13b) obtained from the GPC evaluation based on the 12 PSM fractions.

$$\log \bar{M}_w = 11.13 - 0.1214V_e \qquad (13b)$$

An analysis similar to that involving the PSM fractions was done using the near-monodisperse polybutadienes. The intrinsic viscosity relation was developed from measurements done on samples LF-2 and LF-5 (Table II). The equation obtained follows:

$$[\eta]_{\mathrm{THF}}^{30\,°\mathrm{C}} = 2.56 \times 10^{-4}\bar{M}_w^{0.74} \qquad (14)$$

This equation is in excellent agreement with the one developed by Rochefort and co-workers[17] using the procedure of Kraus and Stacy.[2] The values of A'' and B'' (eq 13b) for polybutadiene were found to be 10.76 and 0.1213, respectively.[18] These may be compared with the values of 10.77 and 0.1214 obtained in the conventional manner utilizing the nine samples of Table II.

In conclusion, we do not wish to imply or claim that the evaluations outlined herein should be used to replace either the usual methods of determining K and α or the calibration techniques for columns used in gel permeation chromatography. However, these methods can serve where a Mark–Houwink–Sakurada relation does not exist for a particular polymer–solvent system and/or in situations where a series of characterized standards are unavailable for GPC calibration.

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(18) The universal calibration expression used for the calculation of these values of A'' and B'' is $\log ([\eta]\bar{M}_w) = 15.14 - 0.2016V_e$. The change in the constants from the values in eq 13 was occasioned by a shift in the calibration during the 5-month interval between the measurements involving the PSM fractions and the polybutadienes.

Influence of Aqueous Salt on Triphase Catalytic Activity[1]

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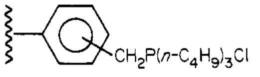
In this note we provide evidence that (1) salt present in the aqueous layer plays a major role in defining the hydration state of polymeric triphase catalysts and (2) imbibed water substantially influences resin activity.

We have previously described the kinetic features of the triphase displacement by chloride ion on n-decyl methanesulfonate using polymers **1a** and **1b** (reaction 1).[2-9] In the present investigation we have examined this reaction further under comparable biphase stoichiometric, triphase stoichiometric, and triphase catalytic conditions.[10]

$$n\text{-}C_{10}H_{21}OSO_2CH_3 + Cl^- \xrightarrow{\mathbf{1a}\text{ or }\mathbf{1b}} n\text{-}C_{10}H_{21}Cl + CH_3SO_3^- \qquad (1)$$



functionalized microporous polystyrene–1% divinylbenzene (200–400 mesh)

1a, 52% ring substitution: 2.23 mequiv g^{-1}
b, 17% ring substitution; 1.23 mequiv g^{-1}

All reactions reported herein were carried out under pseudo-first-order conditions with a 20-fold excess of resin. Biphase stoichiometric reactions were performed in the following manner. A 50-mL culture tube (Corning no. 9826, 25 × 150 mm) containing a $^1/_2 \times {}^5/_{16}$ in. octagonal Teflon-coated stirring bar with pivot ring was charged with 0.45 mequiv of dry polymer. A limited volume of distilled water was then injected directly into the resin, followed by addition of 4.0 mL of toluene containing n-hexadecane (30 μL) as an internal standard. The tube was then sealed with a Teflon-lined screw cap and placed in an oil bath maintained at 70 °C, and the mixture was stirred (ca. 1000 rpm)[11] for 0.25 h. n-Decyl methanesulfonate (4.9 μL, 0.02 mmol) was then injected into the toluene layer and its disappearance was followed as a function of time by GLC.[12] Observed pseudo-first-order rate constants, k_{obsd}, are reported in Table I. Incremental addition of water to **1a** resulted in a reduction in resin activity. When the polymer was fully hydrated, the activity was approximately 0.6% of that found in the absence of water. Results obtained for **1b** were similar but less dramatic; i.e., a maximum water uptake led to a 92% loss in activity. These data clearly show that resin activity is highly dependent on the imbibed water content.

Triphase stoichiometric reactions were carried out by equilibrating 0.45 mequiv of polymer with 4.0 mL of toluene plus 4.0 mL of water at 70 °C for 0.5 h and then injecting 0.02 mmol of n-decyl methanesulfonate into the organic layer. For **1b**, the triphase stoichiometric rate was, within experimental error (±10%), identical with that of a biphase reaction using the fully hydrated polymer. In contrast, the activity of **1a** was reduced by 67% when an external aqueous layer was present. These results indicate that under triphase stoichiometric conditions **1b** maintains contact with the organic phase but that **1a** does not.[13]

The activity of **1a** and **1b** was next examined under catalytic conditions, with procedures similar to those of the triphase stoichiometric reactions except that a satu-

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Table I
Influence of Imbibed Water on Resin Activity[a]

entry	reaction conditions	resin	imbibed toluene,[b] g/g of polymer	imbibed water,[b] g/g of polymer	hydration state[c] n	activity[d] 10^5k_{obsd}, s^{-1}
1	biphase stoichiometric	1a		0.0	0	30
2		1a		0.036	0.9	20
3		1a		0.150	3.7	12
4		1a		0.360	8.9	3.5
5		1a		0.750	18.5	0.9
6		1a		11.910[e]	297	0.17
7	triphase stoichiometric	1a	0.43	11.910	297	0.06
8	triphase catalytic	1a	0.37	0.440	11.0	4.4
9	biphase stoichiometric	1b		0.0	0	52
10		1b		0.019	0.9	37
11		1b		0.079	3.7	29
12		1b		0.189	8.9	11
13		1b		0.395	18.5	4.5
14		1b		0.780[e]	96	3.9
15	triphase stoichiometric	1b	0.55	0.780	96	4.2
16	triphase catalytic	1b	0.56	0.420	18.9	12

[a] Reaction of 4.0 mL of 0.005 M *n*-decyl methanesulfonate in toluene with 0.45 mequiv of polymer at 70 °C, using procedures described in the text. [b] Analytical methods used for determining imbided toluene, water, and sodium chloride are described elsewhere.[15] [c] n = mol of water/mol of phosphonium groups. [d] Observed pseudo-first-order rate constant. Biphase reactions generally showed a slight acceleration with time due to evaporation of water from the resin. In these cases, k_{obsd} was determined from the initial slope. [e] Maximum volume of water uptake.

rated aqueous sodium chloride solution was employed. In the case of **1a**, the presence of salt substantially reduced the amount of imbibed water (osmotic shrinkage)[14] and increased its activity. Of particular significance was the fact that the activity and hydration state under catalytic conditions were nearly identical with those of a biphase reaction (compare entries 4 and 8). This shows that a major role of the salt in influencing catalytic activity is to define the hydration state of the resin. While a similar comparison made for **1b** qualitatively supports this conclusion, the numbers do not closely coincide. Specifically, if entries 12 and 16 are compared, the activities are essentially the same but the apparent hydration state is higher under catalytic conditions. Quantitative analysis of the sodium chloride associated with **1a** and **1b** under catalytic conditions has yielded values of 0.02 and 0.11 g of salt/g of polymer, respectively.[15] Is seems likely, therefore, that the higher hydration state for **1b** in entry 16 is due to the presence of adsorbed sodium chloride.

References and Notes

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(10) Biphase reactions are reactions carried out with a limited volume of water plus excess toluene; i.e., only a polymer and an external aqueous phase are visible. Triphase catalytic reactions are performed with excess toluene and an excess aqueous sodium chloride solution; imbibed solvents reside within the polymer.
(11) Monitored by a Cole-Parmer Strobette stroboscope tachometer.
(12) Analytical methods have been previously described.[9]
(13) Kinetic experiments using a 20-fold excess of *n*-decyl methanesulfonate relative to **1a** and **1b** have also been carried out under triphase stoichiometric conditions at 70 °C. In both cases clean pseudo-first-order kinetics were obtained (over 3 half-lives), indicating that all of the chloride ions in each polymer are uniformly active.
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Concept of Order Parameters in the Glass Transition. Nonequilibrium State of Glass along the Transition Line

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When an equilibrium liquid solidifies to a glass, the first derivatives of the Gibbs free energy, G, with respect to temperature, T (i.e., entropy, S), and pressure, P (i.e., volume, V), remain continuous whereas the second derivatives, the isobaric heat capacity, C_p, the coefficient of thermal expansion, α, and the isothermal compressibility, β, show a final discontinuity. The behavior of these thermodynamic quantities along the line of transition $T_{\text{tr}} = T_{\text{tr}}(P)$ is usually considered from the point of view of Ehrenfest relations,[1] originally derived for a second-order phase transition:

$$\mathrm{d}T_{\text{tr}}/\mathrm{d}P = \Delta\beta/\Delta\alpha \tag{1a}$$

$$\mathrm{d}T_{\text{tr}}/\mathrm{d}P = TV\Delta\alpha/\Delta C_p \tag{1b}$$

where the symbol Δ represents the discontinuity.

A more realistic model of the glass transition is a freezing-in process where the order parameters in the

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