

# Surface Modification of Polybutadiene Facilitated by Supercritical Carbon Dioxide

Truc T. Ngo, Jonathan McCarney, James S. Brown, Michael J. Lazzaroni, Karl Counts, Charles L. Liotta, Charles A. Eckert

*Schools of Chemical Engineering & Chemistry and Specialty Separations Center, Georgia Institute of Technology, Atlanta, Georgia 30332-0100*

Received 26 November 2001; accepted 21 January 2002

**ABSTRACT:** The hydrophilicity of polymers can be improved through surface modification, traditionally done with conventional organic solvents, but these may cause the deterioration of polymer bulk properties due to irreversible polymer swelling. However, supercritical carbon dioxide (scCO<sub>2</sub>) not only swells the polymer reversibly, but also acts as a convenient transport medium for monomeric solutes, which may be subsequently polymerized. Thus we are able to modify the polymer surface without affecting its bulk strength and durability. Here we report scCO<sub>2</sub> surface mod-

ification of polybutadiene using ultraviolet-visible (UV/Vis) and Fourier transform infrared (FTIR) spectroscopy. Monomers such as 3-vinylbenzoic acid and crotonic acid are used to study the effects of pressure, solute structure, and reaction mechanism on the diffusion rates and partitioning of monomers between the fluid phase and the polymer. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 522–530, 2003

**Key words:** polybutadiene; surface modification; spectroscopy; supercritical carbon dioxide; acid dimerization

## INTRODUCTION

Polymer surfaces have been modified by plasma treatment, chemical etching, ozone treatment, ion beam modification, and surface grafting.<sup>1–5</sup> More recent approaches include grafting of monomers to polymer surfaces in supercritical carbon dioxide (scCO<sub>2</sub>),<sup>6</sup> which overcomes the disadvantages encountered by traditional methods, such as polymer degradation and bulk strength deterioration. Supercritical CO<sub>2</sub> is a poor solvent for many polymers, but it can be an effective swelling agent, and this swelling process is completely reversible. Moreover, scCO<sub>2</sub> also can act as a superlative transport medium for monomeric solutes and photoinitiators to diffuse onto polymer surfaces. These monomers can polymerize with themselves and crosslink with the primary polymer matrix to form a chemically different polymer surface. Another advantage of using scCO<sub>2</sub> for surface grafting is total control of the degree of surface modification by tuning the temperature and pressure of the system. Several research groups have modified polymer surfaces with scCO<sub>2</sub>.<sup>6,7</sup> However, most of the scCO<sub>2</sub> work has been done at high temperatures and pressures to produce polymer blends and composites instead of a chemically reacted surface.

The goal of this work was to increase the hydrophilicity of a polymer surface, particularly polybutadiene, by treating it with hydrophilic monomers in the presence of an appropriate photoinitiator, in an scCO<sub>2</sub> environment. A schematic of this process is shown in Figure 1.

The monomers, upon exposure to an ultraviolet (UV) light source, polymerize and crosslink with the double bond of polybutadiene to form a chemically different polymer surface. The experiments were carried out at relatively low temperature and pressures. The adsorption kinetic data for two different hydrophilic monomers were obtained using UV and Fourier transform infrared (FTIR) spectroscopy. The treated films were then characterized by FTIR spectroscopy and contact angle measurements.

## EXPERIMENTAL APPARATUS AND PROCEDURE

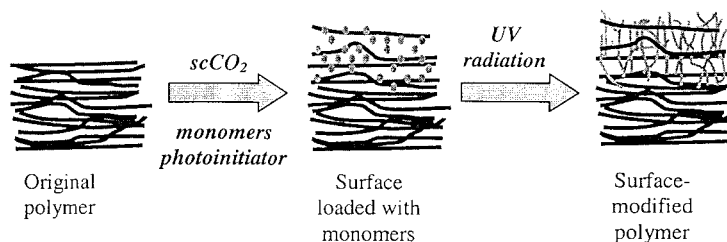
### Apparatus

Adsorption kinetic data were obtained using an HP 8453 UV/Vis and a Bruker Vector 22 IR spectrophotometer. Contact angles were measured with a goniometer. The UV light source was a Kratos LH151 N/2 short-arc lamp with 1000-watt power.

Experiments were carried out in high-pressure optical cells with parallel paths,<sup>8</sup> and quartz, barium fluoride (BaF<sub>2</sub>), or zinc selenide (ZnSe) windows. BaF<sub>2</sub> windows were particularly useful as they have negligible absorption in the UV or IR regions.

During the experiments, the cell was constantly stirred by two stir bars placed at the bottom of the cell,

Correspondence to: C. A. Eckert (charles.eckert@che.gatech.edu).



**Figure 1** Schematic diagram of polymer surface modification process in  $scCO_2$ .

to ensure rapid dissolution of monomer and to keep the conditions uniform inside the cell. Temperature was measured by an Omega type-K thermocouple in contact with the fluid. Pressure was read from a Druck pressure gauge DPI 260 and a Druck pressure transducer PDCR 4010, connected to the cell through a short line of tubing, accurate to  $\pm 0.07$  bar. The cell temperature was controlled to within 0.3 K by an Omega CN9000A temperature controller with six cartridge heaters. Carbon dioxide was introduced into the cell using an Isco syringe pump, Model 500D.

### Materials

All solid chemicals used in the experiments, from Aldrich Chemical Company, are listed in Table I, along with some important physical properties. Purities of these compounds range from 96 to 99+%. (98% *cis*)-Polybutadiene with a weight-average molecular weight range of 2,000,000 to 3,000,000 was used. High performance liquid chromatography (HPLC) grade solvents, including ethanol (200 proof), toluene (99.8%), cyclohexane (99+%), *n*-heptane (99+%), and *n*-hexane (85%), were obtained from Aldrich Chemical Company and J. T. Baker. Supercritical fluid chromatography (SFC)-grade carbon dioxide, from Matheson with at least 99.99% purity, was dried with molecular sieves before use.

### Procedure

All experiments were performed at 308 K, with pressures ranging from 80 to 95 bar. Most polymer films were solvent-cast on either quartz or ZnSe substrates from solution of (*cis*)-polybutadiene in cyclohexane. Some other films were made by a spin coating technique in various solvents, including toluene, *n*-hexane, and *n*-heptane. Film thicknesses varied from 0.005 to 0.040 cm. Films were dried under vacuum for at least 24 h before use.

First, the polymer film, on a crystal substrate, was placed in one path of the parallel-path cell. It was held in place between the two windows by a small spring. Solutes, including monomers and photoinitiator, were weighed and added to the cell. After loading, the cell was placed under vacuum for 30 min at room temper-

ature. Then, the cell was heated to 308 K and pressurized with  $CO_2$ . The cell was constantly stirred throughout the experiment. Once a desired pressure was reached, spectra were collected through both optical paths using either a UV or an IR spectrophotometer. Spectra were taken periodically for 3–6 h, as needed. Some UV absorption spectra of 3-vinylbenzoic acid in polybutadiene subjected to  $scCO_2$  solution are shown in Figure 2.

After data collection, the optical path with the polymer was subjected to a UV light source (1000-W short-arc UV lamp) for 1 h while still under  $CO_2$  pressure to promote the polymerization reaction. The cell was then depressurized slowly to prevent foaming of the polymer film. After the depressurization was complete, the polymer film (on the substrate) was exposed to UV light for another 30 min to complete the polymerization process. Finally, the contact angle of water on the treated polymer surface and the IR spectrum of the polymer were measured to characterize property changes. In some cases, Soxhlet extraction was performed, with HPLC ethanol as the solvent, on the treated polymer film to verify that the monomers had actually chemically grafted and crosslinked with polybutadiene matrix.


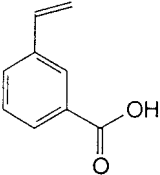
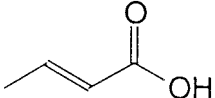
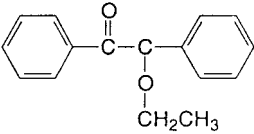
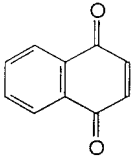
### Chemical reactions

In this study, polymerization reactions were believed to proceed by free-radical mechanisms. However, the initiation stage could be either free-radical addition to a double bond or hydrogen abstraction, depending on which photoinitiator was used. For example, benzoin ethyl ether (or BEE) upon exposure to UV light can be excited to form two free radicals, which can add across a double bond.<sup>2</sup> Conversely, 1,4-naphthoquinone is more likely to facilitate the polymerization with a free-radical hydrogen abstraction mechanism.<sup>9</sup> Detailed mechanisms for different polymerization processes are proposed as in Schemes I–III, where  $B^\bullet$  refers to free radicals formed from photoinitiator BEE and  $R^\bullet$  refers to any free radical present in the system.

## RESULTS AND DISCUSSION

1,4-Naphthoquinone solubility data were reported previously.<sup>10</sup> The solubilities of 3-vinylbenzoic acid

TABLE I  
Physical Properties of Polymer and Solutes

Name	Structure	MW (g/mol)	$T_m$ (K)	$T_b$ (K)	$T_g$ (K)	Solubility Parameter at 298 K, (J/cm <sup>3</sup> ) <sup>1/2</sup>
(cis)-Polybutadiene		2,000,000 — 3,000,000	—	—	171	12.89
3-Vinylbenzoic acid		148	364–368	—	—	22.3
Crotonic acid		86	345	453–454	—	25.34
Benzoin ethyl ether		240	332–334	—	—	—
1,4-Naphthoquinone		158	396–398	—	—	—

and benzoin ethyl ether in scCO<sub>2</sub> were measured using UV/visible (VIS) and FTIR spectroscopy by the same method (Table II). The polybutadiene film surface was treated with photoinitiator and acid monomer separately, or with combinations of both. Table III shows the results of contact angle measurements for all cases. To ensure that the polymer surface was chemically grafted, we extracted the treated polymer films with ethanol (using Soxhlet extraction). IR spectra of the extracted polymer still showed presence of the hydrophilic modifiers, verifying that we did indeed chemically graft the polymer surface.

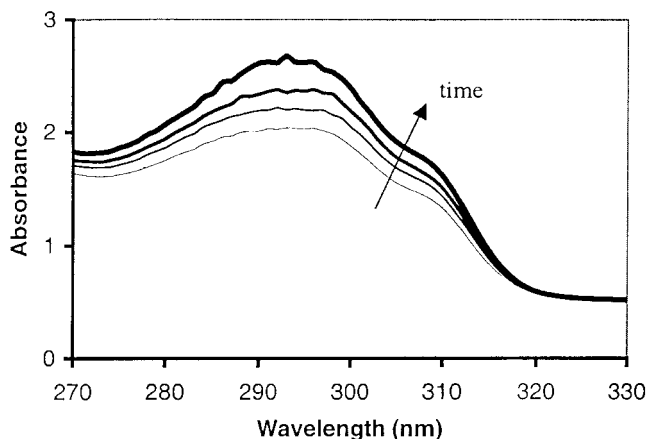
There were several factors affecting the polymer surface properties, including the reaction mechanism, operating conditions, and the solute behavior in the system. Each of these factors is discussed in more detail.

#### Effect of polymerization mechanism on polymer surface property

According to contact angle results reported in Table III, all chemical reagents used in this study showed some increased hydrophilicity. The differences in contact angle could be rationalized based on different reaction pathways of the polymerization process. Several possible scenarios were investigated and compared.

Polybutadiene treated with either 3-vinylbenzoic acid (VBA) or crotonic acid (CA) without photoinitiator (reaction path vii)

When polybutadiene was treated with VBA without any photoinitiator present, we observed neither change in contact angles nor in the IR spectra of poly-



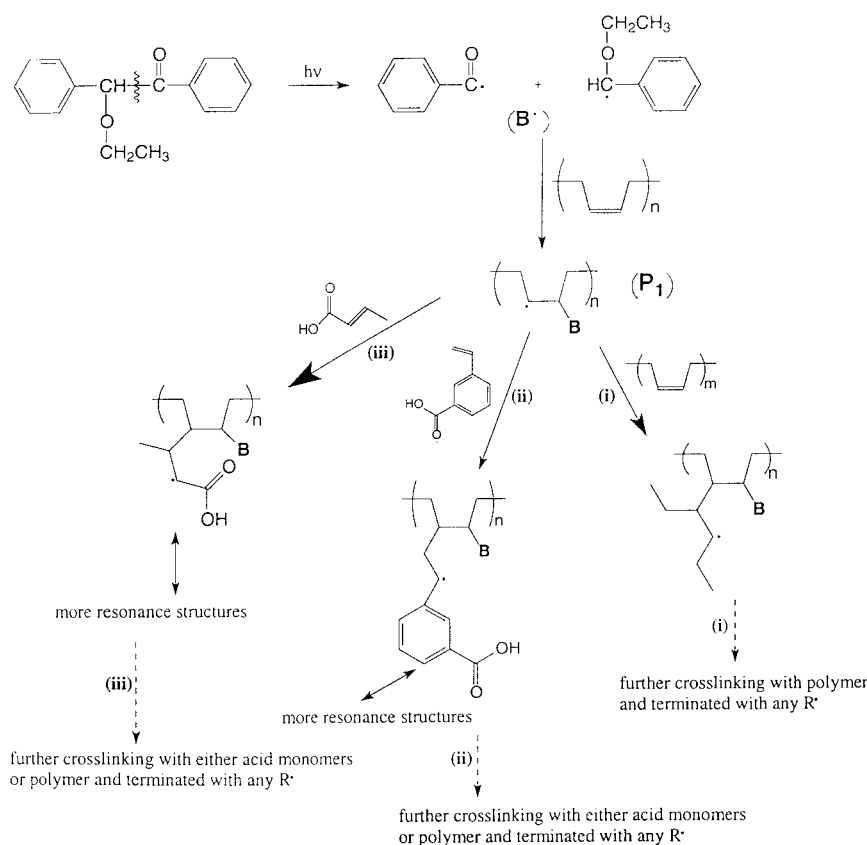
**Figure 2** UV absorption spectra of 3-vinylbenzoic acid in polybutadiene subjected to  $scCO_2$  solution.

mer surface before and after treatment. This evidence suggests that VBA was not able to crosslink with polybutadiene and remain on the polymer surface by itself. Conversely, CA was able to graft onto the polybutadiene surface and to affect its hydrophilicity. The reduction in surface contact angle was quite significant, about  $26^\circ$ , due to the highly hydrophilic nature of CA molecules. One might speculate that when the system was subjected to UV light over a wide range of wavelengths, VBA would be much more

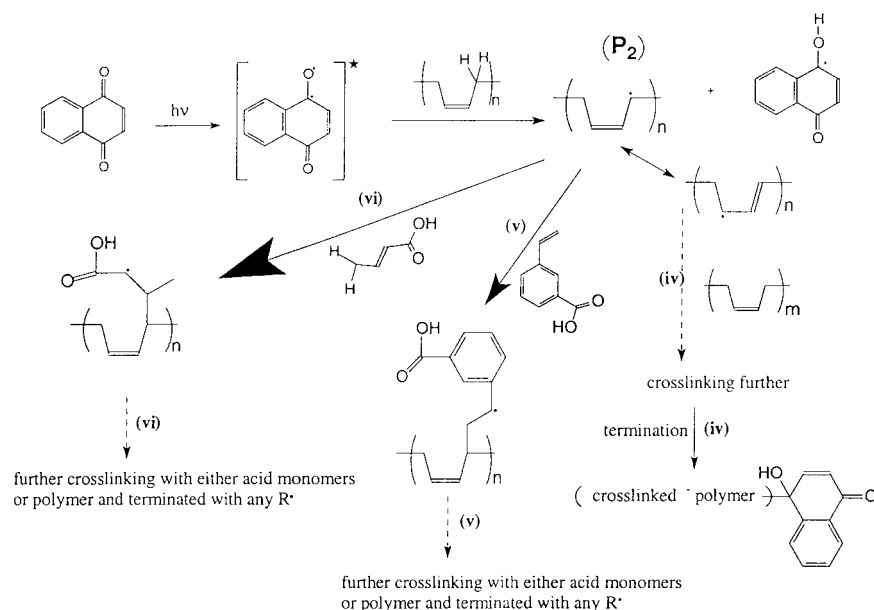
likely to polymerize with itself to form poly(3-vinylbenzoic acid) than with the polybutadiene. As a result, the poly(3-vinylbenzoic acid) formed was not attached chemically to the polymer surface and could be removed easily during the  $CO_2$  depressurization and Soxhlet extraction process. Unlike VBA, CA would be more likely to crosslink with the polybutadiene and remain on the polymer surface, and thus lowering its contact angle.

Polybutadiene treated with benzoin ethyl ether (BEE) or 1,4-naphthoquinone (NAPH) alone (reaction paths i and iv)

As mentioned above, BEE was used to initiate the reaction by breaking up the C—C bond and forming two free radicals ( $B^\bullet$ ) as shown in reaction Scheme I. However, NAPH may initiate the reaction through a hydrogen abstraction route, as shown in reaction Scheme II. In both cases, after the initiation step to form free radicals, the polymer is able to crosslink with itself to form crosslinked polybutadiene, with a few photoinitiator radicals hanging from its surface. The two photoinitiators may be somewhat hydrophilic themselves. Thus, by attaching to the polymer chains, they could affect the polymer surface properties. In fact, we observed a reduction in contact angle of the polymer surface by about  $12^\circ$  for both cases.



**Scheme I** With BEE as the photoinitiator.



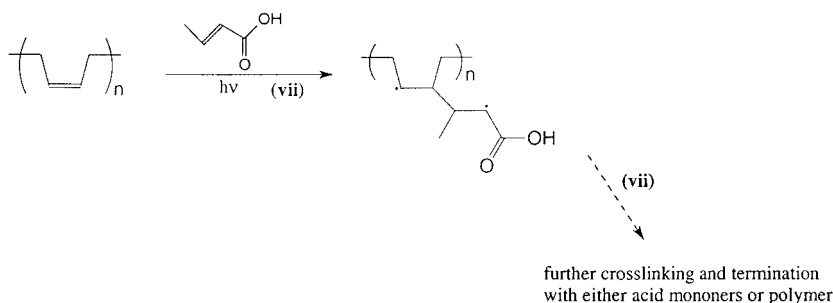
**Scheme II** With 1,4-naphthoquinone as the photoinitiator.

Polybutadiene treated with either VBA or CA in the presence of BEE (reaction paths ii and iii)

In this case, the free-radical  $B^*$  would still be more likely to attack the  $C=C$  bond in polybutadiene first to form  $P_1$ , due to the resonance stability in VBA and CA molecules. Then, a polymer free-radical  $P_1$  can react with  $C=C$  bonds in either VBA or CA molecules to form graft copolymers (as shown in reaction Scheme I). Our contact angle measurements indicate that the reduction in the case with CA was more significant than with VBA. One possible explanation for this is that the free radical formed in reaction path iii was less resonance stable than the one formed by reaction path ii. Therefore, when the polymer was treated with CA, there was better chance for more CA molecules to graft onto the polybutadiene surface. We also noticed that the hydrophilicity of the polymer surface in these cases was improved when compared to treatment with only BEE. This observation is consistent with the fact that the carboxylic acid monomers are more hydrophilic than the photoinitiators.

Polybutadiene treated with either VBA or CA in presence of NAPH (reaction paths v and vi)

In this case, NAPH was believed to abstract hydrogen from one of the carbons in polybutadiene to form a polymer free-radical  $P_2$ . Hydrogen abstraction from VBA or CA molecules would be less likely due to the formation of much more resonance-stable free radicals. The polymer free-radical  $P_2$  has some resonance stability; thus, it is more selective in its reaction path than the polymer radical  $P_1$  in the case of BEE. Because the terminal  $C=C$  bond in VBA molecule is more accessible than the internal  $C=C$  bond in the CA molecule,  $P_2$  would be expected to react more readily with VBA than with CA. Our contact angle results are consistent with this speculation. The contact angle of polybutadiene surface was reduced by about  $20^\circ$  in the case of VBA. Conversely, in the case of CA, it was reduced by about the same amount as when the polymer was treated with NAPH alone. Including CA in the process in this case did not further improve polymer surface hydrophilicity.



**Scheme III** Crotonic acid with polybutadiene, no photoinitiator.

**TABLE II**  
Solubility of Solutes in CO<sub>2</sub> at 308 K

Solute	<i>P</i> (bar)	CO <sub>2</sub> density (mol/L)	Solubility (mole solute/mole CO <sub>2</sub> )
3-Vinylbenzoic acid	82	12.3	1.67 × 10 <sup>-4</sup>
Benzoin ethyl ether	78	7.6	2.22 × 10 <sup>-5</sup>

### Effect of CO<sub>2</sub> pressure and choice of solutes on the partitioning and diffusivity of acids in polybutadiene/CO<sub>2</sub> system

The adsorption kinetics of 3-vinylbenzoic acid onto a polybutadiene surface was measured for both optical paths of the parallel-path cell; thus, we were able to determine the adsorption kinetics of the solute onto polymer surface. Because the polymer films were relatively thin (0.01 cm) in comparison to the total optical path length, we assumed that the molar absorptivities of the solution in both optical paths of the cell were approximately the same. The error in the molar absorptivity resulting from this assumption was calculated to be about 1%. The kinetic results are shown in Figure 3. From these data, the partition coefficients and the diffusivities of the solute for each system were determined.

### Effect on partition coefficient

The partition coefficient ( $K_c$ ), defined as the ratio between the solute concentration in the polymer and the solute concentration in the fluid phase, of 3-vinylbenzoic acid is reported in Table IV, within 5% error. When the BEE photoinitiator was present, as pressure was increased from 81 to 94 bar, the partition coefficient of 3-vinylbenzoic acid decreased by almost a factor of seven. Because our experimental conditions were in the proximity of the critical region of CO<sub>2</sub>, increasing pressure by 13 bar resulted in an increased fluid density by almost 50%. The change in  $K_c$  was more dramatic when pressure approached the critical point of CO<sub>2</sub>. As pressure increased over the indicated range, the fluid became a much better solvent. Consequently, the solute partitions more into the fluid phase at higher pressures. Therefore, the partition coefficient of the solute decreased significantly as pressure increased.

Comparing the two systems with and without the photoinitiator BEE at CO<sub>2</sub> pressure of 83.5 bar,  $K_c$  values for 3-vinylbenzoic acid were different by about 50%. A possible explanation for this phenomenon was that when BEE was introduced into the system, it could act as a cosolvent for 3-vinylbenzoic acid in CO<sub>2</sub> solution. Such a synergistic cosolvent effect on the solubility of two solids in scCO<sub>2</sub> is well known.<sup>11</sup> As a result, the solubility of 3-vinylbenzoic acid in CO<sub>2</sub>

solution was improved. Therefore, it partitioned more in the fluid phase, or less in the polymer, when BEE was present.

The  $K_c$  for crotonic acid in the polybutadiene/CO<sub>2</sub> system is reported in Table IV, within 20% error (due to very small mass uptake). The  $K_c$  for crotonic acid was found to be substantially lower than  $K_c$  for 3-vinylbenzoic acid. We might speculate that this occurred because the activity coefficient of the crotonic acid in the polymer is greater, due to the fact that the solubility parameter of 3-vinylbenzoic acid [estimated  $\delta = 22.3$  (J/cm<sup>3</sup>)<sup>1/2</sup><sup>12</sup>] was closer to the solubility parameter of polybutadiene [ $\delta = 12.89$  (J/cm<sup>3</sup>)<sup>1/2</sup>] than was crotonic acid [ $\delta = 25.34$  (J/cm<sup>3</sup>)<sup>1/2</sup>].

### Effect on diffusivity

The diffusivity of solute in the polymer was obtained by fitting our data, using Fick's law for mass diffusion:

$$\frac{\partial C_p}{\partial t} = D \frac{\partial^2 C_p}{\partial x^2} \quad (1)$$

where  $C_p$  is the concentration of solute in polymer (mol/L),  $t$  is time (s),  $D$  is diffusivity (cm<sup>2</sup>/s), and  $x$  is the penetration distance (cm). The boundary and initial conditions for eq. (1) are shown as follows:

Boundary conditions:

$$\frac{\partial C_p}{\partial x} = 0 \quad \text{at } x = l, \quad \text{for all time}$$

$$C_p = C_s(t) = K_c C_f(t) \quad \text{at } x = 0, \quad \text{for all time}$$

Initial condition:  $C_p = 0$  at  $t = 0$  for all  $x > 0$ ,

**TABLE III**  
Contact Angles of Polybutadiene Surface, Untreated and Treated at 308 K

VBA	Solute (mole %)			<i>P</i> (bar)	$\theta$ (°)
	CA	BEE	NAPH		
—	—	—	—	—	94 ± 0.5
100	—	—	—	82	95 ± 1
—	100	—	—	81	68 ± 3
—	—	100	—	83	83 ± 2
—	—	—	100	85	79 ± 3
92	—	8	—	81	76 ± 1.5
92	—	8	—	82	75 ± 3.5
92	—	8	—	83.5	73 ± 2
92	—	8	—	85	81 ± 2.5
92	—	8	—	94	71 ± 6.5
92	—	—	8	81	74 ± 1
—	93	7	—	81	69 ± 0.5
—	93	7	—	86	73 ± 1.5
—	93	—	7	81	79 ± 2

VBA: 3-vinylbenzoic acid; CA: crotonic acid; BEE: benzoin ethyl ether; NAPH: 1,4-naphthoquinone.

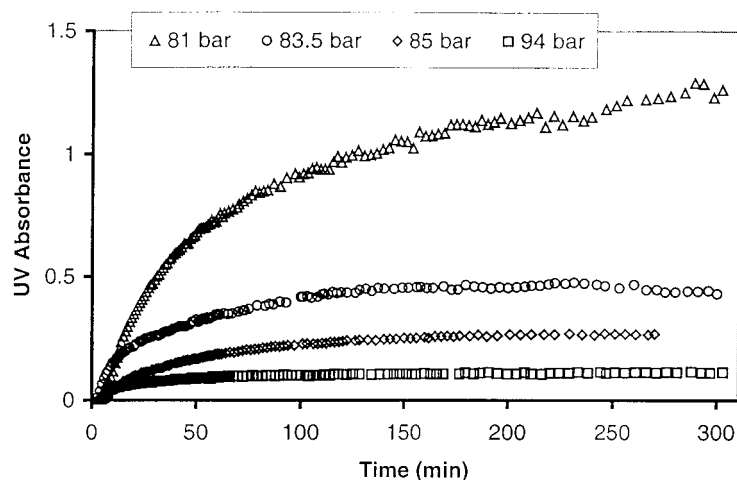


Figure 3 Adsorption of VBA onto polybutadiene surface, at 308 K.

where  $l$  is the thickness of polymer film (cm).  $C_s(t)$  is the concentration of solute at polymer surface (mol/L) at time  $t$ .  $K_c$  is the partition coefficient of solute between the polymer and the fluid phase. Since the concentration of solute in the fluid phase,  $C_f(t)$ , was known for each experiment,  $C_s(t)$  could be calculated for all times. The diffusivity,  $D$ , was determined by solving eq. (1) numerically using the finite difference approximation with five nodes and time step of one second. Since monomers did not dissolve rapidly, it was necessary to include the time-dependent fluid concentration in the model. The results for diffusivity are reported in Table IV and Figure 4 for the cases of treating polybutadiene with 3-vinylbenzoic acid, with and without benzoin ethyl ether photoinitiator, at different  $\text{CO}_2$  pressures.

The calculated diffusivities have large uncertainties, primarily due to large errors associated with the estimated molar absorptivity ( $\epsilon_p$ ) of solute in the polymer (35% uncertainty in estimated  $\epsilon_p$ ). This  $\epsilon_p$  value is implicit in  $C_p(t)$  in eq. (1). As seen in Figure 4, the diffusivity of 3-vinylbenzoic acid in polybutadiene appears to increase with  $\text{CO}_2$  pressures, except for the value at 83.5 bar, with large uncertainty. This trend may be due to the greater  $\text{CO}_2$  swelling of the polymer at higher pressures, creating more free volume to allow faster diffusion of solute molecules. The effect was

more significant around the highly compressible region of  $\text{CO}_2$ .

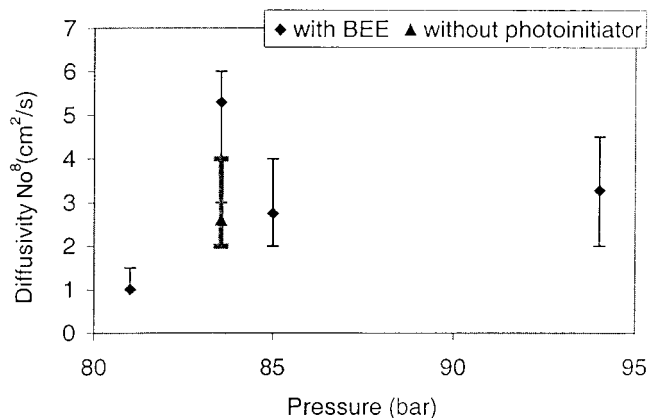
Comparing the diffusivities at 83.5 bar when benzoin ethyl ether was used and when no photoinitiator was present, the photoinitiator seemed to increase the diffusivity of the acid in polymer. This comparison was less certain due to the overlapping error bars shown in Figure 4. However, one might speculate that the photoinitiator BEE helped prevent the dimerization of 3-vinylbenzoic acid molecules before they diffused into the polymer. This dimerization of 3-vinylbenzoic acid will be discussed in more detail below. As a result, when benzoin ethyl ether was present, the sizes of diffusing solute molecules were smaller (monomers, not dimers), and thus their diffusion rate was faster.

#### Dimerization of acids in $\text{CO}_2$ solution

Carboxylic acids have the tendency to form dimers in solution through hydrogen bonding, especially in supercritical fluid systems.<sup>13,14</sup> In this work, we found that both 3-vinylbenzoic acid and crotonic acid underwent dimerization in  $\text{scCO}_2$  solution. This observation was made using FTIR spectroscopy, with dilute acid concentrations,  $4.59 \times 10^{-4}$  mol/L for 3-vinylbenzoic acid and  $8.35 \times 10^{-4}$  mol/L for crotonic acid.

TABLE IV  
Partition Coefficient and Diffusivity of VBA and CA in Polybutadiene/ $\text{CO}_2$  System, at 308 K

Solute	Pressure (bar)	Partition coefficient		Diffusivity	
		$K_c$	% Error	$D$ ( $\text{cm}^2/\text{s}$ )	% Uncertainty
VBA (no photoinitiator)	83.5	762	5	$2.60 \times 10^{-8}$	50
VBA (with BEE)	81	1897	5	$1.01 \times 10^{-8}$	50
VBA (with BEE)	83.5	489	5	$5.30 \times 10^{-8}$	43
VBA (with BEE)	85	346	5	$2.75 \times 10^{-8}$	45
VBA (with BEE)	94	275	5	$3.28 \times 10^{-8}$	39
CA (with BEE)	81–86	49	20	—	—



**Figure 4** Effect of CO<sub>2</sub> pressure on the diffusivity of VBA, at 308 K.

Figure 5 shows the IR absorption spectra of C=O stretching modes for 3-vinylbenzoic acid, where the peak at 1747 cm<sup>-1</sup> represents the C=O band of the monomer. When two acid molecules form a dimer through H-bonding, the C=O band is shifted to a lower frequency (1705 cm<sup>-1</sup>) due to the restricted motion of the bond in the dimer form. Kazarian et al.<sup>15</sup> show comparable results for H-bonding of alcohols in various solvents. Similar to 3-vinylbenzoic acid, C=O peaks for crotonic acid were observed at 1749 cm<sup>-1</sup> for the monomer and 1711 cm<sup>-1</sup> for the dimer.

After solutes were completely dissolved in CO<sub>2</sub> solution, upon increasing CO<sub>2</sub> pressure, or fluid density, we observed that the absorption of C=O band of the monomer increased, whereas the absorption of the dimer band decreased. This behavior is also illustrated in Figure 5. In order to describe the effect of CO<sub>2</sub> density on concentrations of acid monomer and dimer in solution, we assumed that the molar absorptivity ( $\epsilon$ ) of the solution did not change significantly over the studied CO<sub>2</sub> density range. Within this range, our previous work showed that the increase in  $\epsilon$  of the solution due to the increase of fluid density was about 10% for a different solute system.<sup>10</sup> The decrease of  $\epsilon$  due to an increase of fluid density has never been reported previously. Without making the assumption above, we experienced a large decrease in  $\epsilon$  value of the monomer (60% decrease) and a significant increase in  $\epsilon$  value of the dimer (70% increase). Such results would be contrary to our understanding and to established literature. Therefore, we believe that our assumption of constant  $\epsilon$  over the CO<sub>2</sub> density range studied is reasonable. In fact, we doubt that  $\epsilon$  could be calculated separately because it was influenced by two concomitant effects, due to changes in solution concentration and in degree of dimerization.

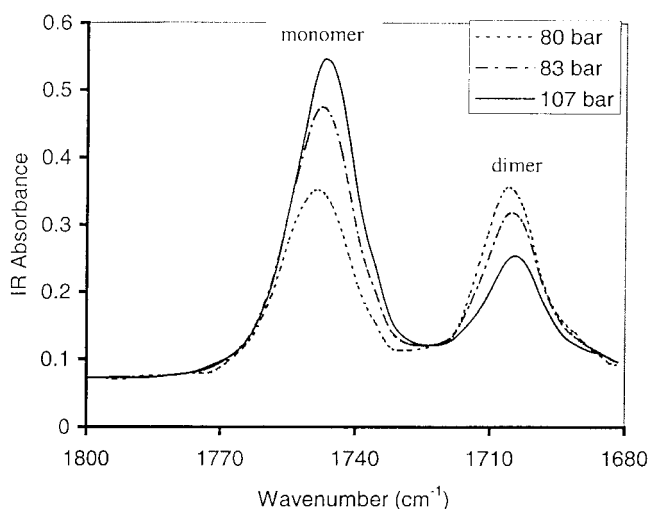
Figure 6 shows the effect of CO<sub>2</sub> density on the monomer and dimer concentrations of 3-vinylbenzoic acid and crotonic acid. The equilibrium constant for

the dimerization reaction,  $K_{eq}$ , was calculated using the formula:

$$K_{eq} = \frac{[\text{dimer}]}{[\text{monomer}]^2} \quad (2)$$

Figure 7 shows the equilibrium constants of the dimerization reactions for both 3-vinylbenzoic acid and crotonic acid. As CO<sub>2</sub> density is increased, the solvent polarity also increases. In other words, the solvation power of the solvent to dissolve the monomers becomes better at higher density. Of course, the solvation power for the dimers is also increased, but we assume that the doubly H-bonded dimer is actually less polar than the monomer, and the effect on the dimer may be less. In any event,  $K_{eq}$  of dimerization decreased as CO<sub>2</sub> density is increased, which is consistent with other studies of dimerization and H-bonding networks.<sup>13-15</sup> The change in standard Gibbs energy associated with dimerization in these cases was calculated to be -5 kcal/mol at most. We also observed that 3-vinylbenzoic acid and crotonic acid behaved more similarly at higher densities and the discrepancies became more apparent at lower densities.

In our kinetic experiments for 3-vinylbenzoic acid, we obtained data by following the absorption peaks of the phenyl ring in its structure (UV  $\lambda_{max} = 297\text{nm}$ , or IR  $\mu = 1585\text{cm}^{-1}$ ). The absorption of this peak should not be affected by the dimerization of acid in CO<sub>2</sub> solution. However, in the case of crotonic acid, the only IR peak that could be isolated from the peaks of polybutadiene and CO<sub>2</sub> was the C=O stretch of the monomer, at 1749 cm<sup>-1</sup>. The behavior of this peak did not provide sufficient information about the amount of crotonic acid being adsorbed onto the polymer surface as a function of time. Therefore, we were unable to follow the true adsorption kinetics of crotonic acid



**Figure 5** Effect of CO<sub>2</sub> pressure on IR adsorption spectra of VBA.



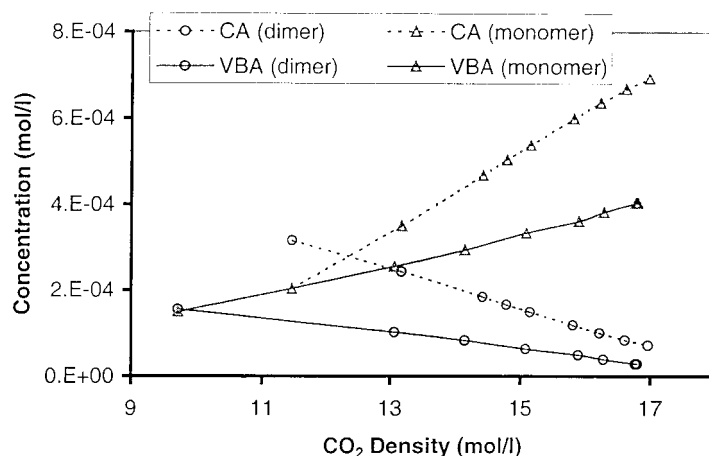


Figure 6 Effect of  $\text{CO}_2$  density on VBA and crotonic acid CA, at 308 K.

onto the polymer surface using the spectroscopic techniques described. In order to obtain these kinetic data, other methods might be used, such as a microbalance system, to measure gravimetrically the mass uptake in the polymer as a function of time.

### CONCLUSIONS

We have shown that the hydrophilic property of a polybutadiene surface could be improved by treating it with a hydrophilic reagent. The method was demonstrated in a  $\text{scCO}_2$  environment, where  $\text{CO}_2$  acted as the swelling agent for the polymer and the transport medium for solutes to diffuse onto the polymer surface. Depending on the chemical structure of the species, we could predict the significance of the effect on polymer surface hydrophilicity. We learned that  $\text{CO}_2$  pressure has a substantial influence on the partition-

ing of the solute between the polymer and the fluid phase, and a smaller effect on the diffusivity of the solute onto polymer surface for the case of polybutadiene. Based on these results, we could optimize the operating conditions of the process to obtain desired surface properties. We also characterized the dimerization kinetics of carboxylic acids in  $\text{CO}_2$  solution. This dimerization behavior significantly affects the solubility and diffusivity of these acids in solution. Therefore, in order to model accurately the solubility of these acids in solution, more extensive studies on the dimerization kinetics and phase behavior would be required.

### References

- Liesegang, J.; Senn, B. C.; Pigram, P. J.; Kang, E. T.; Tan, K. L.; Neoh, K. G. *Surf Interface Anal* 1999, 28, 20.
- Ang, C. H.; Garnett, J. L.; Levot, R.; Long, M. A.; Nguyen, Y. T. *J Polym Sci, Polym Lett Ed* 1980, 18, 471.
- Yao, Z. P.; Ranby, B. *J Appl Sci* 1990, 40, 1647.
- Geuskens, G.; Kanda, M. N. *Eur Polym J* 1991, 27, 877.
- Kang, E. T.; Neoh, K. G.; Shi, J. L.; Tan, K. L.; Liaw, D. J. *Polym Adv Technol* 1999, 10, 20.
- Rajagopalan, P.; McCarthy, T. J. *Macromolecules* 1998, 31, 4791.
- Li, D.; Han, B. *Ind Eng Chem Res* 2000, 39, 4506.
- Kazarian, S. G.; Vincent, M. F.; Eckert, C. A. *Rev Sci Instrum* 1996, 67, 1586.
- Zamotaev, P. V.; Kachan, A. A. *Ukrainskii Khimicheskii Zhurnal* 1986, 52, 1309.
- Ngo, T. T.; Bush, D.; Liotta, C. L.; Eckert, C. A. *AIChE J* 2001, in press.
- Kurnik, R. T.; Reid, R. C. *Fluid Phase Equilib* 1982, 8, 93.
- Fedors, R. F. *Polym Eng Sci* 1974, 14, 147.
- Tsugane, H.; Yagi, Y.; Inomata, H.; Saito, S. *J Chem Eng Jpn* 1992, 25, 351.
- Lu, J.; Han, B.; Yan, H. *Phys Chem, Chem Phys* 1999, 1, 449.
- Kazarian, S. G.; Gupta, R. G.; Clarke, M. J.; Johnston, K. P.; Poliakov, M. *J Am Chem Soc* 1993 115, 11099.

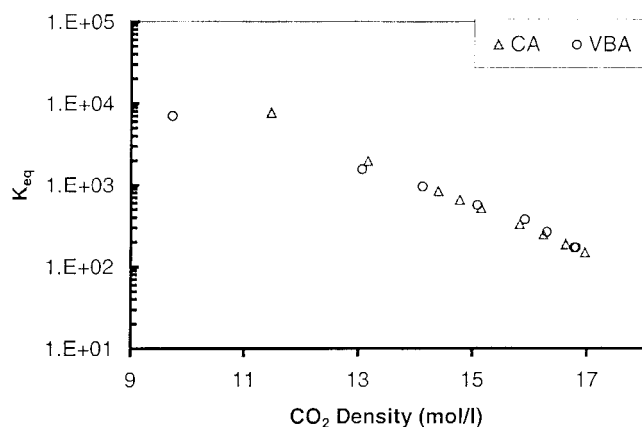


Figure 7 Effect of  $\text{CO}_2$  density on the dimerization equilibria of VBA and crotonic acid CA, at 308 K.