence of PIB−NH$_2$, photobleaching occurs as expected. Figure 4 shows the decrease of the absorption of the PBMA/OH/CO$_2$PC$_{18}$ particles in 4:1 cyclohexane/hexadecane at 249 nm. Without PIB−NH$_2$, this dispersion will begin to flocculate after 4 min of irradiation, roughly after 20% of the total chromophore has reacted. In the presence of the PIB−NH$_2$, the solution remains transparent and the absorbance can be monitored until the reaction goes to completion.

The antiflocculation properties of PIB−NH$_2$ can be attributed to its ability to associate with the particles by hydrogen bonding or salt formation with the newly formed carboxylic acid groups. PIB−NH$_2$ not only blocks the carboxylic groups of the particles from self-association but its long hydrocarbon chains provide steric stabilization of the particles with hydrophilic surfaces formed during the irradiation.

Conclusions

PBMA and PMMA particles ca. 50 nm in diameter, which form stable dispersions in aliphatic-hydrocarbon-containing media, were prepared in a multistep process. Cross-linked particles containing $-COOH$ and $-CH_2OH$ groups were prepared by batch emulsion polymerization in water. After neutralization with $CsCO_3$, the particles were dried and redispersed as microgels in DMF. At this point, hydrocarbon-soluble steric-stabilizer groups were attached, using a photocleavable chromophore as part of the attachment site. When these particles were irradiated in hydrocarbon-containing media, flocculation due to cleavage of the stabilizer arms from the particles occurred. When the irradiation was carried out in the presence of $PIB-NH_2$, flocculation was suppressed. The dispersant action of the polymer most likely occurs through strong adsorption of the amino end onto the particle surface, which after irradiation contains carboxylic acid groups. We see these results as the first step in developing a system to model precursors to sludge formation in motor oil and as a test platform for examining the effectiveness of other dispersants in suppressing flocculation of these precursors.

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