Core–Shell Structured Latex Particles. I. Copolymerization of Styrene/Benzyl Methacrylate as a Choice for Shell Material and Characterization of Poly(n-butyl acrylate) Core Latex Particles

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SYNOPSIS

Composition, molecular weight, and microstructure of the "shell" polymer in core–shell structured latex particles, designed for toughening polycarbonate matrix, should be controlled for enhanced miscibility between the shell polymer and the matrix. Various "shell polymer" systems based on styrene (St) and benzyl methacrylate (BM) were synthesized. Reactivity ratios were determined for (St) and (BM). Chain transfer efficiency studies revealed the susceptibility of styrene to transfer to a chain transfer agent. Benzyl methacrylate was found to have steric and stability factors hindering its tendency to chain transfer with various chain transfer agents. Miscibility tests between P(St/BM) and polycarbonate (PC) indicated different degrees of miscibility, depending upon polymerization conditions. Factors other than molecular weight, such as branching and crosslinking, were found to play a role in the miscibility. Monodisperse poly(n-butyl acrylate) (PBA) seed latex particles of variable degree of crosslinking and particle size were successfully synthesized by batch emulsion polymerization. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Structured latex particles displaying different types of particle morphologies have wide industrial applications. Some of these applications involve enhancing peal strength in adhesives, improving barrier properties and block resistance in coatings applications, and modifying and enhancing the toughness of engineering plastics. The design of particle morphology for a specific application is of paramount importance and is the subject of many recent research efforts, as shown in the patent literature.

In a series of three articles we will report on our systematic studies generating the knowledge base for designing core–shell particle morphology with the specific target of toughening a polycarbonate matrix. The most important feature of this work is our ability to use "monodisperse" latex particles and to vary the core–shell polymer ratios. This allows better interpretation of the influence of various parameters on toughness properties, including the influence of the rubber particle size, without influence of polydispersity in particle sizes.

The toughness of a thermoplastic polymer is a complicated property that depends on many variables such as temperature, loading mode, specimen geometry, and crazing and/or yielding at the micromechanical level. Toughness also depends on phase morphology (size and volume fraction of various phases) on the microstructural level and chain structure at the molecular level.

It was shown by Donald and Kramer[1,2] that the craze-yielding behavior of a glassy polymer is controlled by two chain parameters, the entanglement

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Table I   Basic Recipe for the Polymerization of Poly(styrene/benzyl methacrylate) P(St/BM) Latex Particles

Component	Amount (g)
DDI water	75.0
Dowfax 8390 (35% solids)	0.12
Potassium persulfate	0.3
Styrene	30.0 to 0
Benzyl methacrylate	0 to 30.0
Isooctyl mercaptopropionate	0.03

density (ratio of the density of the amorphous phase and the molecular weight of an entanglement strand), and the characteristic ratio of the chain (a measure of the flexibility, rigidity, or tortuosity of an unperturbed real chain). The entanglement junctions are contact points involving two or more chains. Wu[3] modeled entanglement junctions as binary hooking contacts of Kuhn nodes between two chains. He observed that the "hooking" geometry required to form an entanglement junction may vary somewhat with chain structure, such as tacticity and the effect of the size of pendant groups.

The competition between crazing and yielding determines the predominant mode of fracture. Wu has demonstrated experimentally that for a large number of glassy polymers in an amorphous or semi-crystalline phase, the crazing stress is proportional to the entanglement density and the yield stress is proportional to the characteristic ratio of the chains (a measure of ductility). The toughness of a glassy polymer-rubber blend depends on many factors such as the size, shape, amount, glass transition temperature, and adhesion of the rubber. It was demonstrated that the responsiveness of a matrix to rubber toughening depends on its intrinsic brittleness and ductility (entanglement density and characteristic chain ratio, respectively).

Because of differential thermal shrinkage of the rubber and the matrix during cooling from the melt, internal stresses are generated in the matrix ligaments. Because the rubber shrinks more than and has a glass transition temperature lower than the matrix, compressive stresses and radial tensile stresses are induced on the matrix ligaments. Core-shell type of toughening particles can be highly effective when the chemical constitution and chain structure of the shell are designed so that an interphase layer of entangled miscible chains with a controlled craze-yielding behavior is formed to enhance the adhesion between the rubbery discrete phase and the matrix continuous phase. Therefore, the molec-

ular characteristics of the shell material are very important in selecting the appropriate shell polymer.

In a series of three articles we will report on recent efforts to prepare core-shell latex particles for the modification of polycarbonate thermoplastics. The first article is devoted to the preparation and characterization of styrene/benzyl methacrylate copolymers to be used as the shell polymer. The second article deals with the synthesis and characterization of poly(n-butyl acrylate)/(styrene/benzyl methacrylate) core-shell structured latex particles. The third article centers on the performance of these core-shell structured latex particles in toughening polycarbonate matrix.

When discussing the shell polymer system throughout this article, we do not refer to an actual shell in the structured (core-shell) latex particles, but to the system that will later on constitute the shell material. This article contains: (1) a screening study of different polymerization parameters in order to achieve a stable "shell" latex system with controlled composition and molecular weight; (2) miscibility testing of these latexes with the polycarbonate matrix, and (3) description of the synthesis and characterization of two basic "seed" core PBA particles, "small" and "large."

For the purpose of this project, miscibility is defined in terms of glass transition temperatures as determined by Differential Scanning Calorimetry (DSC).[4,5] Two polymers of distinct glass transition temperatures are considered miscible with each other when their blend yields a single glass transition temperature. A certain degree of miscibility is indicated by a shift in the glass transition temperature of one or all components of the blend towards each other. Miscibility is a function of the affinity between the polymer additive particles and the polymer matrix. Using a specific type of matrix, the affinity with the added particles can be manipulated by the choice of polymer additive or copolymer composition as well

Table II   Molecular Weights and Particle Sizes for Styrene/Benzyl Methacrylate (St/BM) Latex Particles

Sample #	Composition St/BM	$M_w^a \times 10^{-5}$	D_v (nm)
24	100/0	3.0	108
23	75/25	2.4	101
22	50/50	2.6	88
26	25/75	3.0	88
25	0/100	6.7	48

[a] Based on PS calibration curve.

**Table III Glass Transition Temperatures for Blends of 70/30 Polycarbonate/
Poly(benzyl methacrylate/styrene) (PC/P(BM/St)) Weight Ratio**

Sample #	Composition St/BM	T_g^1 (°C)	T_g int[a] (°C)	T_g^2 (°C)
24	100/0	106	—	147
23	75/25	93	—	150
22	50/50	81	—	145
26	25/75	73	—	143
25	0/100	68	88	136

[a] Intermediate.

as by controlling the molecular weight of the added particles. Based on the miscibility tests, the appropriate "shell system" will be chosen for further studies on structured latex particles, where the "shell system" will be the second stage polymer synthesized in the presence of PBA seed latex particles (see Part II in the series).

Poly(n-butyl acrylate) (PBA) was chosen as a model system for the preparation of latex particles to be used as the seed in the preparation of core-shell type latex particles designed for the toughening of a polycarbonate matrix. PBA is a rubbery material, with a relatively low glass transition temperature (-54°C). It can be crosslinked to induce ductility and it is weather resistant.[6] In this article, the synthesis of PBA seed latex particles of different particle sizes and variable degree of crosslinking is described. The particle sizes were designed to be approximately 200 nm and 400 nm in diameter (small and large size particles, respectively). Two monomer–crosslinker weight ratios were used, 93/7 and 99/1 n-butyl acrylate/ethylene glycol dimethacrylate (BA/EGDMA). A thorough study of PBA kinetics of emulsion polymerization was published by Maxwell et. al.[7]

MATERIALS

"Shell"

Styrene (Aldrich), and phenyl methacrylate (Polysciences Inc.) were distilled, benzyl methacrylate (Polysciences Inc.) was passed through an inhibitor remover column with inhibitor remover packing material designed to remove hydroquinone (HQ) and methyl ethyl hydroquinone (MEHQ) (Aldrich). All purified monomers were kept at -2°C until used. Chain transfer agents; tertiary dodecyl mercaptan (tDDM, Pennwalt Corporation), isooctyl mercaptopropionate (IOMP, Evans Chemetics), and n-

butyl mercaptopropionate (nBMP, Evans Chemetics), emulsifiers; Dowfax 8390 (alkylated diphenyl oxide disulfonates, The Dow Chemicals Co.), initiators; potassium persulfate ($K_2S_2O_8$, FMC), sodium bisulfite (NaHSO$_3$, Fisher), azobis(isobutyronitrile) (AIBN, DuPont), solvents; chloroform (CHCl$_3$), tetrahydrofuran (THF), benzene, and methanol (Fisher, ACS certified), and sodium chloride salt (NaCl, Fisher) were all used as received. Water was distilled and deionized.

"Seed"

n-Butyl acrylate (BA, Aldrich) was distilled and the purified monomer was stored at -2°C until used. Ethylene glycol dimethacrylate (EGDMA, Sartomer) was passed through a column containing inhibitor remover packing material designed for the removal of hydroquinone (HQ) and monomethyl ether hydroquinone (MEHQ) (Aldrich). Aerosol MA-80 (sodium dihexyl sulfosuccinate, 80% active ingredients, American Cyanamid Co.), and Aerosol AY-65 (sodium diamyl sulfosuccinate, 65% active ingredients, American Cyanamid Co.) emulsifiers were used as received, potassium persulfate ($K_2S_2O_8$, FMC), and sodium bicarbonate (NaHCO$_3$, Fisher) were also used as received. The water was distilled and deionized (DDI).

EXPERIMENTAL

"Shell" Polymerization

Emulsion polymerizations were carried out in a round-bottom glass vessel equipped with a reflux condenser, a glass stirrer, a nitrogen inlet tube, and a feeding tube. The feeding tube was connected to a syringe operated by a syringe pump with an adjustable feed rate. The DDI water, emulsifier, initiator, and 10–15% of the monomer mixture were
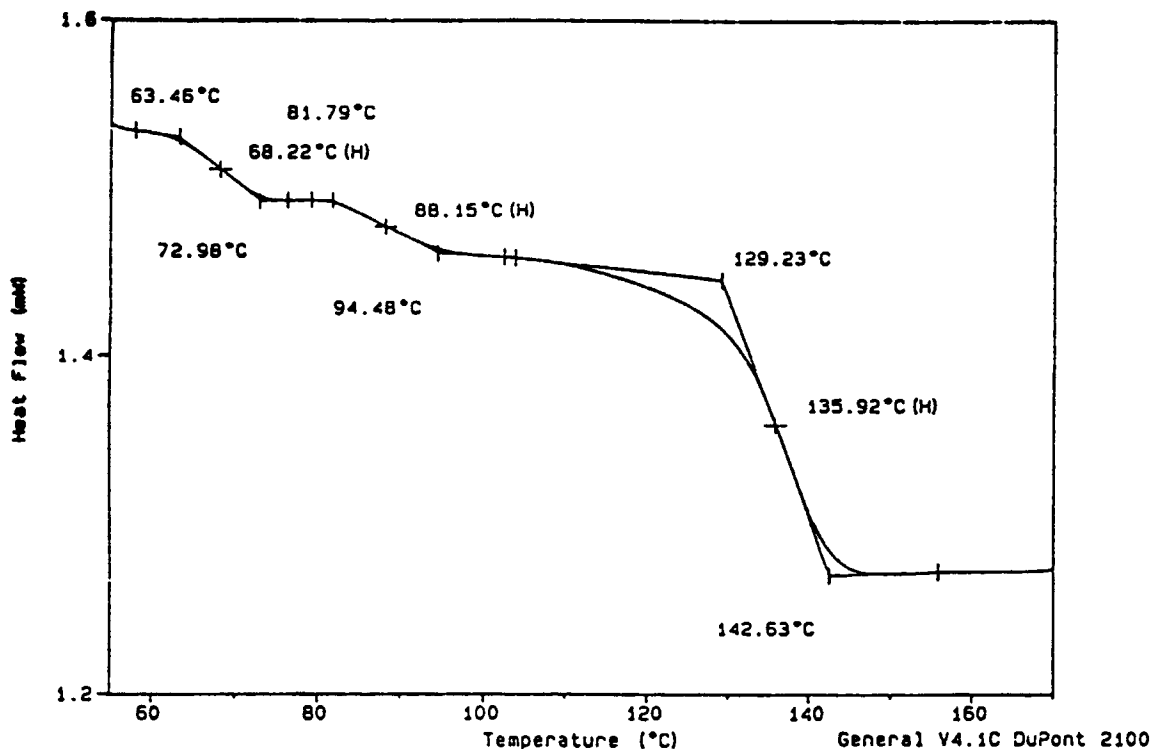
Figure 1 Differential scanning calorimetry curve for 70/30 PC/PBM weight ratio blend.

introduced into the reactor for preseeding. The balance of the monomer mixture was fed into the reactor at a constant rate. Polymerizations were carried out at 70°C. The temperature was held at 70°C for 2 h after the end of the monomer feeding stage and then increased to 90°C for 1 additional hour before the reaction flask was removed from the polymerization bath.
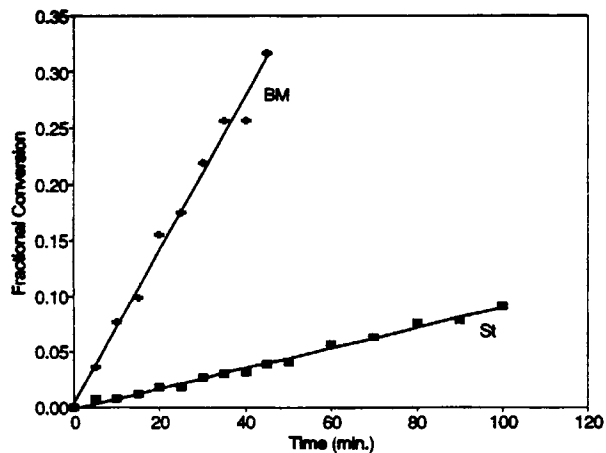

Figure 2 Conversion vs. time curves for bulk polymerized styrene (St) and benzyl methacrylate (BM) monomers; 70°C.

"Shell" Molecular Weight and Particle Size Determination

Molecular weights were determined by Gel Permeation Chromatography (GPC) using 0.15 wt % polymer that had been precipitated in methanol, dried, and redispersed in tetrahydrofuran (THF). Particle sizes were obtained using the Nicomp Submicron Particle Sizer.
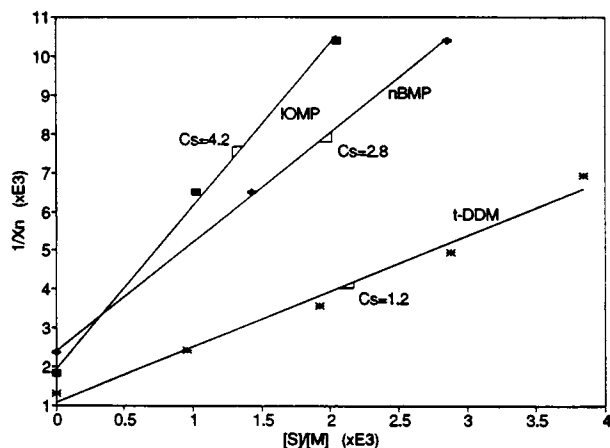
"Shell" Miscibility with Polycarbonate

The St/BM latex particles were dried and blended with PC. Blends of (St/BM)/PC in weight ratios

Table IV Values of Styrene and Benzyl Methacrylate Reactivity Ratios Reported in the Literature[a] (Obtained at 60°C)

r_1 St	r_2 BM
0.48	0.42
0.45	0.51
0.44	0.51
0.46	0.62

[a] Bradrup and E. H. Immergut, *Polymer Handbook*, Wiley & Sons, New York, 1985.

Figure 3   1/Xn vs. [S]/[M] in the bulk polymerization of styrene carried out at 70°C for chain transfer agents: IOMP, nBMP, t-DDM. Slope = chain transfer constant, Cs.

Table V   Experimental Chain Transfer Constants for the Various Chain Transfer Agents with Styrene and Benzyl Methacrylate for Polymerizations Carried Out at 70°C

Chain Transfer Agent	Cs Value	
	Styrene	Benzyl Methacrylate
IOMP	4.2	0.54
n-BMP	2.8	0.68
t-DDM	1.2	0.13

of 70/30 and 30/70 were subjected to Differential Scanning Calorimetry (DSC) measurements to determine their miscibility. DSC runs were carried out on a General V4.1C DuPont 2100 according to the procedure described elsewhere.[8]

"Seed" Polymerization

n-Butyl acrylate, ethylene glycol dimethacrylate, Aerosol MA-80, and DDI water were heated to 75°C under a nitrogen atmosphere, with mechanical agitation in order to form a monomer-in-water emulsion. The potassium persulfate initiator ($K_2S_2O_8$) was dissolved in water, heated to 75°C, and added

to the emulsion in the reaction vessel. Polymerization was allowed to continue at 75°C for 15 h.

RESULTS AND DISCUSSIONS

Emulsion Polymerization I

A series of copolymerizations were carried out using styrene and benzyl methacrylate (BM) covering weight ratios of 0/100, 25/75, 50/50, 75/25, and 100/0 St/BM. The basic recipe is given in Table I.

Molecular Weight and Particle Size Determination

The styrene/benzyl methacrylate copolymers contain a benzyl group and a carbonyl group, both of which have an effect on the hydrodynamic volume. It is difficult to estimate which group has a greater
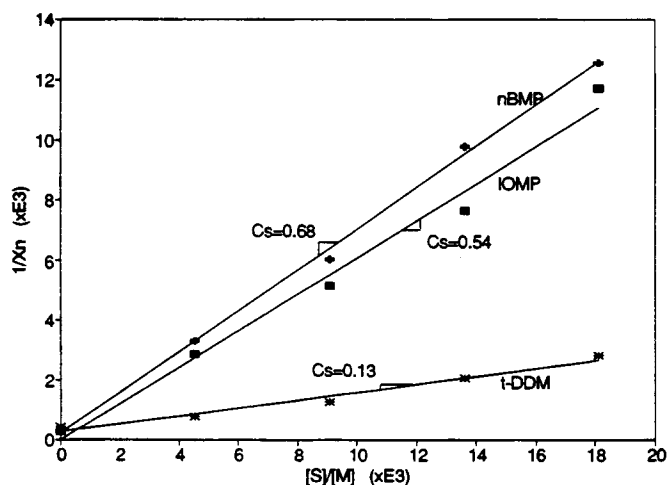
Figure 4   1/Xn vs. [S]/[M] in the bulk polymerization of benzyl methacrylate carried out at 70°C for chain transfer agents: nBMP, IOMP, t-DDM. Slope = chain transfer constant, Cs.

Table VI   Glass Transition Temperatures for Blends of 70/30 Polycarbonate/ Poly(benzyl methacrylate) (PC/PBM) Weight Ratio, Using PBM Polymerized in Bulk

Sample	M_w g/mol	T_g^1 (°C)	T_g int.[a] (°C)	T_g^2 (°C)
PBM-1	1×10^6	63	—	131
PBM-2	1×10^5	62	79	137
PBM-3	6×10^4	63	82	144
PBM-4	4×10^4	62	77	140
PBM-5	3×10^4	65	82	145

[a] Intermediate.

effect. The following discussion will be based on molecular weights determined by using the polystyrene calibration curve, keeping in mind that molecular weights are not absolute but relative to each other. Table II gives the weight average molecular weight (M_w) and particle diameter (D_v) for the resulting styrene/benzyl methacrylate (St/BM) copolymer latexes.

It can be seen from Table II that increasing the amount of benzyl methacrylate in the copolymers resulted in a decrease in the latex particle size (volume average diameter D_v). The decrease in the particle size is usually correlated with a higher polarity of the polymer particles. However, the smaller particle size created a larger surface area with the result that the amount of surfactant used in the polymerization became insufficient to assure complete stability of the latex particles against aggregation. It was necessary to add a small amount of Dowfax 8390 to poststabilize latexes containing 75% and 100% benzyl methacrylate.

Table II shows that all molecular weights, except the one corresponding to 100% benzyl methacrylate, were in the range of 3.0×10^5; the latter had a molecular weight of 6.7×10^5, twofold higher than the rest, despite the use of the same amount of isooctyl

mercaptopropionate chain transfer agent in all cases. These molecular weight differences may result from the styrene being more susceptible to chain transfer reactions than the benzyl methacrylate. However, the benzyl methacrylate homopolymer sample was also the one with the smallest particle size, 40 nm, compared to the other samples having diameters ranging from 88 to 108 nm. Smaller latex particle sizes usually yield higher molecular weights, because there is less chance for termination, because there is less initiator and/or transfer agent radicals per particle.

Miscibility of Styrene/Benzyl Methacrylate (St/BM) Copolymer with Polycarbonate (PC)

Table III contains the first and second glass transition temperatures (T_g) for blends of the 70/30 PC/ X weight ratios, where X represents the St/BM copolymers of different weight ratio compositions. Table III shows that all blends containing PS or P(St/BM) presented two distinct T_gs. No significant shift was observed for the T_g of the components in the blend compared to the parent components (before blending). However, the DSC scan of the blend containing PC and PBM homopolymer, shown in Figure 1, indicated the existence of three T_gs and a shift of the higher T_g (corresponding to the PC) towards lower temperature pointing to the presence

Table VII   Influence of Polymerization Temperature and Initiating System on Molecular Weights of Poly(benzyl methacrylate) Latex Particles

Sample	T (°C)	$M_w \times 10^{-5}$ g/mol	$M_n \times 10^{-5}$ g/mol	PDI
25	70	6.7	1.1	6.1
45*	45	7.3	1.5	5.0
46*	35	2.3	1.0	2.2

* Redox initiator system of persulfate/bisulfite.

Table VIII   Influence of Monomer Addition Mode on the Molecular Weight of Poly(benzyl methacrylate) Latex Particles

Sample	Addition Mode	$M_w \times 10^{-5}$ g/mol	$M_n \times 10^{-5}$ g/mol	PDI
25	Semicont	6.7	1.1	6.1
40	Batch	5.0	1.9	2.7

Table IX Influence of the Methacrylate Ester Monomer Chemical Structure on the Molecular Weight of the Polymer Latex Particles

Sample	$M_w \times 10^{-5}$ g/mol	$M_n \times 10^{-5}$ g/mol	PDI
25[a]	6.7	1.1	6.1
52[b]	2.0	0.88	2.3

[a] Poly(benzyl methacrylate).
[b] Poly(phenyl methacrylate).

of domains of miscibility between the PBM and the PC.

Bulk Polymerization

Bulk polymerization reactions were designed to determine the reactivity ratios of BM with St as well as the chain transfer efficiency of different CTAs in order to obtain a better understanding of the kinetics of copolymerization of the BM with St and the effect of chain transfer agents (CTA) on the polymerization of these two monomers as well as the dependence of molecular weight on comonomer composition.

Bulk polymerizations were carried out in rubber septa capped test tubes, secured with a wire, evacuated, and purged with nitrogen. The test tubes, with AIBN–monomer mixtures were placed in a thermostated water bath at 70°C. When the test tubes were taken out of the water bath, the reaction was stopped by immersing the tubes in ice. Conversion vs. time curves based on refractive index measurements for styrene homopolymerization and BM homopolymerization in bulk are shown in Figure 2.

This study was necessary in order to determine the polymerization time needed for a conversion of monomer to polymer under 10%, so subsequent evaluation of reactivity ratios were not affected by the Trommsdorff or gel effect due to high viscosity.[9] Figure 2 indicates a much faster conversion rate for the BM polymerization with a slope of 6.07, as compared to styrene homopolymerization with a slope of 0.92, which correspond to initial polymerization rates of 6.8×10^{-4} mol/lit s and 1.3×10^{-4} mol/lit s, respectively.

Copolymerization Reactivity Ratios

For the reactivity ratios determination, six test tubes with varying styrene/benzyl methactylate monomer ratios were placed in a thermostated water bath at 70°C. The resulting copolymers were precipitated

in methanol and redispersed in chloroform at a known concentration of approximately 0.05 g/mL, for FTIR measurements.

Methacrylate polymers exhibit a peak on an infrared (IR) spectrum at a wavelength of approximately 1723 cm^{-1}, due to the absorbance of carbonyl groups. Polystyrene does not absorb at this wavelength.[10] Therefore, FTIR can be used to detect and determine the methacrylate content present in copolymers with varying St/BM ratios.

The reactivity ratios r_1 and r_2, for St and BM, were calculated by two different methodes[11-13] to be 0.35 and 0.86, respectively. Values of the reactivity ratios reported in the literature[14] for St and BM at 60°C are given in Table IV for comparison.

The order of magnitude of the experimental values as well as the reactivity ratio for BM (r_2) being higher than the reactivity ratio of St (r_1) are in accordance with the literature values given in Table IV for polymerizations carried out at 60°C. There are no reported data on the effect of the temperature on the reactivity ratios that could help predict them at 70°C, the temperature at which the experiments of this work were carried out, to mimic the conditions employed during the emulsion polymerization experiments. The fact that the values of both r_1 and r_2 are lower than unity indicate that both monomers prefer to react with each other rather than with themselves, leading to the synthesis of a random as opposed to block copolymer.

Chain Transfer Efficiency of Different Chain Transfer Agents in Bulk Polymerizations of Styrene and Benzyl Methacrylate

Bulk homopolymerization of styrene and benzyl methacrylate containing varying amounts of different chain transfer agents were carried out at 70°C to evaluate the chain transfer agent efficiency.

The chain transfer constant to chain transfer agent, Cs, is determined from the slope of the linear

Table X Influence of Isooctyl Mercaptopropionate (IOMP) Chain Transfer Agent Concentration [CTA] on Molecular Weight of Poly(benzyl methacrylate) (PBM) Latex Particles

Sample	[CTA] (cc)	$M_w \times 10^{-5}$ g/mol	$M_n \times 10^{-5}$ g/mol	PDI
25	0.003	6.7	1.1	6.1
37	0.015	1.6	1.1	1.5
31	0.030	0.54	0.25	2.1

plot of $1/Xn$ vs. $[S]/[M]$ where Xn is the degree of polymerization (determined from GPC data), and $[S]$ and $[M]$ are the concentrations of chain transfer agent and monomer, respectively. Such plots for PS and PBM are given in Figures 3 and 4, respectively. The resulting values of Cs for the various chain transfer agents with St and BM are given in Table V.

The Cs data in Table V show that in the case of PS, IOMP is the most efficient chain transfer agent; whereas in the case of PBM, nBMP is acting more efficiently than IOMP. However, for the PBM system, the difference in Cs due to the presence of IOMP and n-BMP is small (0.68 vs. 0.54), and, therefore, IOMP was chosen as the chain transfer agent, with the added advantage of being odorless. This is an important factor, especially when a large amount of chain transfer agent is required for a significant decrease in the molecular weight.

It is important to note that the chain transfer agent constants for PS are one order of magnitude higher than the chain transfer agent constants for PBM; indicating that styrene is more prone to transfer to a chain transfer agent than is benzyl methacrylate.

The enhanced degree of chain transfer for styrene is also important in explaining the fact that emulsion BM homopolymerizations yielded molecular weights twice as high as those reported for St/BM copoly-

Table XI   Influence of the Potassium Persulfate Initiator Concentration [I] on the Particle Size (D_v) and Molecular Weights of Poly(benzyl methacrylate) Latex Particles

Sample	[I] (g)	D_V (nm)	$M_w \times 10^{-5}$ g/mol	$M_n \times 10^{-5}$ g/mol	PDI
37	0.03	—	1.6	1.1	1.5
60	0.06	130	1.1	0.46	2.4
61	0.15	193	1.1	0.38	2.8
62	0.30	347	1.3	0.36	3.6

mers (see Table II), despite the fact that all those polymerizations were carried out under the same conditions using the same amounts of chain transfer agent.

Miscibility of Bulk Polymerized Poly(benzyl methacrylate) with Polycarbonate

In order to study the influence of molecular weight on the miscibility between two polymers, miscibility tests were also performed on the bulk polymerized PBM, which were originally synthesized for the purpose of chain transfer efficiency studies. As observed in Table VI, sample PBM-1, which had the highest weight average molecular weight in this series, presented two glass transition temperatures
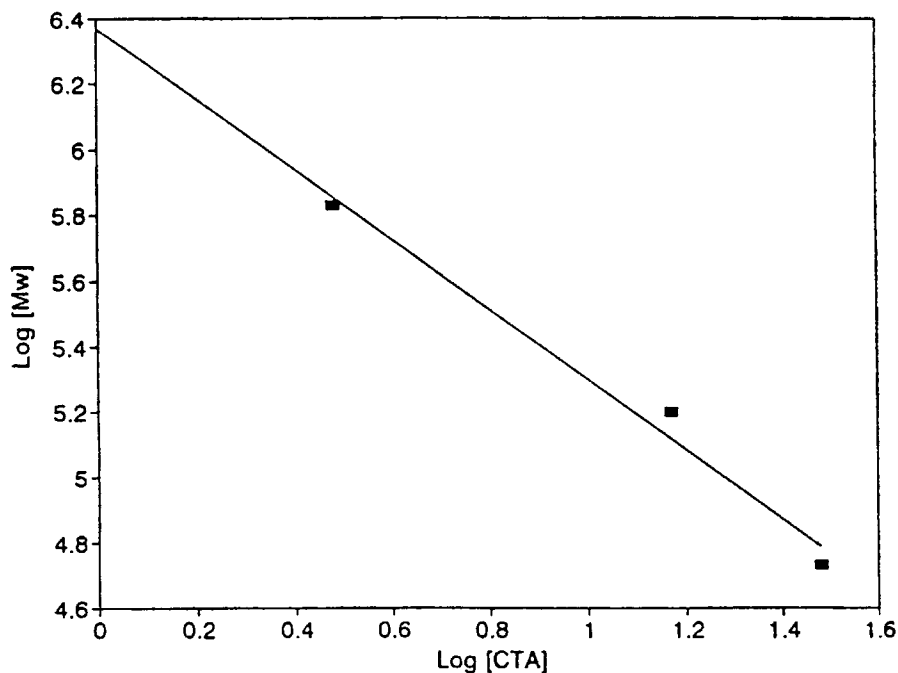
Figure 5   Log M_w vs. log [CTA] for the emulsion polymerization of benzyl methacrylate in the presence of IOMP chain transfer agent at 70°C.

Table XII   Basic Recipe for Benzyl Methacrylate/Styrene (BM/St) Emulsion Copolymerization

Recipe Component	weight (g)
DDI water	7.5
Dowfax 8390 emulsifier (35% solids)	0.012
Potassium persulfate, initiator	0.03
Monomer	3.0 (variable BM/St wt ratios)
Isooctyl mercaptopropionate	0.015

(T_g); while all the others presented three T_gs. However, the shift towards lower temperatures observed for T_g2 (corresponding to the PC, $T_g = 147°C$) for PBM-1 and PBM-2, 131 and 137°C, respectively, is more significant than the shift in T_g2 for samples PBM-3, PBM-4, and PBM-5 (144, 140, and 145°C, respectively). Samples PBM-2 through PBM-5 presented three distinct T_gs, indicating a certain degree of miscibility or domains of miscibility between the PBM and the PC in the blend. It is uncertain at this point which is more favorable, a higher molecular weight for the PBM displaying only two glass transition temperatures for the PBM/PC blend and a big shift in T_g2, or a lower molecular weight of the PBM accompanied by a third, intermediate T_g, where there is no significant shift of the high temperature T_g corresponding to the PC. Generally speaking, "high molecular weight" bulk polymerized samples that have no or low CTA concentration produce longer polymer chains compared to the samples synthesized in the presence of higher CTA concentration. Longer polymer chains, despite their chain entanglements, may interdiffuse further into the PC matrix.

Once the effect of CTA in bulk polymerization of St and BM were better understood, it was time to go back to emulsion polymerization and evaluate the effect of polymerization parameters on the molecular weight of emulsion polymerized BM.

Emulsion Polymerization II

We tried to understand the reason for the high molecular weight of the BM homopolymer by finding an answer to whether this is due merely to the fact that the BM is less prone to react with the chain transfer agent, or is it also due to its tendency towards branching. The following approaches were taken in order to address the above question: (1) conduct polymerizations at low temperatures using a redox initiator; (2) carry out polymerizations by a batch process; (3) polymerize a monomer similar to BM, which differs only by one less $-CH_2-$ group, such as phenyl methacrylate (PHM), making it less prone to branching.

Effect of Polymerization Temperature

Two redox initiated emulsion homopolymerizations of benzyl methacrylate were carried out at 35°C and 45°C, by semicontinuous emulsion polymerization. Table VII shows the molecular weight and polydispersity index (M_w/M_n) for samples 25, 45, and 46, polymerized at 70°C, 45°C, and 35°C, respectively. For the redox polymerized latexes (samples 45 and 46) the same basic recipe as given in Table I was used; only sodium bisulfite was added (0.015 g), one-half at the beginning of the polymerization, the other half 30 min later, when the semicontinuous feed was started. Comparison of results for samples 45 and 46 show a significant drop in the weight average molecular weight from 7.3×10^5 to 2.3×10^5, which seemed to be the result of a 10°C decrease in the polymerization temperature.

Sample 25 had a weight average molecular weight of 6.7×10^5, slightly lower than the molecular weight obtained by redox initiation at 45°C, and about threefold higher than the molecular weight of sample

Table XIII   Influence of Copolymer Composition on Molecular Weight of Poly(benzyl methacrylate/styrene) Latex Particles

Sample	Composition BM/St (wt %)	D_v (nm)	$M_w \times 10^{-4}$ g/mol	$M_n \times 10^{-4}$ g/mol	PDI
63	95/05	109	9.3	4.1	2.3
64	90/10	98	8.2	4.4	1.9

Table XIV Basic Recipe for Benzyl Methacrylate Emulsion Polymerization

Component	Amount (g)
DDI water	7.5
Dowfax 8390 (35% solids)	0.012 ± 0.1 (1 h later)
Potassium persulfate	0.03
Sodium bisulfite	0.015
Benzyl methacrylate	3
Isooctyl mercaptopropionate	variable (0.015 or 0.03 g)

46, polymerized at 35°C. The reason may not only be due to the actual temperature difference, but to the change in the initiator's radical flux caused by the presence or absence of a reductant ($NaHSO_3$) in the system.

Effect of Monomer Addition Mode

The influence of the mode of monomer addition is reflected in the results shown in Table VIII, where sample 25, polymerized by semicontinuous addition under monomer starved conditions at 70°C, is compared with sample 40, polymerized in batch at the same temperature, giving weight average molecular weights of 6.7×10^5 and 5.0×10^5, respectively. As expected, the batch polymerized latex had a lower weight average molecular weight. The higher molecular weight for the semicontinuous monomer addition case is attributed to a greater degree of branching, which takes place under monomer starved conditions. The number average molecular weight indicated a greater fraction of low molecular weight chains in the batch polymerized latex, where branching is not favored.

Effect of Monomer Chemical Structure

In order to determine the effect of the monomer chemical structure, polymerizations of benzyl methacrylate and phenyl methacrylate (recipe given in Table I) were carried out at 70°C. The results given in Table IX reflect a significant decrease in the weight average molecular weight from 6.7×10^5 to 2.0×10^5, by using a different methacrylate ester monomer, phenyl methacrylate (PHM, sample 52), which contains one less $-CH_2-$ group than the BM monomer used in sample 25. The chemical structure of the PHM monomer used for the polymerization of sample 52 restricts its ability for branching due to steric effects and stability factors.

The above-mentioned experimental results allowed us to conclude that BM is prone to branching, and, therefore, yields higher molecular weights. Keeping in mind the objective of reducing the molecular weight of the PBM, studies were conducted on the effectiveness of changing the concentration of the chain transfer agent (IOMP) and initiator used.

Effect of Chain Transfer Agent Concentration

Studies of chain transfer agent concentration effect on the molecular weight of emulsion polymerized PBM were carried out by using the recipe given in Table I and a polymerization temperature of 70°C. The only difference from one polymerization to the next was in the concentration of the IOMP chain transfer agent. The influence of the chain transfer agent concentration on the molecular weights of PBM latexes is given in Table X. It is observed that as the chain transfer agent concentration was increased, the weight average molecular weight dropped exponentially. This effect is represented by the straight line obtained when plotting log M_w as a function of log CTA concentration and can be seen in Figure 5.

Effect of Initiator Concentration

The influence of potassium persulfate initiator concentration on the particle diameter and the molecular weight of BM homopolymer latexes is given in

Table XV Molecular Weights Obtained for Semicontinuous and Batch Benzyl Methacrylate Redox Initiated Emulsion Polymerizations at 35°C

Sample	Addition Mode	IOMP[a] wt %	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	PDI
74	Semi[b]	1.0	41	19	2.1
75	Semi[b]	0.5	64	29	2.2
68	Batch	1.0	45	20	2.2
70	Batch	0.5	95	40	2.4

[a] Isooctyl mercaptopropionate, based on monomer.
[b] Feed rate = 0.018 mL/min.

Table XI. The polymerizations were carried out at 70°C according to the recipe given in Table I. It can be seen that the particle diameter, D_v, as measured by the Nicomp Submicron Particle Sizer, consistently increased with an increase in the amount of initiator used. The weight average molecular weight decreased from 1.6×10^5 to 1.1×10^5 when doubling the initiator concentration, going from sample 37 to sample 60. Sample 61, containing five times the basic initiator concentration, had the same weight average molecular weight as sample 60; whereas sample 62 had an even higher weight average molecular weight, 1.3×10^5, despite a tenfold increase over the basic initiator concentration. The number average molecular weight shows a consistent, but not significant, drop with the increase in the initiator concentration.

The conclusion drawn from the above results is that at higher initiator concentrations, branching is favored due to the higher radical flux. The increase in the latex particle size with higher initiator concentrations is induced by the increase in the electrolyte content of the continuous phase by the initiator ($K_2S_2O_8$) levels, which in turn, lead to limited aggregation and reduction in the number the latex particles. Based on the above results, the most effective way to reduce the molecular weight of the polymers is by increasing the amount of chain transfer agent in the basic recipe.

Effect of Copolymer Composition

Latexes with copolymer compositions of 95/5 and 90/10 BM/St were synthesized using chain transfer concentrations equivalent to five times the standard amount shown in Table I. The basic recipe is given in Table XII. The particle size and molecular weight results given in Table XIII indicate that weight average molecular weights of 9.3×10^4 and 8.2×10^4,

Table XVII   Recipe for the Preparation of Batch Poly(n-butyl acrylate) Latex Particles with a 93/7 Monomer/Crosslinker Weight Ratio

Monomer Phase:	(g)
n-Butyl acrylate	27.9
Ethylene glycol dimethacrylate	2.1
Aerosol MA-0	0.43
DDI water	80.0
Aqueous Phase:	
Potassium persulfate	0.1
DDI water	8.32

are within the targeted range of 100,000. Also, it is worth mentioning that the higher the styrene fraction in the copolymer, the lower is the molecular weight, due to a greater ability of St to transfer to the chain transfer agent and a lower tendency to branching when compared with the benzyl methacrylate, as discussed previously.

Emulsion Homopolymerization Using Redox Initiators

Based on the results reported previously, and in an attempt to further lower the molecular weight, conditions were chosen for a series of emulsion homopolymerization experiments initiated by a redox system at 35°C. The process was carried out under a N_2 blanket, in a 50 mL Erlenmeyer flask with a magnetic stirrer, varying the amount of isooctyl mercaptopropionate (IOMP) chain transfer agent (0.5% and 1.0% by weight based on monomer), and the monomer addition mode (batch and semicontinuous). The polymerizations were carried to high conversion (96–99%) using the basic recipe reproduced in Table XIV. For the batch polymerization, all the ingredients were initially placed in the re-

Table XVI   Glass Transition Temperatures for Poly(benzyl methacrylate) (PBM) Latex Particles and its Blends with Polycarbonate (PC)

	T_g (°C)			
	PBM	Blend Ratio (PC/PBM)[a]		
Sample	Homopolymer	70/30	30/70	$M_w \times 10^{-3}$
74	65	63, 134	62, 135	41
75	67	63, 140	61, 129	64
68	66	64, 142	62, 135	45
70	68	123	93, 114	95

[a] By weight.

Table XVIII Particle Sizes as a Function of Crosslinker Amount for Batch Polymerized Poly(n-butyl acrylate) Latexes

| | | NICOMP | | TEM | |
Sample	BA/EGDMA Wt Ratio	$D_v{}^a$ (nm)	Coefficient Variation (%)	$D_w{}^b$ (nm)	PDI
108	93/7	177	26	187	1.03
109	99/1	158	9	176	1.04

ᵃ Volume average particle diameter.
ᵇ Weight average particle diameter.

actor. An additional charge of 0.1 g Dowfax 8390 surfactant was added after 1 h to prevent coagulation. For the polymerization employing semicontinuous monomer addition, DDI water, 0.012 g Dowfax 8390 surfactant, and 15% of the monomer were introduced into the reactor at first. Half of the sodium bisulfite was added at the beginning of the polymerization, with the other half added 1 h later when the continuous monomer feed at 0.018 mL/min was started. The additional 0.1 g Dowfax 8390 emulsifier designed to prevent coagulation was added to the reactor at the end of the monomer feed stage (2-½ h). Molecular weights were calculated from Gel Permeation Chromatography (GPC) measurements based on a polystyrene calibration curve. The results are given in Table XV. Weight average molecular weights between 40,000 and 110,000 were obtained, within the targeted range. The polydispersity index (PDI), calculated as M_w/M_n, varied between 2.0 and 2.4, as expected for radical initiated polymerizations.

Some of the polymerizations were repeated to check for reproducibility. Table XV indicates that batch (B) and semicontinuous (S) polymerizations carried out at a chain transfer agent (CTA) level of 1.0 wt %, based on monomer, yielded similar molecular weights (40,000–45,000), while for polymerizations run at 0.5 wt % CTA based on monomer, the weight average molecular weight of the batch polymerized BM was twofold higher (88,000–110,000) than that of BM polymerized using the semicontinuous monomer addition mode (50,000–64,000).

These results indicate that at a higher CTA concentration (1.0 wt %), the effect of the CTA is greater than the effect of the monomer addition mode, resulting in low and similar molecular weights for samples polymerized by batch and semicontinuous methods. However, at a CTA concentration of 0.5 wt %, the monomer addition mode becomes more important and the molecular weight differences between batch and semicontinuous polymerizations are more apparent.

Miscibility Tests for Emulsion Polymerized Benzyl Methacrylate Blended with Polycarbonate

As mentioned earlier, glassy polymers will ultimately constitute the "shell" polymer in a rubbery core-shell latex system to be used as an impact modifier in a polycarbonate (PC) matrix. A glassy shell is chosen as the particle shell for easy handling of the rubber and to retain particle integrity during handling and processing. In addition, the composition of the glassy shell is chosen such that it provides good interfacial adhesion between the rubber particles and the matrix polymer. Such interfacial adhesion is achieved in the present study through partial miscibility of the glassy shell with the PC matrix. The importance of the interfacial adhesion between the matrix and the rubber particles was studied previously.[15]

For the purpose of this research, two polymers are said to be miscible when blended together if the blend possesses a single glass transition temperature (T_g) as indicated by Differential Scanning Calorimetry (DSC).

Blending was achieved by dissolving PBM (precipitated from the latex) and PC in a common solvent (chloroform) followed by coprecipitation. PC has a T_g of 147°C and PBM has a T_g ranging from 65 to 68°C. When blended, a shift of either one, or both glass transition temperatures towards one another, is an indication of miscibility. The bigger the shift, the greater the miscibility, until the point is reached where both glass transitions overlap, giving a single T_g that is interpreted as complete miscibility.

Table XVI compiles the T_gs of the BM homopolymers listed in Table XV and the T_gs of 70/30 and 30/70 PC/PBM blend ratios by weight. Sample 74 (S/1.0% IOMP) shows slight miscibility at both
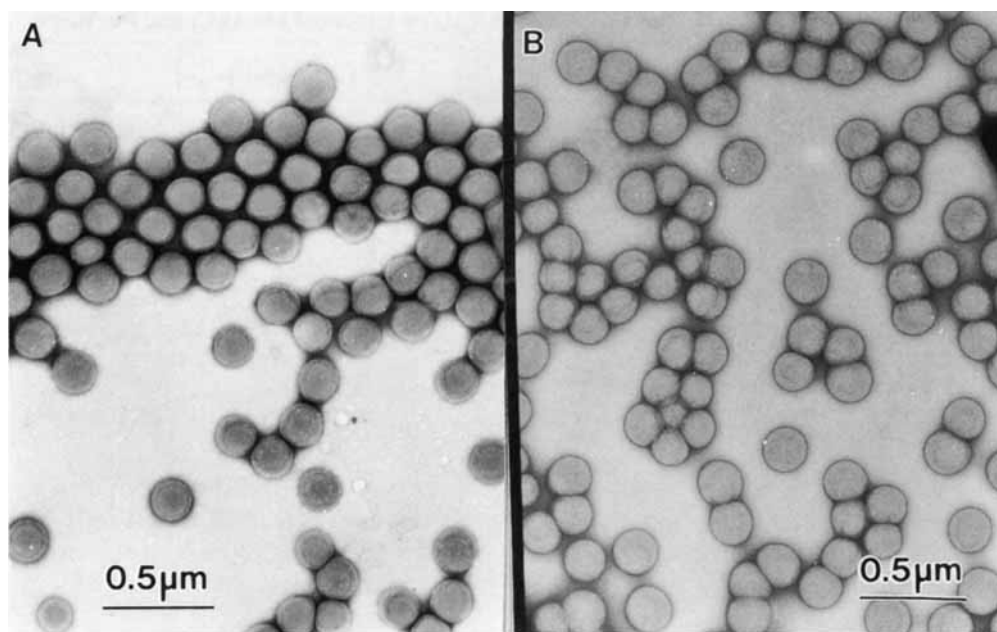
Figure 6   Transmission electron micrographs of small PBA seed latex particles stained with phosphotungstic acid (PTA): (A) 7% crosslinked; (B) 1% crosslinked.

70/30 and 30/70 PC/BM blend ratios. Samples 75 and 68 (S/0.5% IOMP, B/1.0% IOMP) indicate no miscibility at the 70/30 PC/BM blend ratio and only slight miscibility at the 30/70 PC/BM blend ratio (S and B stand for semicontinuous and batch monomer addition modes; the IOMP chain transfer agent concentration given is in wt % based on monomer). The lower T_g for the immiscible blends (samples 74, 75, and 68) seems to be shifted to even lower temperatures than the BM homopolymer T_g, possibly due to degradation. Degradation can result from the heating of the blends up to 275°C prior to the actual DSC miscibility test, performed in order to erase the memory of previous thermal history. Sample 70 (B/0.5% IOMP), however, presents a single T_g at the 70/30 blend ratio and a pronounced shift of both T_gs, indicating a significant degree of miscibility for the 30/70 PC/PBM blend ratio.

Table XIX   Recipe for the Preparation of Crosslinked Poly(n-butyl acrylate) Latex Particles

Component	Amount (g)
n-Butyl acrylate	198.0
Ethylene glycol dimethacrylate	2.0
DDI water	800.0
Potassium persulfate	0.8
Sodium bicarbonate	0.8
Aerosol AY (5% solids)	10.0

The last column in Table XVI lists the weight average molecular weights as determined by GPC. Contrary to what was expected, the best miscibility was achieved for sample 70, the one with the highest weight average molecular weight. These results led to the conclusion that factors other than molecular weight, which leads to polymer chain entanglements such as branching or crosslinking, influence the miscibility of PBM with PC. However, these factors have not been identified during the course of this work.

Poly(n-butyl acrylate) (PBA) Small-Size Particles

The recipe for the batch emulsion polymerization of small size poly(n-butyl acrylate) seed latex particles is given in Table XVII. The same recipe (given in Table XVII) was also used varying the monomer/ crosslinker (BA/EGDMA) ratio from 93/7 to 99/1 wt %. Table XVIII lists the volume average particle sizes, (D_v) determined by the Nicomp Submicron Particle Sizer and weight average particle diameters (D_w) obtained from transmission electron microscopy (TEM) analysis. The results obtained by both methods indicated that particle sizes ranged from 158 to 187 nm, with a consistent trend of smaller particle sizes at lower crosslinker concentrations. It is worth mentioning that for each crosslinker concentration the D_v particle diameters were smaller than the D_w particle diameters, and that the differ-

Table XX Particle Sizes for Crosslinked Poly(n-butyl acrylate) Latex Particles

	NICOMP			CHDF[a]		
Sample	$D_v{}^b$ (nm)	$D_n{}^c$ (nm)	Coefficient Variation (%)	$D_w{}^d$ (nm)	$D_n{}^c$ (nm)	Coefficient Variation (%)
41	505	343	34			
42	482	380	28			
41 + 42	507	363	32	351	349	5

[a] Capillary hydrodynamic fractionation.
[b] Volume average particle diameter.
[c] Number average particle diameter.
[d] Weight average particle diameter.

ence between the particle sizes as a function of crosslinker concentration was more noticeable from the results of the Nicomp Submicron Particle Sizing than from the TEM analysis (see Fig. 6).

Poly(n-butyl acrylate) (PBA) Large-Size Particles

Large-size seed latex particles were synthesized with a 99/1 BA/EGDMA weight ratio (samples 41 and 42). The recipe for this PBA latex preparation is shown in Table XIX. A second polymerization reaction (sample 42) was carried out to check for reproducibility. The resulting particle size as obtained by the Nicomp Submicron Particle Sizer and by Capillary Hydrodynamic Fractionation (CHDF) are listed in Table XX. These results proved the reproducibility of the polymerization process. Latex samples 41 and 42 were mixed together for further use in seeded emulsion polymerization of structured latex particles, to be described in Part II of this series.

SUMMARY AND CONCLUSIONS

Glassy polymer systems were synthesized and their miscibility with PC was tested for potential use as "shell" polymer in a core–shell structured latex for toughening of PC.

PBM and P(BM/St) systems were thoroughly investigated through bulk and emulsion polymerizations to better understand the effect of polymerization parameters on final molecular weight and miscibility with PC. It was found that BM is less sensitive to chain transfer with a chain transfer agent than St, and leads to high molecular weight polymers due to steric and stability factors. The studies also indicate that CTAs have a greater effect on reducing molecular weight than polymerization temperature, monomer addition mode, or initiator

concentration. IOMP was found to be an efficient, odorless chain transfer agent for both St and BM. Reactivity ratios of St and BM were found to be lower than unity, yielding a random rather than block copolymer.

Miscibility tests of the P(BM/St) system indicated different degrees of miscibility, depending on the polymerization conditions, leading to the conclusion that factors other than just molecular weight, such as branching and crosslinking also affect the miscibility of PBM with PC.

The overall study of the "shell system" led to the choice of BM to be used as the second-stage monomer for the polymerization of core–shell PBA/PBM latex particles. The synthesis and characterization of such structured latex particles will be described in Part II of this series.

Monodisperse PBA latex particles of the desired particle sizes were successfully obtained by batch emulsion polymerization. Small particles, 200 nm in diameter, were produced with BA/EGDMA monomer–crosslinker weight ratios of 93/7 and 99/1. Large particles, 400 nm in diameter, were also synthesized, with a 99/1 monomer–crosslinker weight ratio.

Repeated polymerizations using the same recipe indicate good reproducibility of the polymerization process. Particle size analysis by the Nicomp Submicron Particle Sizer, TEM, and CHDF showed similar trends in terms of particle sizes. The Nicomp Submicron Particle Analyzer, however, seems to give unreasonably high volume average diameters for particles larger than 300 nm in diameter. The number average particle size obtained by the Nicomp Submicron Particle Sizer is not too far off from the CHDF values.

The 200 nm (1 and 7% crosslinked) and 400 nm diameter (1% crosslinked) latex particles were used as seeds for subsequent emulsion polymerizations

to prepare structured latex particles as described in Part II of this series.

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