Table I
Activation Energies for the Decomposition of Some Sulfonyl Radicals

sulfonyl radical	activation energy, kcal/mol	ΔE,[a] kcal/mol
$CH_3SO_2\cdot$[9]	22.4 ± 1.8	20.0 ± 2
$CH_3CH_2SO_2\cdot$[14]	19.9	
$CH_3CH(Cl)SO_2\cdot$[b]	13.4 ± 2.0	11.0 ± 1.5
$PhCH_2SO_2\cdot$[15]	12.0 ± 3.2	
$CH_2{=}CHCH_2SO_2\cdot$[15]	8.4 ± 3.2	

[a] The difference in activation energies between the decomposition and addition of sulfonyl radicals to styrene measured in this work. [b] Our estimated activation energy for decomposition.

For comparison purposes, data on the decomposition of some sulfonyl radicals reported by other workers are listed in Table I together with our results on the α-chloroethanesulfonyl radical. The decomposition of benzyl- and allylsulfonyl radicals is associated with low activation energy since the radicals formed in the decomposition are resonance stabilized. It is interesting to note that the activation energy for the decomposition of ethanesulfonyl radical is 6.5 ± 2 kcal/mol higher than that of α-chloroethanesulfonyl radical, which we attribute to the electrostatic repulsion between chlorine atom and SO_2 group.

Experimental Section

A solution of the catalyst (acetonitrile, 5 mL; $CuCl_2$, 0.175 g; $N(Et)_3HCl$, 0.250 g; AIBN, 0.150 g) was prepared.[8] A required amount of the catalyst solution (10 vol % of the total volume of reaction mixture) was then added to the reaction vessel containing benzene, styrene, and sulfonyl chloride. The molar ratio of styrene to sulfonyl chloride was 2. Benzene as diluent was used to vary the initial styrene concentrations, which were 1.0, 1.3, 2.0, and 3.5 M. The sample was thoroughly mixed and degassed. Reaction was homogeneous and was stopped at the desired times by cooling in a precooled methanol bath. A small amount of the reaction mixture was removed for determination of sulfone II by gas chromatography (GE-SE-30, 20% silicone oil on Chromosorb, 60–80 mesh, stainless steel column (2 m × 4 mm o.d.), column oven temperature 250 °C, injector temperature 300 °C). All the remainder was used for determination of SO_2 by iodide–thiosulfate titration.[16]

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Equation of State for Crystalline Polyethylene

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In a recent paper[2] a quantum mechanical version of the cell theory for polymeric solids, including the effect of anharmonicity in the cell potential to a first approximation, was given. The resulting equation of state was shown to describe quite nicely the variation of volume with temperature at atmospheric pressure for the crystal phase of polyethylene and poly(chlorotrifluoroethylene) over a wide range. It was also found that the isotherms of the semicrystalline polymer, on the basis of some plausible assumptions, were in accord with theory for temperatures sufficiently below the normal melting point. The direct data for the isotherm of the polyethylene crystal at room temperature of Ito[3] and Sham et al.[4] (SNP) have now become available to us. In the present note we examine the validity of our theory vis-â-vis their experimental results and the information about the P–V–T surface which was previously available. In doing so we have taken a fresh look at the values to be assigned to various parameters from the point of view of consistency regarding the values of the ratio c/n (the number of volume dependent degrees of freedom per repeat unit) derived from either (i) the assignment made for the scale factors for pressure (P^*), for volume (V^*), and for temperature (T^*) or (ii) the assignments for the reduced characteristic temperature $\tilde{\theta}_0$, T^*, and V^*.

In our earlier work[2] it was shown that the equation of state has the form

$$\tilde{P} = \tilde{P}(\tilde{V},\tilde{T},\tilde{\theta}_0,s/c) \tag{1}$$

where $\tilde{P}$, $\tilde{V}$ and $\tilde{T}$ are the reduced pressure, volume, and temperature respectively, while s and c are respectively the number of force centers and the number of volume dependent degrees of freedom per chain. For full details about the equation of state reference should be made to the previous paper.[2] In comparing theory with experiment, the values of parameters adopted there for polyethylene crystal, for $s/c = 1$, were $T^* = 6918$ K, $V^* = 0.9954$ cm^3 g^{-1}, $P^* = 18$ kbar, and $\tilde{\theta}_0(\tilde{V}_0) = 0.054$, $\tilde{V}_0$ being the reduced volume for $P = 0$ and $T = 0$ K. Using eq 2a and 4 of ref 2, it can be shown that

$$c/n = \frac{M_r}{N_A}\left\{\frac{1.5874\pi^2 k}{h^2}\right\}\frac{(T^*)^{3/5}(V^*)^{2/5}\tilde{\theta}_0{}^{6/5}\tilde{V}_0{}^{8/5}}{(A_1\tilde{V}_0{}^{-2} - 2B_1)^{3/5}} \tag{2a}$$

where M_r is the molecular weight of the monomer repeat unit and N_A is the Avogadro's number. On the other hand, from the expressions for the scaling factors P^*, V^*, and T^* one gets

$$c/n = \frac{P^*V^*}{T^*}(M_r/R) \tag{2b}$$

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Table I
Values for V^*, T^*, and P^* [a]

source of P-V-T results	$\tilde{\theta}_0$	V^*, cm^3 g^{-1}	T^*, K	P^*, kbar	c/n
Ito[3] and Davis et al.[5]	2.100×10^{-3}	1.0163	7880	16.23	0.3599
SNP[4] and Davis et al.[5]	2.400×10^{-3}	1.0152	7850	19.12	0.4250

[a] Values of parameters of eq 1 needed for obtaining the best fit between theory and the reported P-V-T results from X-ray measurements for polyethylene subject to the consistency condition; in all cases here $s/c = 1$.

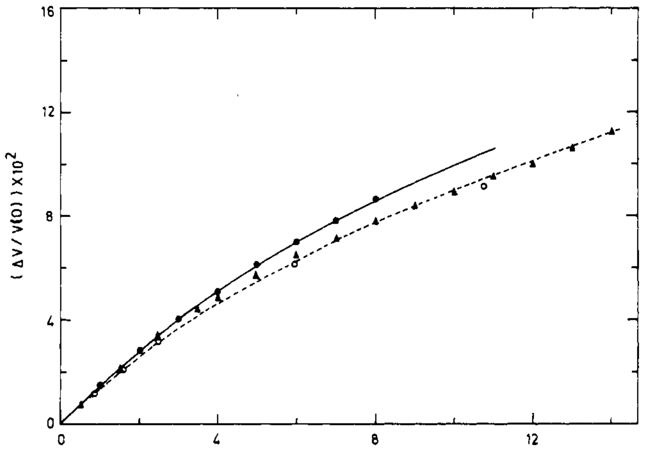

Figure 1. Theoretical plots of $\Delta V/V(0)$ vs. pressure; full curve (20 °C) and dashed curve (25 °C) are drawn using respectively the first and second set of parameter values from Table I and eq 1. Open circles are results of Pastine's theory.[7] Other points represent the experimental results: (●) Ito[3] and (▲) SNP.[4]

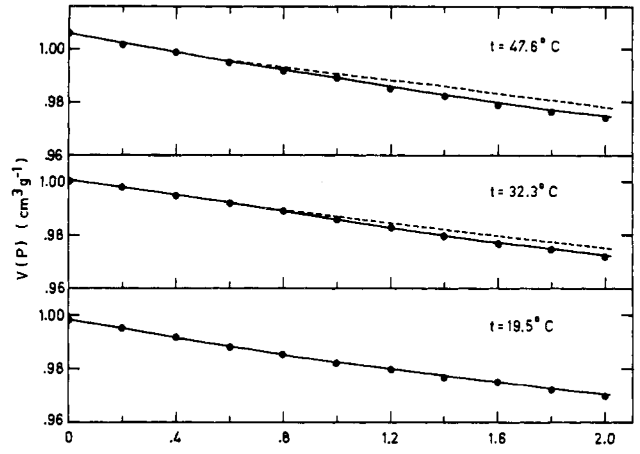

Figure 2. Theoretical plots of $V(P)$ as a function of P at different temperatures. Full curves and dashed curves are drawn as in Figure 1; (●) crystal data deduced from P-V-T measurements on semicrystalline polyethylene.[2,6]

where R is the universal gas constant. The value of $\tilde{V}_0$, for $s/c = 1$ and $\tilde{\theta}_0 = 0.054$, is found from equation of state to be 0.9610. Substituting the values quoted above for various quantities in eq 2a and 2b, one finds that c/n has the values 1.15 and 0.436, respectively. Evidently this discrepancy has to be removed for a proper check of the validity of the theory.

The choice $s/c = 1$, which has been found[2] to provide a representation for V-T results of Davis et al.[5] over the widest range of temperature, will be retained here. The remaining parameters of eq 1 are to be chosen, subject to the consistency conditions 2a and 2b, so that the best representation (through least-squares analysis) of the X-ray P-V-T data is obtained. While doing this, it has to be kept in mind that the present theory is expected to agree closely with V-T data in the intermediate temperature region. It would show deviations on the low-temperature side ($T < \theta_0$) because of the neglect of correlations inherent in a cell-type theory while close to the melting temperature deviations are expected due to our approximate treatment of the effect of anharmonicity. In actual practice a problem is encountered because the reported ΔV ($= V(P) - V(0)$) values of Ito are systematically higher than that of SNP. The two sets of high-pressure data have therefore been used separately with the V-T results of Davis et al. for the determination of optimum values of $\tilde{\theta}_0$, V^*, T^*, and P^*. The values found are given in Table I.

A comparison between theoretical and experimental values is shown in Figure 1. It is noted that the theoretical solid curve, based on the first set of parameter values of Table I, provides a very good representation for the experimental results of Ito (solid circles). The representation of SNP values (triangles) by the theoretical dashed curve, using the second set of parameter values, however, is not as good, there being some noticeable departures between 2 to 6 kbar. The open circles, which represent the results of Pastine's theory,[7] are generally quite close to the SNP values but a trend which shows gradually increasing deviations at higher pressures is noticeable. It may also be mentioned that our theory, using parameters of Table I, agrees with the V-T results of Davis et al.[5] (deviations below 0.04%) in the range 165 (175 K for the second set) to 333 K instead of 130 to 320 K as found earlier.[2] No V-T data for polyethylene crystal above 333 K are available. At the melting point, however, the experimental crystal volume is reported[8] to be 1.034 cm^3 g^{-1} as compared to the theoretical values 1.029 cm^3 g^{-1} (parameters of Table I) and 1.024 cm^3 g^{-1} (parameters of ref 2). Thus the use of the consistency condition in the selection of parameter values leads to better agreement with experiment on the high-temperature side.

In Figure 2, comparisons of theoretical isotherms with the crystal data generated[2] from the P-V-T measurements[6] on semicrystalline polyethylene are shown at three different temperatures. It is noted that the theoretical results using the first set of parameters in Table I (full curves) are in good agreement with experiment at all temperatures. On the other hand, theoretical results using the second set of parameter values (dashed curves) show deviations from experiment which increases with temperature.

It may be concluded that our theory, using the first set off parameter values in Table I, suitably describes not only the P-V-T data of Davis et al. and Ito based on X-ray measurements but also the crystal data generated from the isotherms of semicrystalline polyethylene. The negative deviations of the reported results of SNP from the full curve in Figure 1 are perhaps due to the neglect of strain along the c axis of the crystal in their determination of volume changes as a function of pressure. Measurements of crystal isotherms over a wide range of pressure and temperature would serve to define the range of validity of the present theory.

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Solvation–Desolvation Effect in Polyelectrolyte Catalysis: Cyanoethylation of Amino Acid in Aqueous Me_2SO Mixtures

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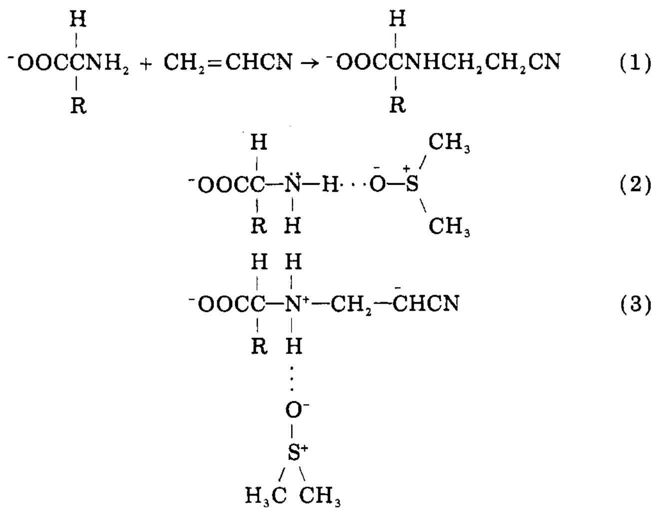
Catalytic influence of polyelectrolytes has been studied by various research groups and it has been found that reactions between similarly charged ionic species could be enormously accelerated by oppositely charged polyions and those between cationic and anionic species could be hindered by both cationic and anionic polyions.[1] With regards to the cause of this distinct polyelectrolyte effect, we pointed out that desolvation and solvation of the reactant and/or activated complex by the polyions might be important, in addition to the purely electrostatic interaction between the polyions and the reactants and/or activated complex.[2] The pressure effect studied was not inconsistent with the solvation–desolvation hypothesis.[3] In this paper, we wish to report the selective solvation effect, which affected clearly the catalysis by polyelectrolytes on cyanoethylation of an amino acid (eq 1 in Scheme I).

This reaction system (in the absence of polyelectrolyte) was studied by Friedman et al. in the 1960's.[4,5] They found that the reaction rates in the mixed solvent, especially in the Me_2SO–H_2O equal volume mixture, were much larger than in pure water, and this phenomenon was attributed to the increase in the nucleophilicity of the amino group of the amino acid by hydrogen-bond formation between Me_2SO oxygen and NH_2 hydrogen (eq 2). If the catalysis by polyelectrolytes is partly attributable to desolvation of the reactants by polyions, the rate-enhancing effect of Me_2SO would be weakened if the polyions can be strongly solvated by Me_2SO. Thus, in the present work, the experiment was designed to check this anticipation by using quaternized poly(vinylpyridine) derivative, a cationic polymer which may be solvated by Me_2SO preferentially.

Experimental Section

L-Phenylalanine (L-Phe), ninhydrin, and other reagents were obtained from Wako Pure Chemical Co. Acrylonitrile and Me_2SO were distilled before use. The details about the preparation of poly(4-vinyl-*N*-benzylpyridinium chloride) (BzPVP) and sodium poly(styrene sulfonate) (NaPSt) were described elsewhere.[6] The procedure of kinetic measurement followed was described by Friedman et al.[5] A Hitachi UV spectrophotometer (EPS-3T) was used in order to follow the ninhydrin reaction.

Scheme I



$$^{-}OOC\overset{H}{\underset{R}{C}}NH_2 + CH_2{=}CHCN \rightarrow {}^{-}OOC\overset{H}{\underset{R}{C}}NHCH_2CH_2CN \quad (1)$$

$$^{-}OOC\overset{H}{\underset{R}{C}}{-}\overset{\cdot\cdot}{\underset{H}{N}}{-}H\cdots\overset{-}{O}{-}\overset{+}{S}(CH_3)_2 \quad (2)$$

$$^{-}OOC\overset{H}{\underset{R}{C}}{-}\overset{H}{\underset{H}{N^+}}{-}CH_2{-}\overset{-}{C}HCN \quad (3)$$

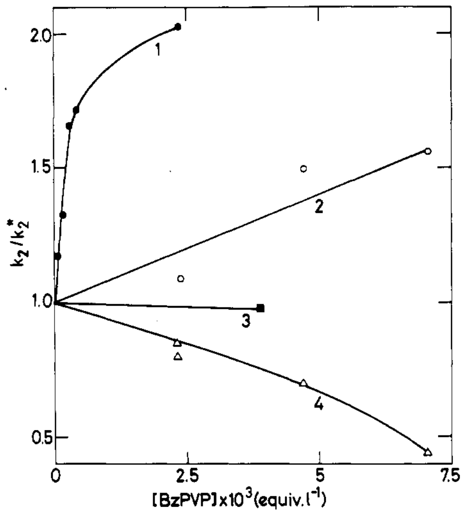


Figure 1. Polyelectrolyte influence on the cyanoethylation of L-phenylalanine at 30 °C ([acrylonitrile] = 0.2 M, [L-Phe] = 1 mM): (1) pH 10.06 buffer; (2) 50(v/v)% pH 10.06 buffer–Me_2SO; (3) pH 8.48 buffer; (4) 50 (v/v)% pH 8.48 buffer–Me_2SO.

Results and Discussion

The influence of the cationic polyelectrolyte, BzPVP, on this reaction system is shown in Figure 1, where k_2 and k_2^* are the second-order rate constants in the presence and absence of polyelectrolyte, respectively. k_2^* were 2.1×10^{-3}, 5.3×10^{-3}, 0.48×10^{-3}, and 5.0×10^{-3} M^{-1} s^{-1} for pH 10.06 buffer, 50(v/v)% pH 10.06 buffer–Me_2SO, pH 8.48 buffer, and 50(v/v)% pH 8.48 buffer–Me_2SO, respectively. These were in agreement with literature values[5] (k_2^* were 0.35 $\times 10^{-3}$ and 5.0×10^{-3} M^{-1} s^{-1} under slightly different conditions, namely, for pH 8.4 buffer and 50(v/v)% pH 8.4 buffer–Me_2SO, respectively). Clearly Me_2SO accelerates the reaction. By the addition of BzPVP, the reaction rate was increased by a factor of 2 at most in the pH 10.06 buffer solution (curve 1). This can be explained by the electrostatic interaction between anionic L-Phe (pK_2 = 9.0[4]) and cationic BzPVP and hydrophobic interaction between acrylonitrile and BzPVP.

In the 50(v/v)% pH 10.06 buffer–Me_2SO, however, the reaction rate was increased only slightly. This can be understood as follows: BzPVP accumulates the reactants in its domain similarly as in the pH 10.06 buffer. Me_2SO, which accelerated the reaction rate in the absence of polyelectrolyte, solvates the cationic polyions (as will be discussed below) in such a way that it does not so strongly