Characterization of the Interphase in Poly(divinylbenzene)/ Poly(n-butyl acrylate) Core/Shell Latexes by High-Resolution Solid-State NMR Relaxation Studies

V. NELLIAPPAN,[1,3] M. S. EL-AASSER,[1,2,*] A. KLEIN,[1,2] E. S. DANIELS,[1] and J. E. ROBERTS[3]

[1]Emulsion Polymers Institute, [2]Department of Chemical Engineering, and [3]Department of Chemistry, Lehigh University, 111 Research Drive, Iacocca Hall, Bethlehem, Pennsylvania 18015

SYNOPSIS

Poly(divinylbenzene)/poly(n-butyl acrylate) core/shell latexes were investigated using solid-state ^{13}C-NMR. The $(H)T_{1\rho}$ relaxation time was found to be substantially affected by many of the seeded emulsion polymerization parameters, such as the core/shell ratio, the mode of addition of the second-stage monomer, the addition rate of the second-stage monomer, and the level of conversion of the seed latex at the time of addition of the second-stage monomer. The existence of an interphase region between the core and shell polymers was detected. Maximum interphase region thickness was achieved when the butyl acrylate was added under starved conditions. The thickness of this interphase layer was calculated to be 5–7 nm based on a model proposed by McBriety.[1] Solid-state NMR was found to be an excellent spectroscopic technique to probe the interphase region in core/shell latexes. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The incorporation of core/shell latex particles consisting of a rubbery core surrounded by a glassy shell into a thermoplastic glassy matrix is known to increase the impact resistance of thermoplastics. For example, multilayered core/shell particles comprised of radially alternating layers of rubbery and glassy layers have been used to toughen brittle thermoplastics such as PMMA.[2] Different emulsion polymerization process variables including surfactant concentration, solids content, mode of addition, and monomer addition rate, etc., have been shown to affect the particle morphology of the core/shell latexes.[3] Grafting and interdiffusion between the boundary layers of the core and shell polymers results in the formation of an interphase between them. This interphase zone is one of the most important features of the core/shell particles, as it plays an important part in their success as impact modifiers.

The miscibility and the interphase regions of multiphase polymer blends were investigated over the past decade via spin-lattice (T_1), spin-spin (T_2), and spin-lattice relaxation in the rotating frame ($T_{1\rho}$) measurements using solid-state Nuclear Magnetic Resonance (NMR).[4-17] The $(H)T_{1\rho}$ measurements yield information about molecular dynamics. Information about the spatial relationships (e.g., domain sizes, extent of the interphase, etc.) can also be obtained using the $(H)T_{1\rho}$ relaxation measurements. The spin-lattice relaxation time in the rotating frame is sensitive to molecular motions in the midkilohertz region; also, the spin-lattice (T_1) and rotating frame spin-lattice ($T_{1\rho}$) parameters are sensitive to short-range spatial proximity of the interacting dipole moments, and, thus, to spin-diffusion phenomena. Previous work has demonstrated that solid-state NMR is an excellent means to probe the structure of the interphase in a variety of core/shell latexes including polybutadiene/poly(methyl methacrylate),[17,18] poly(n-butyl acrylate)/polystyrene,[19] and polybutadiene/polystyrene.[17,18] These systems have applications as impact modifiers for thermoplastics. Hidalgo et al. have characterized the films formed from structured core/shell latexes of

Table I Recipes Used for the Polymerization of PDVB Seed and PDVB/PBA Core/Shell Latexes at 70°C

Components	Amount Used in Seed[a] (g)	Amount Used in Polymerization Stage II (g)
Divinylbenzene-HP	100.0	—
Hexadecane	5.123	—
n-Butyl Acrylate[b]	—	2.5–22.5
Ethylene glycol dimethacrylate[b]	—	0.37
Distilled-deionized water	567	52.5
Potassium persulfate	0.3122 [2 mM][c]	0.1125 [8 mM][c]
Aerosol AY 65	1.099 [3.4 mM][c]	0.5981 [6 mM][c]
PDVB seed latex (14% solids)	—	150

[a] Particle sizes (CHDF): seed D_w = 173.0 nm; D_n = 151.5 nm; Stage II D_w = 219.2 nm; D_n = 204.5 nm.

[b] Added semicontinuously under monomer-starved conditions.

[c] Based on the aqueous phase.

poly(n-butyl acrylate)/polystyrene and have detected the existence of an interphase between the two components.[19]

One goal of this work was to extend the investigation to other types of latex systems including poly(divinylbenzene)/poly(n-butyl acrylate) (PDVB/PBA) core/shell latexes. In this work, the influence of different emulsion polymerization process parameters on the interphase characteristics has been investigated using (H) $T_{1\rho}$ measurements. The thickness of the core/shell interphase region was also estimated based on (H) $T_{1\rho}$ measurements.

EXPERIMENTAL

Materials

DVB-HP (Divinylbenzene-High Purity, The Dow Chemical Company) composed of p-divinylbenzene (25.9%), m-divinylbenzene (54.1%), p-ethylvinylbenzene (7.6%), m-ethylvinylbenzene (10.6%), and napthalene (0.6%) was purified by passing the monomer through an alumina column to remove the inhibitor (methoxyethyl hydroquinone). n-Butyl acrylate and ethylene glycol dimethacrylate (EGDMA, Aldrich) were also passed through an inhibitor-removal column (Aldrich) to remove the inhibitor. Potassium persulfate (Aldrich) and Aerosol AY 65 (sodium diamyl sulfosuccinate in ethyl alcohol, Cytec Industries) were used as received. Distilled-deionized water (DDI) was used in all polymerizations.

Synthesis

Crosslinked poly(divinylbenzene) seed latex was synthesized by a miniemulsion polymerization procedure[20] according to the recipe listed in Table I. The use of conventional emulsion polymerization resulted in the formation of microgels,[21] while the miniemulsion polymerization process produces particles with sizes near 200 nm.[22] Hexadecane, one of the key components present in the miniemulsion recipe, is known to act as a swelling promoter[23] and helps to produce crosslinked particles in the 200 nm range. Different core/shell latexes were prepared using the recipe given in Table I either by a batch or a semicontinuous emulsion polymerization process at 70°C. The butyl acrylate monomer (BA) was added at a rate of 2.5 mL/h, which was lower than the maximum polymerization rate for BA, and also at a rate of 4 mL/h. For the batch polymerization, the seed latexes were mixed with the second-stage monomer and allowed to tumble at room temperature for 6 h before adding the initiator. The concentration of the potassium persulfate initiator was 0.5% by weight in all cases, based on the BA phase. The sample preparations for NMR measurements were carried out by drying the latex at room temperature for 2 days, followed by drying in a vacuum oven at room temperature for 2 additional days. All of the core/shell latexes were characterized by NMR within 4 weeks of their preparation.

Transmission electron micrographs were obtained after staining the samples with phosphotungstic acid (negative stain) and ruthenium tetroxide (positive stain). All of the micrographs were obtained at a magnification of 36,000.

Table II   Particle Size Characterization Using Capillary Hydrodynamic Fractionation

Wt Ratio PDVB/PBA	D_w (nm)	$D_{(Calculated)}$ (nm)	Mode of Addition	$(H)T_{1\rho}$ (ms)[a]
1 : 0.1	173.4	178.6	Semicontinuous (2.5 mL/h, starved)	5.1
1 : 0.25	183.2	186.4	Semicontinuous (2.5 mL/h, starved)	5.9
1 : 0.4	190.7	193.5	Semicontinuous (2.5 mL/h, starved)	8.0
1 : 1[b]	219.2	224.3	Semicontinuous (2.5 mL/h, starved)	13.2
1 : 1	197.8	224.3	Batch	8.4, 15.9
1 : 1	201.4	224.3	Semicontinuous (4.0 mL/h, flooded)	17.1

[a] The relaxation times of the PDVB and PBA homopolymers were 4.2 ms and 23.5 ms, respectively.
[b] *n*-Butyl acrylate added at 75% and 100% conversion of the PDVB seed.

NMR Measurements

Solid-state ^{13}C-NMR measurements were obtained using crosspolarization, dipolar decoupling, and magic angle sample spinning (CP/DD/MASS) on a General Electric GN 300 spectrometer operating at a carbon frequency of 75.47 MHz. The crosspolarization experiments with variable contact times were used to determine $(H)T_{1\rho}$.[17,18] The rotating frame spin-lattice relaxation time of the proton spin is monitored from its effect on the decay of the magnetization of carbon to which it is bonded. A radiofrequency field of 20.8 kHz was used for the spinlock crosspolarization transfers. The Hartman-Hahn match was set by adjusting the power levels for proton and carbon so as to maximize the signal for adamantane. Ten contact times ranging from 100 µs to 21 ms were used in 10 separate experiments with a recycle delay of 2.5 s between individual acquisitions. Approximately 200 µL of the samples were spun at a speed of 2400 ± 100 Hz at the magic angle; depending on the composition, 320–640 scans were acquired for each contact time for a satisfactory signal-to-noise ratio. All of the spectra were acquired at a temperature of 21°C.

For each experiment at least 1024 data points were acquired. The acquisition time for each spectra was 20.48 ms and the data were zero filled once before processing. The peak intensities that were used to monitor the $(H)T_{1\rho}$ values were 126 ppm (benzylic carbons) for PDVB and 12.6 ppm (methyl carbon, C1, of the butyl side chain) for PBA, respectively. Sixty-four acquisitions were made at each contact time and the process was repeated 10 times to average out any fluctuations that might occur

during the course of the experiment. The $(H)T_{1\rho}$ of the PDVB and PBA (crosslinked with 1.5% by wt EGDMA) homopolymers were obtained from vacuum-dried samples of the homopolymers.

RESULTS AND DISCUSSION

Characterization of the Latexes

The weight average (D_w) and number average (D_n) particle sizes were determined using Capillary Hydrodynamic Fractionation (CHDF). These values for the PDVB seed and the core/shell latexes are listed in Table II. In the cases where the BA was added semicontinuously under starved conditions, the theoretical value for the weight average particle diameter agreed closely with the measured value, indicating the absence of secondary particles. In the cases where the BA was added in a batch mode or in a semicontinuous mode under flooded conditions, the measured value of the D_w was less than the calculated value indicating the presence of secondary particles.

Characterization of the Latexes Using Solid-State NMR

Figure 1 shows stacked plots of the ^{13}C-NMR spectra of the PDVB/PBA core/shell latex (core/shell ratio 1 : 1) obtained with contact times varying from 0.5–20 ms. The prominent features of the NMR spectra obtained from the PDVB correspond to the aromatic carbons centered at 126 ppm and the methylene carbons at 44 ppm. For the PBA spectra, the methyl
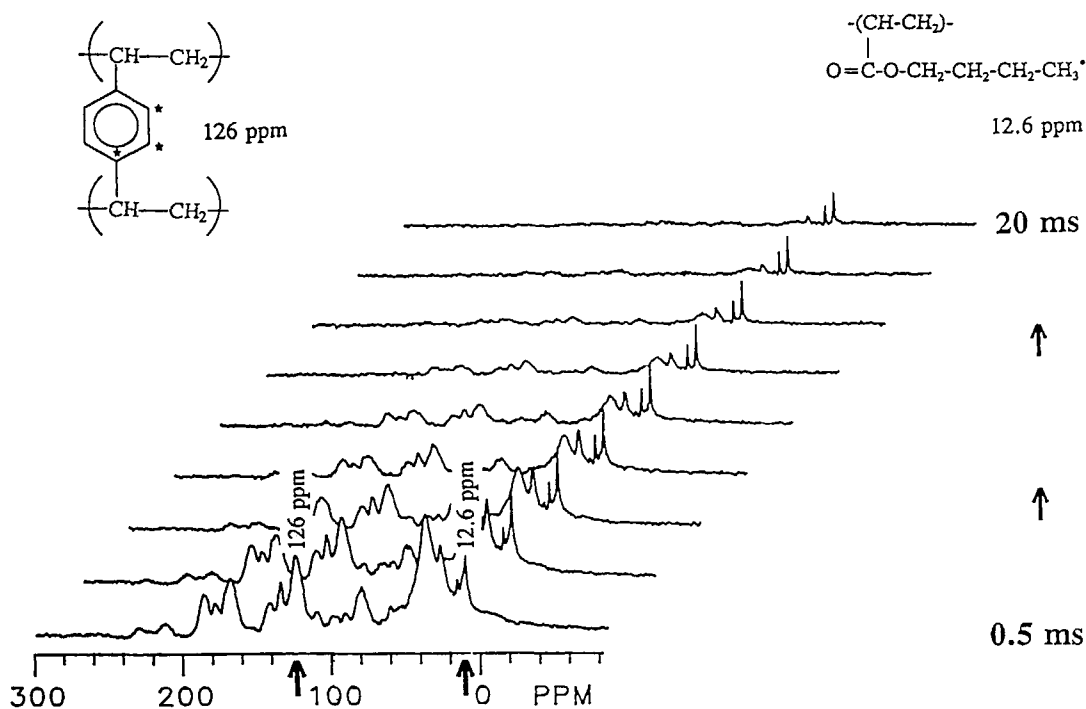
Figure 1 Stacked plots of the ^{13}C-NMR spectra of PDVB/PBA core/shell latex.

carbon of the butyl side chain yields a resonance at 12.6 ppm, the methylene carbons and the carbonyl carbons appear at 40 ppm and 177 ppm, respectively. The $(H) T_{1\rho}$ values for PDVB are very close to each other because of the phenomenon of rapid spin-diffusion, while in the case of PBA it was found that the spin diffusion between protons is not very efficient due to the mobile nature of the PBA homo-

polymer $(T_g = -56°C)$ and accounted for the fact that each carbon exhibits a unique $(H) T_{1\rho}$.

Crosspolarization experiments with varying contact times were performed on several different samples; the variation of the carbon magnetization of the glassy core and the rubbery shell is shown in Figure 2 as a function of contact time. The relaxation time is obtained from the negative of the inverse of
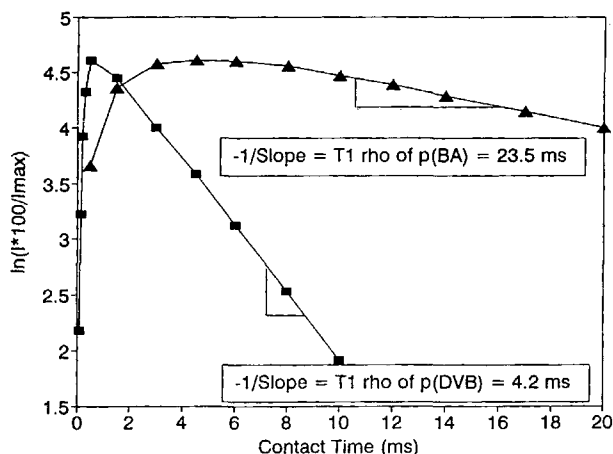

Figure 2 The scaled natural logarithm of the peak intensities of the carbon magnetization of the PDVB (126 ppm) and PBA (12.6 ppm) vs. the contact time; [(H)$T_{1\rho}$ = −1/slope]; PDVB (■): benzyl carbon (126 ppm); PBA (▲): methyl carbon of the butyl side chain (12.6 ppm).
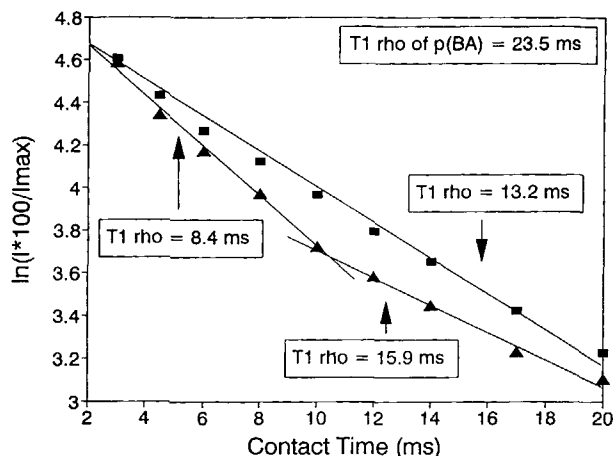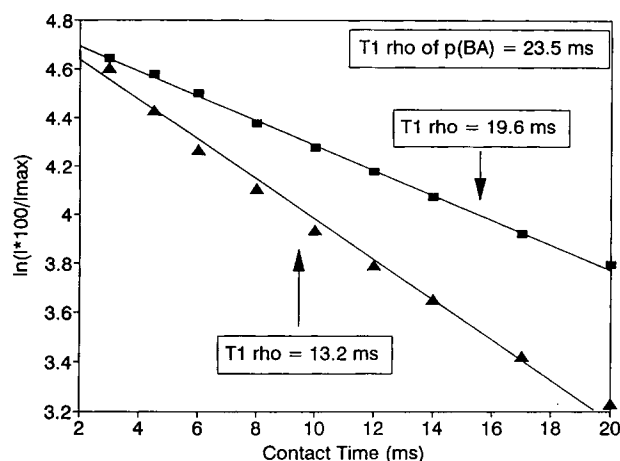
Figure 3 The scaled natural logarithm of the peak intensities of the PBA component of the core/shell latexes prepared via semicontinuous addition of BA monomer. The level of conversion of the PDVB seed at the time of addition of BA are 75 (▲) and 100 (■)%.

Figure 4 The scaled natural logarithm of the peak intensities of the PBA component of the core/shell latex prepared via semicontinuous (▲) and batch (■) modes of addition of BA.

the slope $(-1/\text{slope})$ of the descending part of the curve. Multiple measurements of $(H)T_{1\rho}$ on the same sample demonstrated that the precision of these measurements is $\pm 6\%$. The $(H)T_{1\rho}$ relaxation times of the PBA homopolymer (crosslinked with 1.5% EGDMA) and the PDVB homopolymer were found to be 23.5 ms and 4.2 ms, respectively.

## Influence of Process Parameters in the Interphase Zone

The process parameters that were studied during the seeded emulsion polymerization included the mode of addition of the second stage monomer, the rate of addition of the second stage monomer, and the extent of conversion of the PDVB seed latex at the time of addition of the second stage monomer.

Effect of Adding PBA at Different Levels of Conversions of the Seed Latex

Figure 3 compares the $(H)T_{1\rho}$ relaxation data for the PBA C1 carbon obtained with the core/shell latex that was synthesized via the semicontinuous addition of BA using PDVB seed particles at two different conversion levels (75% and 100%). There is a break in the plot for the case in which BA was added to the seed latex at 75% conversion of the PDVB seed. The $(H)T_{1\rho}$s obtained in this case are 8.4 ms and 15.9 ms. The existence of two different slopes represent the existence of two populations of PBA with regimes of different mobility. The population, which has a faster relaxation time, is probably crosslinked by divinylbenzene and is also grafted to the PDVB seed,

and the population of PBA with a relaxation time of 15.9 ms is more mobile and is probably only grafted to the PDVB seed and has only minimal physical interaction with the PDVB seed. Consequently, this domain of PBA has a relaxation time that is closer to that of the PBA homopolymer.

In the case where BA was added semicontinuously to the completely converted seed, some of the PBA is grafted to the seed PDVB and also has extensive physical interactions with the PDVB seed. However, in this case, the PBA is not crosslinked by divinyl-
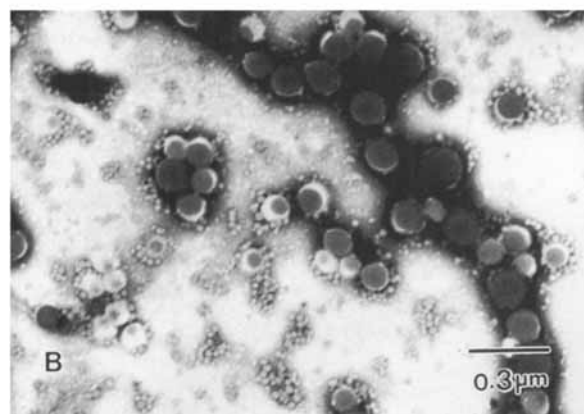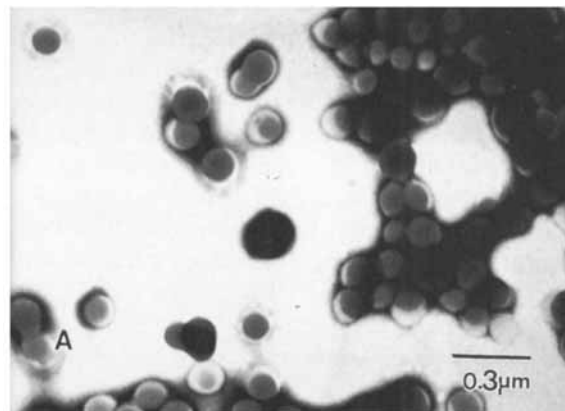
Figure 5 Transmission electron micrographs of the core/shell latexes made using (A) a semicontinuous process and (B) a batch emulsion polymerization process showing the presence of a secondary crop of PBA particles.

benzene, and the relaxation time of PBA in this case is 13.2 ms. This is demonstrated in Figure 3.

Effect of the Mode of Addition of the BA on the Interphase

Figure 4 compares the relaxation times of PBA in the core/shell latexes prepared using batch and semicontinuous modes of second-stage monomer addition. The PDVB seed used in these experiments was at 100% conversion prior to the addition of the second stage monomer. In the case in which the BA is added semicontinuously, the $(H) T_{1\rho}$ value is significantly lower (13.2 ms) compared to the relaxation time obtained from the batch mode sample (19.6 ms). This is related to the higher incidence of grafting reactions in the case in which PBA is added semicontinuously. When the BA was added in a batch mode, a crop of secondary particles of PBA homopolymer was formed that contributed to an increase in the observed relaxation time. The transmission electron micrograph showing the presence of secondary particles is shown in Figure 5(B). Also, the molecular weight is expected to be higher in this case, which consequently results in a higher number of chain entanglements and an increase in the relaxation time. Figure 5(A) illustrates the presence of a core/shell morphology in a latex made by the semicontinuous process and the absence of secondary particles, which should be contrasted with the presence of secondary particles in the latex prepared by a batch process [Fig. 5(B)].

Effect of the Addition Rate of BA on the Relaxation Time

The effect of the monomer addition rates (2.5 mL/h and 4.0 mL/h) on the relaxation times of PBA present in the core/shell latexes were compared at the same weight ratio of PDVB/PBA of 1 : 1. The results in Table II shows that in the case where the BA is added under monomer-starved conditions, the relaxation time is lower (13.2 ms) than that obtained
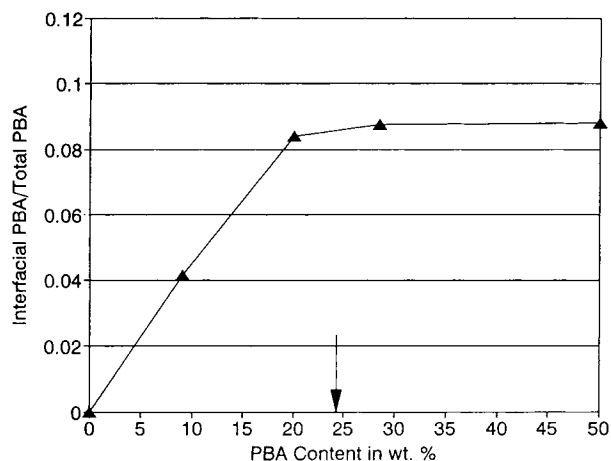
Figure 6   Plot of the interfacial PBA/total PDVB vs. the PBA content in the core/shell latexes prepared by a semicontinuous addition of BA showing the growth in the amount of the interfacial PBA.

where the BA is added under flooded conditions (17.1 ms). This is due to the formation of a secondary crop of particles under monomer-flooded conditions, which was confirmed by electron microscopy.

Estimation of the Thickness of the Interphase Zone

The $(H) T_{1\rho}$ values of the PBA phase are sensitive to the composition of the core/shell latex.[17,18] The $(H) T_{1\rho}$ of the PDVB homopolymer and the PDVB component present in the 1 : 1 PDVB/PBA core/shell latex are 4.2 ms and 5.3 ms, respectively. The difference between these values indicates that the $(H) T_{1\rho}$ is not very sensitive to the composition. As shown recently, the change in the $(H) T_{1\rho}$ of the PBA shell component of the core/shell latex particles compared to the pure polymer may be due to two reasons:[18] (1) the PBA protons interact with the neighboring PDVB protons by direct dipole–dipole interactions, or (2) the presence of sufficient PDVB alters the molecular motions of the neigh-

Table III   The Percentage of Interfacial PBA and Interfacial PBA/PDVB

PDVB/PBA Weight Ratio in Core/Shell Latexes	$T_{1\rho}(H)_m$ of the C1 Carbon in PBA (ms)	Percentage of Interfacial PBA ($M_1 \times 100$)	Percentage of Interfacial PBA/ Total PDVB
1 : 0.1	5.1	41.5	4.2
1 : 0.25	5.9	33.5	8.4
1 : 0.4	8.0	21.9	8.7
1 : 1	13.2	8.8	8.8
1 : 0 (PBA Homopolymer)	23.5	—	—

boring PBA component because of grafting and crosslinking. There was no break in plots of the ln(PBA magnetization) against contact time as noticed by Hidalgo for the PBA/PS system.[19] This indicates the presence of strong spin diffusion between the protons of PBA present in the interfacial as well as noninterfacial regions. A linear increase of the $(H)T_{1\rho}$ relaxation time of the PBA component with PBA content in the PDVB/PBA core/shell latexes in the range of weight ratios of 1 : 0.1–1 : 1 is observed in the data given in Table II.

The PBA component of the core/shell latex can be thought to be composed of two populations of PBA: (1) the interfacial PBA "perturbed" portion that interacts with the PDVB seed both physically and also via grafting and crosslinking reactions, and (2) the unperturbed PBA, which has no interaction with the seed PDVB; this has a value of the relaxation time for the PBA homopolymer. To a first approximation, the $(H)T_{1\rho}$ value of the "perturbed" portion of PBA can be obtained by extrapolating the $(H)T_{1\rho}$ values of the PBA component in core/shell latexes to zero PBA concentration. The extrapolated value of the $(H)T_{1\rho}$ for the PBA component is 2.4 ms. Unlike PDVB, the spin-diffusion is not expected to be strong in the case of PBA so as to equalize the relaxation time of all carbons; however, the spin-diffusion between the "unperturbed" and the "perturbed" portions of the PBA is strong enough to average their relaxation times to $(H)T_{1\rho m}$, which is the observed relaxation time of PBA in the core/shell latexes.

A model has been proposed for compatible blend systems with relaxation times that change with composition.[24,25] This model has been applied to our core/shell latex systems to calculate the percentage of the interfacial PBA using eq. (1):

$$M_1 = \frac{[1/(H)T_{1\rho m} - 1/(H)T_{1\rho 2}]}{[1(H)T_{1\rho 1} - 1/(H)T_{1\rho 2}]} \quad (1)$$

where M_1 is the mol fraction of phase 1, which is the perturbed PBA phase, $(H)T_{1\rho m}$ is the experimentally determined $(H)T_{1\rho}$ value of the core/shell latex, $(H)T_{1\rho 1}$ is the value of the relaxation time extrapolated to zero concentration of PBA, and $(H)T_{1\rho 2}$ is the relaxation time of pure PBA homopolymer. The amount of interfacial PBA with respect to the total PBA calculated from this model is listed in Table III. The interfacial PBA content has been normalized with respect to the PDVB weight, which remains constant in the core/shell latexes. The variation of the interfacial PBA is plotted against the PBA content in the core/shell latex

in Figure 6. The interfacial PBA content grows until the PBA content in the core/shell latexes reaches about 20–25% by weight; beyond this, the further addition of PBA to the core/shell latexes does not result in an increase in the amount of interfacial PBA, and the quantity of interfacial PBA reaches a plateau value. The maximum amount of the interphase is formed when the PBA content in the core/shell latex is approximately 20 to 25% by weight. This corresponds to a particle radius in the region of 92–94 nm; by using the radius of the seed particle (86.5 nm) one is able to estimate the thickness of the interphase region as 5–7 nm.

CONCLUSIONS

Solid-state NMR is a powerful technique to study the interphase region in PDVB/PBA core/shell latexes. The $(H)T_{1\rho}$ of the PBA phase was sensitive to a number of seeded emulsion polymerization parameters. Taking advantage of the change in $(H)T_{1\rho}$ of the perturbed portion of the PBA as a function of changes in the shell/core ratio, it was possible to calculate the thickness of the interphase layer using a model proposed by McBriety.[1] The length scale of this interphase region was found to be 5–7 nm, when the BA was added at 100% conversion of the seed PDVB latex in a semicontinuous process under monomer-starved conditions.

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