Reactive Latex Studies. 1. Kinetics of Reactions of Poly(vinylbenzyl chloride) Latex with Water-Soluble Amines[1]

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ABSTRACT: Monodisperse poly(vinylbenzyl chloride) latexes were prepared in the presence or absence of detergents. Reaction with trimethylamine or *N,N*-dimethylethanolamine leads to essentially complete conversion of chloromethyl groups with dissolution of the polymer. Reaction with amines that are insoluble or very slightly soluble in the polymer phase restricts the reaction to the surface of the latex particle. The kinetics of the reaction with glycinate and diethanolamine were studied for latex prepared in the absence of detergents as a function of surface charge density and the concentration of added surfactant.

Introduction

The surface properties of organic polymers are of considerable importance in many industrial, biological, and technological applications.[2-4] For example, in wettability, adhesion, electrostatic charging, and dye adsorption, the chemical properties of the surface play an important role. The surface analysis of solid organic polymers benefited greatly from the introduction of various modern instrumental techniques, for example, electron microscopy, AES, ESCA, ISS, SIMS, etc., as well as some new developments in IR, Raman, and UV–visible spectroscopy.[4,5] These methods have given detailed information on the chemical composition and structure of surfaces, and Whitesides and his collaborators have shown[6] that reactions of acid chloride groups on the surface of a polyethylene sheet with nucleophiles in aqueous solution can be monitored by highly sensitive spectroscopic techniques.

In this paper, we describe the kinetics of reactions of a polymer latex with a reactive surface; since this surface is very large, conventional analytical methods could be used to follow the chemical transformation. In particular, we used monodisperse poly(vinylbenzyl chloride) latex, where the particle size and the surface charge density[7-9] can be varied systematically over a wide range. The latex was prepared by either conventional or surfactant-free methods. The nucleophilic attack by amines in the aqueous phase was then followed by the amount of chloride released. Conditions were emphasized that restricted the reaction to the surface of the latex particles.

Experimental Section

Materials. The vinylbenzyl chloride monomer (VBC) (Dow Chemical) was a mixture of the meta (60%) and para (40%) isomers. It was extracted with 0.5% NaOH solution to remove inhibitors. Sodium lauryl sulfate (SLS) (Aldrich), analytical grade potassium persulfate (Mallinckrodt), sodium bisulfite (Aldrich), and sodium acetate (Fisher Scientific) were used as received. Glycine (Aldrich) was recrystallized twice from water, diethanolamine (Aldrich) was purified by zone refining, and trimethylamine (Aldrich), tris(hydroxymethyl)aminomethane (Aldrich), and triethanolamine (Aldrich) were used without further purification.

Latex Preparation. Polymerization followed Ono's method,[10] with some modifications: (1) Conventional latex: The polymerizations were carried out at 45 °C in a 500-mL three-neck flask. After 200 mL of distilled water was charged into the reaction vessel, nitrogen gas was bubbled through the water for about 30 min in order to exclude the dissolved oxygen. Vinylbenzyl chloride (32 g) and 0.0896 g of sodium lauryl sulfate were than added under stirring. Next, 0.096 g of sodium bisulfite (in 20 mL of H_2O) and 0.1274 g of potassium persulfate (in 30 mL of H_2O) were added dropwise. Polymerization was allowed to proceed overnight in a stream of nitrogen with the stirrer maintaining 300 rpm. The unreacted monomer was removed by steam distillation, and the ionic impurities were eliminated by dialysis against distilled water for 7 days, changing the dialyzate every 24 h. During the polymerization, unreacted monomer was analyzed by extracting the solution with hexane and measuring the optical density of VBC at 252 nm. (2) Surfactant-free latex was prepared in a similar manner except that no surfactant was added and the system was buffered with sodium acetate.

Particle Size. The PVBC latex particle size was determined by transmission electron microscopy, using a HU-11C-1 Hitachi electron microscope. A highly dilute sample of the latex was dried on a film of Formvar coated with a thin layer of carbon mounted on a copper gauze. The particle diameter, d, is specified in μm.

Surface Charge Densities of the Latex Particles. The latex prepared by both conventional and surfactant-free methods contains chemically bound sulfate groups whose number could be determined by conductometric titration.[11] Conductometric titrations under a nitrogen atmosphere were carried out on latex samples dialyzed first against M/1000 HCl and then against water until the dialyzate was free of chloride. A dip-type cell (cell constant $\kappa = 1$ cm^{-1}) was used and the conductivity was measured with a conductivity bridge (Industrial Instruments, Model RC 16B2).

Kinetic Measurements. The chloride ion released in aliquots of the system was determined after acidification with concentrated HNO_3 by using a chloride-selective electrode (Corning Glass Works, catalog no. 13-641-604) to locate the end point.

Results and Discussion

From the residual monomer analysis and the amount of acid released, it was found that the polymerization conversion was 90% and that 2.4% of the chloromethyl groups had been hydrolyzed during the polymerization. The latex is quite stable when stored in the refrigerator; see Figure 3 for a comparison of the rates of chloride release in the presence and absence of added nucleophiles.

Poly(vinylbenzyl chloride) (PVBC) Latex Reaction with Trimethylamine and *N,N*-Dimethylethanolamine. Figures 1 and 2 show the results obtained in the reaction of the PVBC latex (d = 0.16 μm) with trimethylamine and *N,N*-dimethylethanolamine. An approximate measure of the ability of these nucleophiles to penetrate into the polymer phase is their distribution coefficient between water and toluene. This was found to be 3.0 for *N,N*-dimethylethanolamine and 2.6 for trimethylamine, indicating that they can enter the latex particles. Thus, the attack of the amino groups on the chloromethyl groups is governed by the diffusion of the nucleophile from the aqueous to the polymer phase. These reactions exhibit an initial acceleration and proceed almost to completion, with the system undergoing a dramatic change from an opaque milky appearance to a clear viscous solution. Apparent conversions were possibly less than 100% because some of the chloromethyl groups had hydrolyzed before reaction with the amine. The conversion of PVBC latex by reaction with trimethylamine to a

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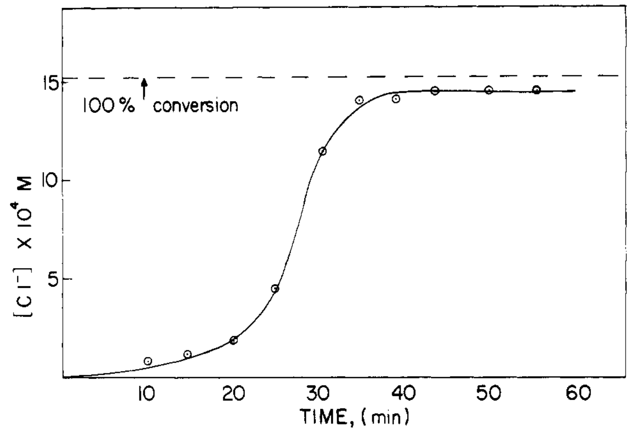

Figure 1. Reaction of PVBC latex with 0.14 M trimethylamine. Latex concentration 0.23 g/L, d = 0.16, temperature 32 °C.

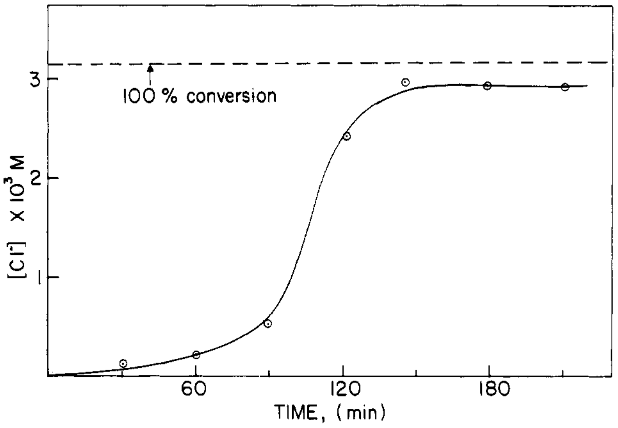

Figure 2. Reaction of PVBC latex with 1.0 M *N*,*N*-dimethylethanolamine. Latex concentration 0.51 g/L, d = 0.16, temperature 35 °C.

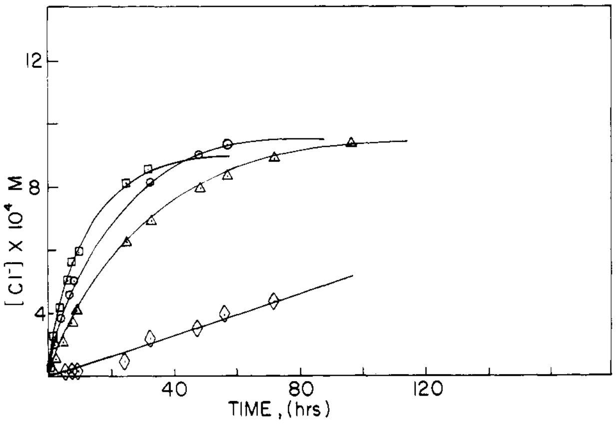

Figure 3. Reaction of PVBC latex with 0.24 M glycine. Latex concentration 3.85 g/L, d = 0.17, temperature 35 °C. NaOH/glycine ratio: 0.75 (□); 0.50 (○); 0.25 (△); 0 (◇).

water-soluble polymer had previously been described by Lloyd and Durocher,[12] who followed the process by acid–base titration.

Reaction with Glycinate. Figure 3 shows the time dependence of chloride ion release when latexes were reacted with glycine to which different proportions of sodium hydroxide had been added. The first-order rate constants (Figure 4) were found to be proportional to the degree of neutralization as would be expected since only the deprotonated amine can function as a nucleophile. The very slow reaction rate for unneutralized glycine is possibly due to hydrolysis. Since glycinate could not dissolve in the organic phase of the latex particle, the reaction involved only the surface of the latex particle. The reaction leveled off at a conversion of 2.96%, leading to attachment of one glycinate residue per 30 Å^2 of surface area. It is surprising that the reaction follows closely first-order kinetics in spite of the increasing charge density of the surface of the latex particles.

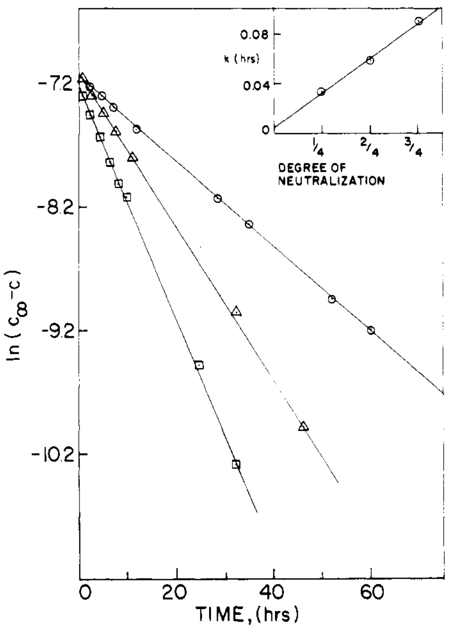

Figure 4. First-order plots for reaction of PVBC latex with glycinate. (Conditions and symbols same as in Figure 3.)

Table I
Reaction of PVBC Latex[a] with Amines[b]

reagent	init rate × 10^5, M/h
diethanolamine	3.4
tris(hydroxymethyl)aminomethane	1.4
triethanolamine	1.4
glycinate	3.6

[a] Latex concentration, 3.85 g/L. [b] Amine concentrations 0.12 M, d = 0.17, temperature 35 °C.

Reaction with Various Amines. Table I shows the initial rates for the reaction of various amines with the PVBC latex. The distribution coefficients between water and toluene are 32.4 (diethanolamine), 2460 (triethanolamine), 2380 (tris(hydroxymethyl)aminomethane). In view of this large preference for the aqueous medium, attack by these nucleophiles is limited to the surface of the latex particles. The reaction rates seem to depend on the size of the amines and not on their basicity. In the case of the half-neutralized glycinate, the lower than expected reaction rate can be explained by the repulsion between the negatively charged latex surface and the carboxylate groups on the glycinate.

Effect of the Interfacial Tension on the Reaction Rates. When methanol is added to the latex, the interfacial tension should decrease and it seemed possible that this would make it easier for a reagent in the aqueous phase to attack functional groups attached to the nonpolar polymer surface. However, results showed that methanol addition had no substantial effect on the initial rates. The reaction rate did not change at a methanol content as high as 12.5% by volume. A small increase was noted when the methanol content was raised to 25%.

Effect of Surfactant on the Reaction Rate. Latex particles prepared in the presence of detergents are surrounded by adsorbed surfactant, the charges of the surfactant and charges from the initiating radical attached

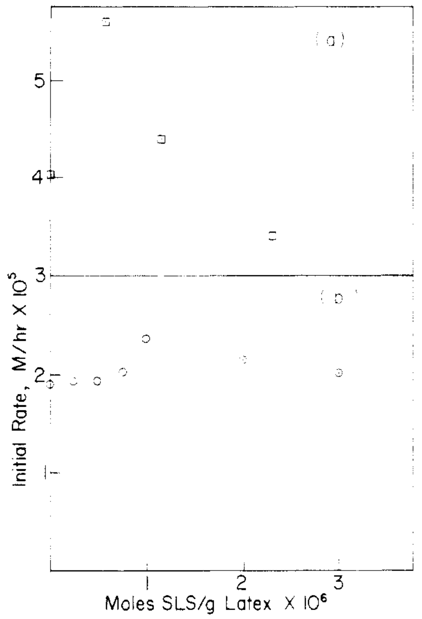

Figure 5. Effect of SLS on the reaction of PVBC latex with (a) 4.1 g/L latex (*d* = 0.4) with 0.32 M glycinate (temperature 35 °C) and (b) 8.0 g/L latex (*d* = 0.4) with 0.12 M diethanolamine (temperature 31.5 °C).

Table II
Surface Charge Density of Latex

	surfactant-free latex				conv latex
	SFL-B	SFL-1	SFL-2	SFL-10	L-12
diam, μm	1.0	0.72	0.40	0.24	0.17
surf charge, μC/cm^2	1.44	0.96	0.48	0.23	0.40

to the polymer chain[7,13] providing the stabilization for the latex against coagulation. When surfactant was added to a latex prepared in the absence of detergents, a different effect was observed for the reaction rates with the neutral diethanolamine and the negatively charged glycinate (Figure 5). This could be attributed to three effects caused by the surfactant: (1) it decreases the interfacial tension between the nonpolar surface and the aqueous medium; (2) it increases the charge density of the surface (this effect will be discussed in more detail later); (3) it shields the reactive chloromethyl groups from being attacked. In the reaction of diethanolamine, factors 1 and 2 counterbalance factor 3, and this is why the reaction rates first increase; at a certain point factor 3 becomes dominant and the reaction rate decreases on further surfactant addition. In the case of glycinate, both the initial acceleration and the later decline of the reaction rate with increasing detergent concentrations are much more pronounced.

Charge Density Effect on the Initial Reaction Rates. The conductometric titration results are shown in Table II. In surfactant-free latexes the surface charge density increases with increasing particle size. This may be understood by assuming that the number of initiator fragments attached to the latex particles is proportional to the particle volume. The conventional latex L12 has a higher charge density than the corresponding surfactant-free latex due to the adsorbed surfactant. Table III shows the initial reaction rates of detergent-stabilized and detergent-free latex with glycinate and diethanolamine. In both cases the initial rate decreases with decreasing particle size. Table IV lists relative initial rates per unit surface of the latex particles. The reaction rates are approximately proportional to the charge densities. This suggests that the more hydrophilic latex particle surface, obtained at higher charge densities, favors the nucleophilic attack on the chloromethyl groups. It is however surprising that an increase in the negative charge density of the latex particles favors the reaction with anionic glycinate even more than the reaction with neutral diethanolamine. We have no explanation for this feature.

Table III
Reaction Rates of Latexes with Glycinate and Diethanolamine

	init rate × 10^5, M/h	
latex[a]	glycinate[b]	diethanolamine[b]
SFL-B	2.01	1.27
SFL-1	1.50	1.07
SFL-2	1.08	0.82
SFL-10	*c*	0.68
L-12	1.98	1.65

[a] Latex concentration [b] Concentration 0.12 M, temperature 35 °C. [c] Too slow to be measured.

Table IV
Effect of the Surface Charge Density on the Reaction of Latexes with Glycinate and Diethanolamine

			rel init rate	
sample	particle diam, μm	rel charge density	with glycinate	with diethanolamine
SFL-B	1.0	3	4.7	3.8
SFL-1	0.72	2	2.5	2.3
SFL-2	0.40	1	1	1
SFL-10	0.24	0.54	*a*	0.50
L-12	0.17	0.83	0.79	0.85

[a] Too slow to be measured.

Concluding Remarks

This study showed that a polymer latex with a very high surface density of groups reacting with nucleophiles in the aqueous phase can easily be prepared and that the reaction is restricted to the surface of the polymer particles if the reagent is characterized by a low solubility in the polymer phase. Reactive latex particles have been previously coupled with antibodies for serological tests[14] and the present work was to provide background information for the possible use of the PVBC latex in this application. Studies of protein attachment to PVBC latex will be reported at a later date.

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Registry No. Poly(vinylbenzyl chloride) (homopolymer), 9080-67-5; glycine, 56-40-6; diethanolamine, 111-42-2; tris(hydroxymethyl)aminomethane, 77-86-1; triethanolamine, 102-71-6; trimethylamine, 75-50-3; *N*,*N*-dimethylethanolamine, 108-01-0.

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Pressure Dependence of Secondary Transitions. 6. T_{α_c} and T_{α_a} in Polyethylenes

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ABSTRACT: Isotherms of branched and linear polyethylenes from 20 to 200 °C at P = 1–2000 bars have been examined by a linear form of the Tait equation, $Y = P/b$, where Y is an exponential function of volume and b is the normalizing constant in the Tait equation. Isothermal V–P data from ca. 175 to 200 °C follow the linear Tait equation exactly with a single value of b. Lower temperature isotherms in the region of the secondary α_a (intercrystalline) and the α_c (intracrystalline) relaxations ($T_{\alpha_c} > T_{\alpha_a}$ at constant P) do not follow a single $Y = P/b$ line because of pressure-induced α_a and α_c relaxations. Instead, $n + 1$ $Y = P/b$ lines per isotherm are required with n intersections at pressures P_1^{i}, $P_2^{\mathrm{i}} - P_n^{\mathrm{i}}$, where $1 < n \le 3$ for $P_{\max}$ of 2 kbars. A computerized intersection search method based on minimizing the standard error has been employed to locate these intersection pressures and to calculate the intercepts and slopes of the $n + 1$ lines needed to define each isotherm. The step increase in b at each pressure-induced transition is readily calculated. Results of the intersection search method were verified by linear regression analysis with residuals. Past practice in the literature with Tait analysis of isothermal V–P data tended to obscure the existence of secondary relaxations. Use of the linear form $Y = P/b$ with the statistical procedures used herein greatly extends the utility of the Tait equation in search for weak secondary transitions. Hence we judge the empirical Tait equation to be remarkably useful for representing isothermal V–P data when properly used. Values of T_{α_c} and T_{α_a} obtained by the above procedures and independently from isobaric V–T data are linear in P with pressure coefficients of 48–56 K/kbar for α_c and 50–60 K/kbar for α_a. The linear Tait method was applied to isothermal V–P data on two n-alkanes with P up to ca. 5 kbars. Exact linearity obtains with no evidence of transitions. Residuals, while small, are nonrandom.

Introduction

Previous papers in this series have employed variations of and approximations to the Tait equation to determine the pressure dependence of the T_{ll} transition in amorphous polymers,[1-3] the temperature dependence of the Tait parameter, b, above T_g,[4] the change in coefficient of expansion at $T_{ll'}$ and $\mathrm{d}T_{ll}/\mathrm{d}P$ from isobaric V–T data.[5] Isotactic PMMA has been studied to locate $T_{ll'}$ using a linear form of the Tait equation.[6]

Here we employ this same linear variation of the Tait equation to analyze the P–V–T behavior of branched and linear polyethylenes (PE) with several objectives in mind: (1) to provide a rigorous test of the Tait equation using isothermal V–P data in the melt of PE where we anticipated no pressure-induced transitions other than T_m, (2) to study the premelting or intracrystalline process, designated as the α_c transition, lying at about $(0.85–0.90)T_m$; as well as the amorphous intercrystalline or α_a process lying just below the α_c event, and (3) to search the lower temperature isotherms from room temperature to T_m for amorphous-phase transitions, in particular for T_{ll}. In addition, we examine isobaric V–T data for confirmatory and/or supplementary information, especially in regard to the α_a and α_c processes.

A note on nomenclature: While melting at temperature T_m is a thermodynamic first-order transition, the glass-to-liquid transition, designated T_g, has relaxational character or frequency dependence. Still it has been designated as a transition by Fox and Flory.[7] Likewise the α_a and α_c processes have a relaxational aspect but are clearly revealed herein by P–V–T data. Various designations have been used in the literature for these two processes, e.g., α', α'', mechanism 1, mechanism 2, $\alpha_c(1)$, and $\alpha_c(2)$. We prefer α_a to symbolize an amorphous-phase event and α_c to symbolize the crystalline-phase event, especially since the molecular mechanisms are now well-known, as will be shown later. In treating isothermal V–P data we use the symbol P_n^{i} to indicate an intersection pressure corresponding to a transition or relaxation. n is a small integer denoting the number of the intersection along any isotherm going from low to high pressure. n seldom exceeds 3 for any polymer and in this study does not exceed 2. The corresponding symbol for isobaric V–T data is T_n^{i}, again with n not exceeding 2 for P not greater than 2 kbars.

Motivation for this study arose from the fact that we have been questioned on several occasions about the reliability of the Tait equation for locating weak secondary events, in part because of its empirical nature and in part because of a paucity of isobars. Even though it has been widely employed with polymers, major emphasis has always been on T_g and T_m, which are strong primary transitions. We concede however that a rigorous test of the Tait equation is desirable. One possibility is to locate a polymer that is completely free of secondary transitions in some region of P–V–T space. The melt of PE seemed, a priori, to meet this requirement, and indeed it does.

It apparently had been considered by some authors[8-12] that the seeming constancy of b across an isotherm constituted a verification of the Tait equation although Quach and Simha did find departure from Tait in the β region

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