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On the Gelation Rates of Thermoreversible Poly(vinylidene fluoride) Gels

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ABSTRACT: The gelation rates of poly(vinylidene fluoride) (PVF_2) gels have been measured for three commercial samples each in two different solvents at different polymer concentrations and also at different temperatures. The rate has been expressed as a combination of temperature-dependent function $f(T)$ and concentration-dependent function $(\phi)^n$; ϕ is the reduced overlapping concentration of the polymer chains. ϕ has a resemblance with the $P - P_c$ term of percolation theory, P being the conversion factor and P_c its critical value. Exponent n has been measured from double logarithmic plots of t_{gel}^{-1} and ϕ, and it lies between 0.45 and 0.6 which is closer to percolation exponent β (0.45) of a three-dimensional lattice. This indicates that three-dimensional percolation is a suitable model for this thermoreversible gelation process. The temperature-dependent function of the gelation rate has been found to be analogous to the temperature-dependent function of the nucleation rate of crystalline polymers in dilute solutions. There is some dependency of the gelation rate on the amount of H−H defect ($-CF_2CF_2-$) structures present in the polymers and also on the molecular weight of the samples. Solvents also have a significant influence on the gelation rate of the polymer: the poorer the solvent, the faster is the gelation rate. The critical gelation concentration ($C_{t=\alpha}^*$) measured from gelation kinetics by an extrapolation procedure increases with temperature in each case. Thermodynamic analysis of the variation of $C_{t=\alpha}^*$ with temperature reveals that about three to six crystallites (depending on the solvent and sample) are involved to produce a single crosslink in the gel.

Introduction

Thermoreversible polymer gels are a continuous network of polymer chains crosslinked by physical junctions through various types of processes.[1] For amorphous polymers liquid−liquid phase separation and/or liquid−liquid phase separation arrested by vitrification play the major roles. In the case of crystalline polymers apart from the above two processes, crystallites, a folded chain, or a fringed micelle act as points of physical junctions. Sometimes the gelation is also accompanied by conformational changes of the chains.[2] Thus, gelation of crystalline polymers is more complex than that of amorphous polymers, and its true nature depends on the chain structure of the polymer, on its molecular weight, and also on the solvent. In this paper these aspects of polymer gelation have been delineated from gelation rate measurements.

The choice of poly(vinylidene fluoride) (PVF_2) to study the above objectives in this work is 2-fold. First, it is a technologically important polymer because of its piezo- and pyroelectric properties.[3] No gelation study of this polymer is reported except the very recent one by Cho et al.[4] in a γ-butyrolactone solution. Second, this polymer is available commercially with different chain structures,[5] because PVF_2 is not completely isoregic with all head-to-tail ($-CF_2CH_2-$) addition.[6] It has some syndioregic structure with occasional head-to-head ($-CF_2CF_2-$) and tail-to-tail ($-CH_2CH_2-$) linkages which are usually referred to as the head-to-head (H−H) defect structure. One of the objectives of this work is to study the influence of H−H defects of PVF_2 on the gelation rate of PVF_2.

Due to the complex nature of the gelation process, it is very difficult to find a simple relation of the gelation rate complying with all the physical processes as mentioned above. Recently, Ohkura et al.[7] expressed the gelation rate (t_{gel}^{-1}) as a combination of two factors: (i) temperature-dependent factor $f(T)$ and (ii) concentration-dependent factor ϕ^2. The exponent "2" of ϕ in their expression was attributed to the bimolecular nature of the crosslinking process between the overlapping polymer segments during gelation. But it is very difficult to believe that gelation is a bimolecular process because, if one considers gelation simply as a classical tree model (e.g., Bethe lattice) of Flory[8] and Stockmayer,[9] it should be presented as a chain reaction.[10] Recently, gelation has been considered as percolation in a three-dimensional lattice.[10,11] In this paper we want to apply the relations of percolation theory to explain the gelation rates.

Table 1. Characteristics of the Samples Used

sample	source	$\overline{M}_n \times 10^{-5}$	$\overline{M}_v \times 10^{-5}$	$\overline{M}_w \times 10^{-5}$	PDI	H−H−defect (mol %)
Sol-10	Solvey Corp.	2.14	3.96	4.48	2.09	4.19
Sol-12	Solvey Corp.	3.01	6.27	7.74	2.57	4.06
KY-201	Pennwalt Corp.	3.12	6.71	8.81	2.82	5.31

Experimental Section

Materials. Unfractionated commercial samples were used in this work. The characteristics of the PVF_2 samples used here are presented in Table 1. From the table it is clear that Sol-10 and Sol-12 PVF_2 samples have almost the same amount of H−H defects but have different molecular weights. The Sol-12 and KY-201 have almost the same molecular weight but have different head-to-head defect concentrations. The head-to-head defects were measured from ^{19}F NMR spectroscopy in an *N,N*-DMF-d_7 solution.[12] The samples were recrystallized from dilute solutions of acetophenone, repeatedly washed with methanol, and dried in vacuum at 80 °C for 3 days. The viscosity-average ($\overline{M}_v$) molecular weights were determined from intrinsic viscosity measurements in *N,N*-dimethylacetamide at 25 °C, and the number-average ($\overline{M}_n$) and weight-average ($\overline{M}_w$) molecular weights were determined from gel permeation chromatography (Waters) using a μ-Styragel col-

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umn in *N*,*N*-dimethylformamide at 90 °C. Polystyrene samples were used as standards.

The solvents acetophenone (E. Merck) and ethyl benzoate (E. Merck) were dried over $CaCl_2$ and fractionally distilled before use in the gelation study.

Gelation Rate. Appropriate amounts of polymer and solvent were taken in glass tubes (1 cm i.d.). The tubes were degassed by a repeated freeze–thaw method and sealed under vacuum (10^{-3} mmHg). Polymer concentrations varying from 0 to 9% (w/v) were used for each sample. The tubes were initially kept in an air oven at 175 ± 2 °C for about 20 min to make the system homogeneous. They were then quickly transferred into a silicon oil bath kept at a predetermined temperature controlled within ±0.1 °C. The gelation times were visually measured by observing cessation of the liquid flow inside the tube when it was tilted. The time (t_{gel}) was monitored just after the tube was placed into the thermostatic bath. The reciprocals of the gelation times were referred to as the gelation rates. If the tubes of the Sol-10 and Sol-12 samples were melted at ≤150 °C, solution crystals with partial gelation were observed, but when they were melted at 175 °C, complete gelation under identical conditions was observed.

Dissolution temperatures used for temperature coefficient analysis of kinetic data and for measurement of polymer–solvent interaction were determined using annealed crystals (for 10 days) at ~5 °C below the melting temperatures measured in a differential scanning calorimeter at a heating rate of 10 °C/min. Appropriate amounts of polymer and solvent were encapsulated in glass tubes as stated earlier and were heated slowly from 100 °C at a rate of 1 °C/h until a homogeneous solution was produced. The temperatures were recorded as dissolution temperatures.

The X-ray diffractograms of the dried gels were taken from a Philips wide-angle X-ray diffractometer (PW 1710) with Cu Kα radiation.

Results

The critical gelation concentration (C^*) is the concentration of polymer below which gelation does not occur, and it is an important parameter to analyze the gelation rate. The C^* values can be experimentally measured by different procedures.[7,13,14] Here, we have measured it from the plots of t_{gel}^{-1} vs polymer concentration by extrapolation of each curve to zero gelation rate. Parts a–c of Figure 1 show the nature of such plots for KY-201/acetophenone, Sol-12/acetophenone, and Sol-12/ethyl benzoate systems, respectively. The critical concentrations determined in this way have been designated as $C_{t=\alpha}^*$ following the previous workers.[7] It is apparent from the figures that $C_{t=\alpha}^*$ varies with temperature. In Figure 2 the variation of $C_{t=\alpha}^*$ with temperature has been shown for both the solvents. With an increase in temperature $C_{t=\alpha}^*$ increases for all the samples in both the solvents, and a similar variation[14] was observed earlier for polyethylene gels. It is also clear from the figure that at a particular temperature $C_{t=\alpha}^*$ depends on the solvent. As, for example, at 65 °C, the $C_{t=\alpha}^*$ of Sol-12 in ethyl benzoate is 0.76 g/dL, while that in acetophenone is 1.6 g/dL. A similar trend is observed at other temperatures also. Such a solvent dependency of $C_{t=\alpha}^*$ is possibly due to the different solvent powers of each solvent. The dissolution temperature at each volume fraction of KY-201 PVF_2 in ethyl benzoate is higher compared to those in acetophenone, and the polymer–solvent interaction parameter determined from melting point depression has been found to be 0.09 for acetophenone and 0.31 for ethyl benzoate.[15] It may, therefore, be surmised that in poorer solvents the critical concentration required for gelation is lower than that in good solvents. The gels produced in both the solvents for each sample are turbid at all temperatures, and this indicates that crystallites are involved in the gelation process. This is also confirmed from the X-ray

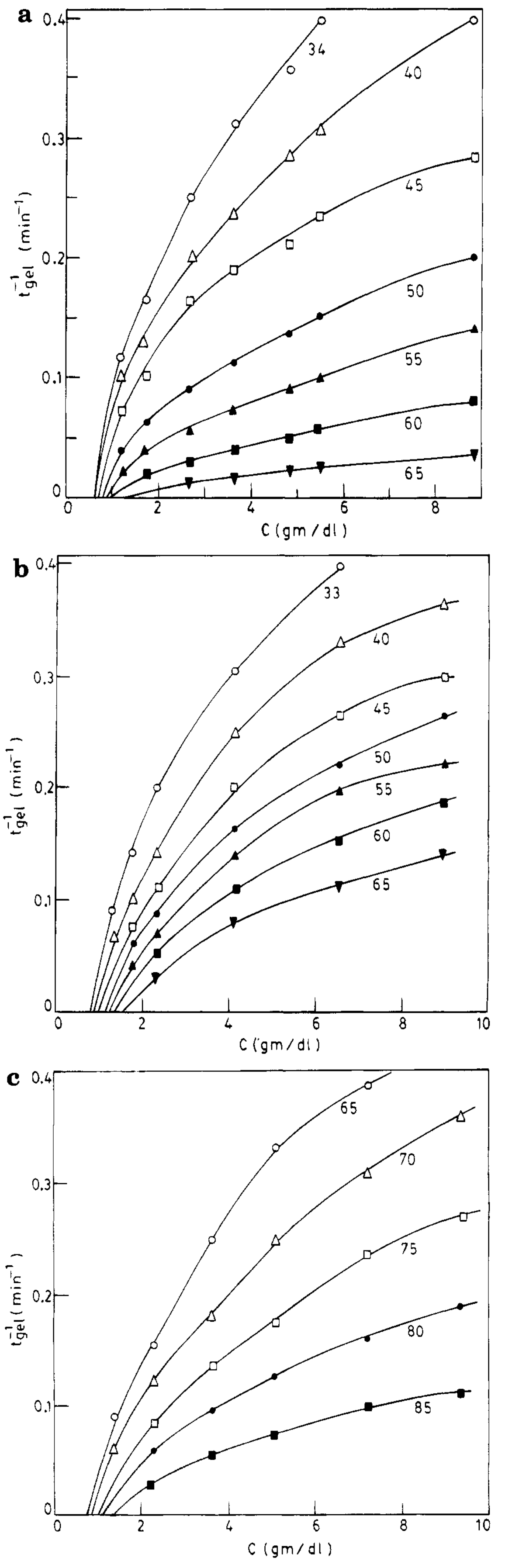

Figure 1. (a) t_{gel}^{-1} vs concentration plot of KY-201 PVF_2 in acetophenone at indicated temperatures (°C). (b) t_{gel}^{-1} vs concentration plot of Sol-12 PVF_2 in acetophenone at indicated temperatures (°C). (c) t_{gel}^{-1} vs concentration plot of Sol-12 in ethyl benzoate at indicated temperatures (°C).

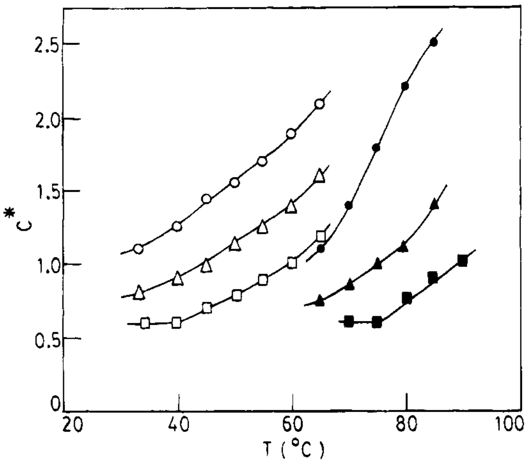

Figure 2. Variation of $C_{t=\alpha}^*$ with temperature: (○) KY-201 in acetophenone; (△) Sol-10 in acetophenone; (□) Sol-12 in acetophenone; (●) KY-201 in ethyl benzoate; (▲) Sol-10 in ethyl benzoate; (■) Sol-12 in ethyl benzoate.

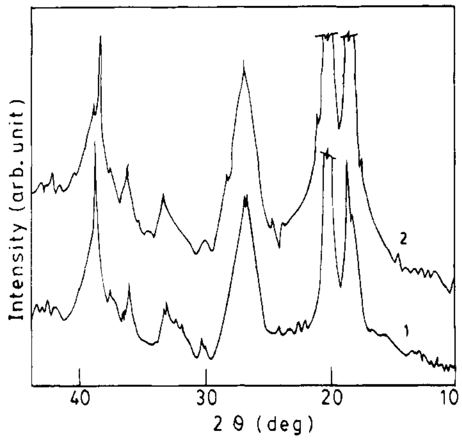

Figure 3. X-ray diffractograms of dried gels of PVF$_2$ from acetophenone: (1) Sol-12; (2) KY-201.

diffraction patterns of dried gels in Figure 3. Clearly these diffractograms correspond to the α crystallites produced in these gels.[16] In poor solvents crystallite formation of the chains is much easier than in the good solvents. This causes lower $C_{t=\alpha}^*$ values in poorer solvents. In good solvents an increased concentration of the polymer increases the undercooling at the same temperature, and this favors the crystallite formation required for a three-dimensional crosslink to produce gels. The increase of $C_{t=\alpha}^*$ values with temperature of each sample in the solvents may be due to the decrease of undercooling with an increase of temperature.

Eldridge and Ferry[17] proposed a relationship between the polymer concentration (C) and the gelation (or melting) temperature (T) as

$$\log C = \Delta H^0/2.303RT + \text{constant} \qquad (1)$$

where ΔH^0 is the heat of reaction to produce 1 mol of cross-links. In the approximation that this relation is valid at the critical gelation concentration ($C_{t=\alpha}^*$), plots of log $C_{t=\alpha}^*$ vs $1/T$ have been made with data of Figure 2 and are presented in Figure 4. It is apparent from the figure that the data fit well in a straight line for each case, and this also supports the theory that the critical gelation concentration ($C_{t=\alpha}^*$) is a temperature-dependent parameter. The ΔH^0 values have been calculated from the least-square slopes of the above plots and are presented in Table 2. It is clear from the table that ΔH^0 values in ethyl benzoate are higher than those in acetophenone and all these data are much higher than the literature reported value of 12.47 kJ/mol in γ-butyrolactone.[4] The ΔH^0 values are, therefore, solvent dependent as observed earlier for atactic polystyrene, though no definite trend in the variation of ΔH^0 with the polymer–solvent interaction parameter was noted.[18] It is now pertinent to compare the enthalpy of fusion (ΔH_u^0) of pure PVF$_2$ with the ΔH^0 values. The reported values of ΔH_u^0 are 6.69[19] and 5.95 kJ/mol[20] for two different samples of PVF$_2$ by two different groups of workers. The values are much lower than the ΔH^0 values of Table 2. Since crystallites act as primary points of physical junction in these gelation processes, as stated earlier, it may, therefore, be argued that about three to six crystallites (depending on the solvent and sample) are involved in producing a single crosslink in the gel. This junction size is not similar to the size of the critical nucleus of the nucleation process. The former represents the size of a crosslink in the gel, and the later represents the minimum size of a nucleus above which it grows thermodynamically.

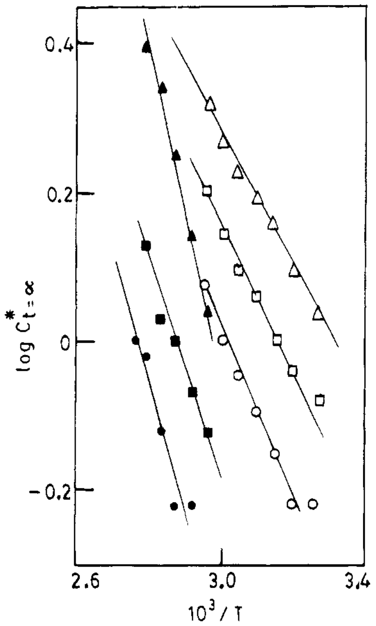

Figure 4. Plot of log $C_{t=\alpha}^*$ vs $1/T$ of PVF$_2$ gels: (○) KY-201 in acetophenone; (△) Sol-10 in acetophenone; (□) Sol-12 in acetophenone; (●) KY-201 in ethyl benzoate; (▲) Sol-10 in ethyl benzoate; (■) Sol-12 in ethyl benzoate.

Table 2. ΔH^0 (in kJ/mol) Values of PVF$_2$ Samples in Acetophenone and Ethyl Benzoate Gels

solvent	Sol-10	Sol-12	KY-201
acetophenone	17.4	18.2	20.1
ethyl benzoate	42.4	28.4	29.7

Parts a and b of Figure 1 compare the influence of H–H defects on the gelation rate of PVF$_2$, while parts b and c of 1 compare the gelation rate of PVF$_2$ (Sol-12) with the solvents. In the Sol-12/ethyl benzoate system the gelation at ambient temperature is so fast that gelation time cannot be measured with accuracy. A comparison of the gelation rates of PVF$_2$ for different amounts of head-to-head defect content samples and for different molecular weights is better presented in parts a and b of Figure 5 for both the solvents in a 4% (w/v) solution of PVF$_2$. The gelation rate of lower molecular weight Sol-10 is slower than that of the higher molecular weight Sol-12 sample at each temperature. The $C_{t=\alpha}^*$ of Sol-12 is lower than that of Sol-10, and thus gelation of Sol-12 occurs more rapidly at identical conditions. A comparison of the rate–temperature

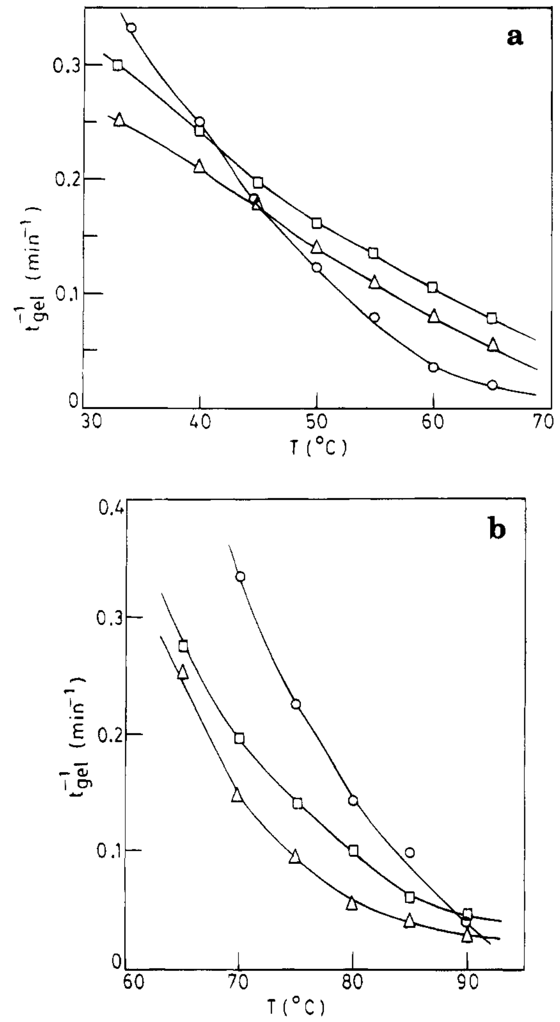

Figure 5. (a) t_{gel}^{-1} vs temperature plot of PVF$_2$ (4 g/dL) in acetophenone: (○) KY-201; (△) Sol-10; (□) Sol-12. (b) t_{gel}^{-1} vs temperature plot of PVF$_2$ (4 g/dL) in ethyl benzoate: (○) KY-201; (△) Sol-10; (□) Sol-12.

curves of KY-201 PVF$_2$ and Sol-12 PVF$_2$ reveals that at lower temperatures KY-201 has a higher rate than the lower defect content Sol-12 sample. But with an increase in temperature the situation becomes reversed for both the solvents. Such behavior is not common and might be due to both liquid–liquid and liquid–crystal phase separation involved in the gelation process. There is also evidence that PVF$_2$ gels by liquid–liquid phase separation.[4] Since KY-201 PVF$_2$ has a greater chain irregularity, liquid–liquid phase separation is more likely than the more regular Sol-12 PVF$_2$. Again as the solvent becomes poorer, the tendency of liquid–liquid phase separation increases.[8] In the acetophenone gels, therefore, the t_{gel}^{-1} temperature curve of KY-201 PVF$_2$ intersects that of Sol-12 PVF$_2$ at the very initial stage, while in ethyl benzoate (a poorer solvent than acetophenone) the crossing occurs almost at the end of the temperature scale studied here. The lower gelation rates at higher temperatures of KY-201 PVF$_2$ compared to those of the more regular Sol-12 PVF$_2$ are due to difficulty of crystallite formation of higher defect content KY-201 at those temperatures because of the lower undercooling of the higher defect content sample. The dissolution temperatures of KY-201 and Sol-12 PVF$_2$ in acetophenone are 120 and 130 °C, respectively, for 4% (w/v) composition.

Theoretical Development

Thermoreversible gelation is the formation of a three-dimensional physical network in the polymer solution through a crosslinking process. Like the process of chemical transformation it may be assumed that it (physical crosslinking) is passing through a potential energy barrier. According to the theories of chemical kinetics, the reaction rate is proportional to the fraction of molecules overcoming the activation energy barrier. Similarly gel fraction G, which is the ratio of the molecular content of a gel macromolecule to that of the total molecular content (gel macromolecule plus sol molecule), is proportional to the gelation rate expressed as t_{gel}^{-1}, t_{gel} being the gelation time. Thus, t_{gel}^{-1} α G.

From percolation theory[10,11] G α $(P - P_c)^\beta$ where P is the conversion factor (i.e., it is the ratio of the actual number of bonds at any given moment to the maximally possible number of such bonds in the three-dimensional lattice), P_c is the critical conversion factor required for gelation, and β is a critical exponent and has a value 0.45 for the three-dimensional lattice.[11] So,

$$t_{gel}^{-1} \propto (P - P_c)^\beta \propto \Delta p^\beta \tag{2}$$

where $\Delta p = P - P_c$.

It is now well-known that gelation rates of thermoreversible polymer gels depend on temperature and also on concentration. Thus following Ohkura et al.[7]

$$t_{gel}^{-1} \propto f(T)\, f\{C - C_{t=\alpha}^*(T)\}$$

where $C_{t=\alpha}^*(T)$ is the critical gelation concentration at a particular temperature and $C - C_{t=\alpha}^*(T)$ is the overlapping concentration at that temperature. To give a general character of the concentration function, it should be reduced by $C_{t=\alpha}^*(T)$, and an exponent n is introduced as $\{(C - C_{t=\alpha}^*(T))/C_{t=\alpha}^*(T)\}^n$, which may be replaced by ϕ^n, ϕ being the reduced overlapping concentration. ϕ is, therefore, a positive number, and multiplication of $f(T)$ with a number ϕ^n expresses the gelation rate at different temperatures for a given concentration of polymer.

Therefore,

$$t_{gel}^{-1} \propto f(T)\, \phi^n$$

and at a particular temperature

$$t_{gel}^{-1} \propto \phi^n \tag{3}$$

A comparison of eqs 2 and 3 can be done in the following way. If $C < C_{t=\alpha}^*(T)$ gelation is not favored but if $C/C_{t=\alpha}^*(T) > 1$, there is a finite rate of gelation. The reduced overlapping concentration $C - C_{t=\alpha}^*(T)/C_{t=\alpha}^*(T)$ is, therefore, analogous to $P - P_c$ of the percolation theory, because if $P < P_c$, no gelation takes place. Therefore, Δp of eq 2 is similar to ϕ of eq 3. A possible support may be arrived at if n has a value equal to β, i.e., 0.45, for percolation in the three-dimensional lattice.

The nature of $f(T)$ will now be evaluated considering that crystallites are primary points of physical junctions to produce a three-dimensional network. The gelation rate of this polymer is very much dependent on temperature and has a negative temperature coefficient. Since crystallites are major points of physical junctions, as evidenced from X-ray diffractograms of dried gels, the temperature coefficient of gelation may be related to that of nucleation of crystalline polymers in solution.

The nucleation rate at v_2 volume fraction of polymer in its solution is given by the expression[21]

$$N(v_2) = N_0 v_2 \exp\left[\frac{E_D(v_2) - \Delta F^*(v_2)}{kT}\right] \tag{4}$$

where N_0 is a preexponential factor, $E_D(v_2)$ is the activation energy of transport at v_2 volume fraction, and $\Delta F^*(v_2)$ is the free energy of formation of a nucleus at the same volume fraction. The $\Delta F^*(v_2)$ is given by the expression:[21]

$$\Delta F^*(v_2) = \frac{8\pi\sigma_u^2\sigma_e - 4\pi kT\sigma_u^2 \ln v_2}{(\Delta H_u^0 \Delta T)^2} T_m^2 \tag{5}$$

where ΔH_u^0 is the enthalpy of fusion (2.01×10^9 ergs/cm^3 for this polymer),[19] ΔT is the undercooling ($T_m - T$), T_m is the equilibrium melting temperatures of the crystal at that composition, and σ_u and σ_e are the lateral and end surface free energies of the crystal. At a low concentration of the polymer ($v_2 \leq 0.1$) the change in undercooling with crystallization at a fixed temperature is negligible because T_m is insensitive to the polymer concentration in this region. Further, in this dilute region v_2 does not necessarily represent the nominal concentration but rather the polymer concentration within the swollen coil.[21]

Discussion

The exponent n obtained from double-logarithmic plots of eq 3 has been discussed in the following part. For the sake of brevity only two such plots, e.g., KY-201/acetophenone and KY-201/ethyl benzoate, are presented in parts a and b of Figure 6, respectively. It is necessary to mention here that for the calculation of ϕ different $C_{t=\alpha}^*$ values at different temperatures are taken into account. From the figures it is clear that all the points at each temperature represent parallel straight lines for both solvents. The least-squares slopes of the straight lines are presented in Table 3. Averages of the data for all temperatures and the standard deviations are also presented. From the table it is clear that the n value varies from 0.45 to 0.61, and it is independent of the solvent–polymer sample and also of temperature. The values are quite different from that of Ohkura et al.[7] for poly(vinyl alcohol) gels in a dimethyl sulfoxide–water mixture (60:40) and are very close to the exponent β (=0.45) of percolation theory[11] for a three-dimensional lattice. From the Flory–Stockmayer theory β has a value of unity.[10,11] So the measured exponent values are closer to the percolation value, and this small discrepancy might be due to experiments not carried out extremely close to the gel point. This is because the gelation rate near the gel point is much slower and difficult to measure in a reasonable time period. Nonetheless, the exponent values clearly support that percolation in a three-dimensional lattice is a satisfactory model to explain the gelation rate of thermoreversible PVF$_2$ gels. However, it is necessary to mention here that gels produced by covalent bonds (thermoirreversible gels) usually obey the Flory–Stockmayer theory which is a special case of the percolation theory applied to the Bethe lattice.[10,11] Therefore, it may be concluded that percolation theory is a suitable tool for understanding both types of gels.

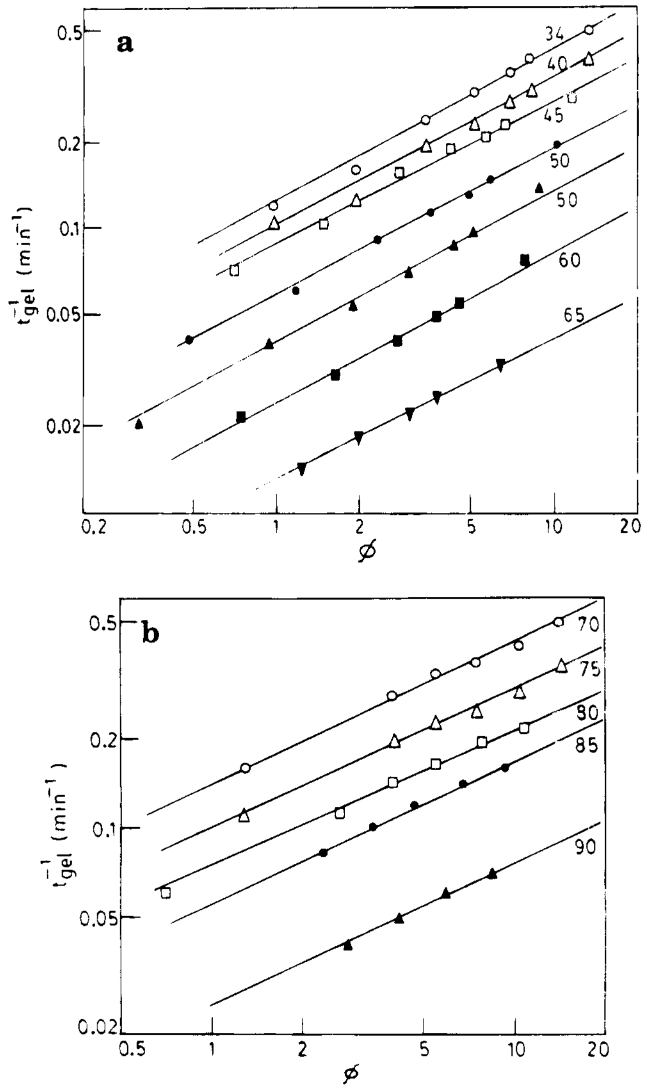

Figure 6. (a) log t_{gel}^{-1} vs log ϕ plots of KY-201 PVF$_2$ gels in acetophenone at indicated temperatures. (b) log t_{gel}^{-1} vs log ϕ plots of KY-201 PVF$_2$ gels in ethyl benzoate at indicated temperatures.

Table 3. Exponent n Values of PVF$_2$ Gels in the Solvents Determined from Least-Squares Slopes of Double-Logarithmic Plots of t_{gel}^{-1} and ϕ

gels in acetophenone				gels in ethyl benzoate			
temp (°C)	KY-201	Sol-10	Sol-12	temp (°C)	KY-201	Sol-10	Sol-12
34	0.56	0.48	0.59	65		0.56	0.60
40	0.53	0.57	0.58	70	0.45	0.60	0.61
45	0.50	0.50	0.59	75	0.46	0.61	0.58
50	0.53	0.51	0.58	80	0.49	0.58	0.59
55	0.57	0.54	0.60	85	0.46	0.56	0.61
60	0.55	0.51	0.58	90	0.55		
65	0.55	0.55	0.59				
av	0.54	0.52	0.58		0.48	0.58	0.59
st dev	0.02	0.03	0.01		0.03	0.02	0.02

To justify the nature of $f(T)$ as presented in eq 4, semilogarithmic plots have been made for t_{gel}^{-1} vs $T_m^2/T(\Delta T)^2$ like those in polymer–dilute solution systems.[21] The ΔT values are calculated from the equilibrium melting temperature at each composition. The plots are well fitted in straight lines as shown in the representative Figure 7 for a PVF$_2$–acetophenone system at 4% (w/v) composition. The straight line nature of the plots clearly suggests that the gelation rate is basically a nucleation-controlled process and the logarithmic term of $\Delta F^*(v_2)$ may be regarded as independent of T.[7] At a first approximation, equating the slope values to $8\pi\sigma_u^2\sigma_e/k\Delta H_u^{0\,2}$, $\sigma_u^2\sigma_e$ values are calculated and are presented in Table 4. The $\sigma_u^2\sigma_e$ values of PVF$_2$ from a melt are also presented in Table 4. The mean interfacial energies

Table 4. $\sigma_u^2\sigma_e$ Values (in erg^3 cm^{-6}) of PVF$_2$ Samples during Gelation in Various Solvents

		Sol-10			Sol-12			KY-201		
solvent	conc (% w/v)	T_m (°C)	$\sigma_u^2\sigma_e$	$\sigma_\pm$ (erg/cm^2)	T_m (°C)	$\sigma_u^2\sigma_e$	$\sigma_\pm$ (erg/cm^2)	T_m (°C)	$\sigma_u^2\sigma_e$	$\sigma_\pm$ (erg/cm^2)
acetophenone	4	129	576.8	8.1	130	571.7	8.1	120	760.6	8.9
	6	129	530.9	7.9	130	513.5	7.8	120	709.6	8.7
	9	130	520.7	7.9	131	505.3	7.8	121	689.1	8.6
ethyl	4	143	561.0	8.1	144	551.3	8.0	134	531.0	7.9
benzoate	6	143	501.8	7.8	144	504.3	7.8	134	460.0	7.5
	9	144	489.0	7.7	145	487.1	7.7	135	439.0	7.4
from melt	100				205	863.0[a]	9.3	178	305.0[b]	6.60

[a] From ref 22. [b] From analysis of the kinetic data[23] of KY-301 with T_m = 178 °C.[20]

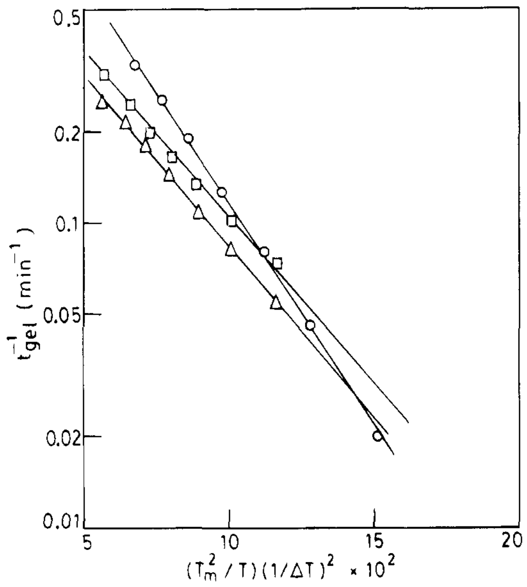

Figure 7. log t_{gel}^{-1} vs $(T_m^2/T)(1/\Delta T)^2$ plots of PVF$_2$ gels (4 g/dL) in acetophenone: (○) KY-201; (△) Sol-10; (□) Sol-12.

$\sigma_\pm = (\sigma_u^2\sigma_e)^{1/3}$ are also presented in the table, and the values, though lower than those determined by other methods,[23] appear to be reasonable in comparison with those of other polymers determined by this method.[21] There are two different values of $\sigma_u^2\sigma_e$ for two groups of workers obtained from melt crystallization of the polymer.[22,23] The $\sigma_u^2\sigma_e$ values calculated here from gelation rates are in between them and are, therefore, reasonable. This supports the theory that gelation is a nucleation-controlled process, with crystallites primarily acting as points of physical junction.

In conclusion, this paper attempts to explain the gelation rate of thermoreversible PVF$_2$ gels with the help of percolation theory in a three-dimensional lattice. The exponent of ϕ is found to be very close to the exponent β of percolation theory, and this signifies that thermoreversible PVF$_2$ gels can be well explained by the percolation theory. The higher the molecular weight of the PVF$_2$ sample, the higher is the gelation rate at a particular temperature, both in acetophenone and in ethyl benzoate. Head-to-head defects also influence the gelation rate, and it depends on the gelation temperature. Thermoreversible gelation shows negative temperature coefficients which are very similar to nucleation rates of crystalline polymers in dilute solution. The critical gelation concentration determined from kinetic data has both a temperature and solvent dependency. It increases with increasing solvent power and temperature. Thermodynamic treatment of these critical gelation concentrations with temperature reveals that about three to six crystallites (depending on the nature of the solvent and polymer samples) are involved in producing a single crosslink in the gel.

References and Notes

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