Diluent–Gel Point Relationships for the Reaction of Tetra-(β-carboxyethyl)-cyclohexanone with Diethylene Glycol

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In his basic investigation of gel points, Flory[2] found that the experimental values for the extent of reaction at which gelation occurred, the critical extent of reaction, were higher than the values predicted from his theoretical analyses for such systems. He ascribed the discrepancy to the small amount of intramolecular reaction which occurs, this reaction not contributing to the formation of infinite networks.

Stockmayer and Weil[3,4] have used the dilution principle as a means of excluding the error due to the intramolecular reaction. They reasoned that since the cyclization reaction assumes more importance at higher dilutions, a series of gel points obtained at increasing dilutions in an inert solvent should show ever increasing values for the extent of reaction at which gelation occurs. Using the system pentaerythritol–adipic acid and dimethoxytetraethylene glycol as the inert diluent, they plotted the extent of reaction at the gel point as a function of the volume of the system and found the observed points to fall on a straight line which when extrapolated to zero volume, a so-called "infinite concentration," gave a value for the critical extent of reaction equal to 0.578 in excellent agreement with the predicted value of 0.577. This then appears to be a device for eliminating the error due to cyclization reactions.

During the course of some work on polyesters, we had occasion to use this same technique on the system tetra-(β-carboxyethyl)-cyclohexanone[5] and diethylene glycol,[6] and using dimethoxytetraethylene glycol[7] as the diluent. The data of Table I were obtained by use of the falling sphere method for observing the gel point and by titrating unreacted carboxyl groups to follow the extent of reaction. The values for the critical extent of reaction, Flory's[3] p_c, were plotted as a function of the volume of the system. The points were found to fall on a straight line, enabling extrapolation to zero volume, the intercept giving a value for p_c of 0.585 as compared with the calculated value of 0.577 from the Flory equation.

TABLE I

POLYCONDENSATION OF EQUIVALENT QUANTITIES OF TETRA-(β-CARBOXYETHYL)-CYCLOHEXANONE AND DIETHYLENE GLYCOL AT 110.8° USING DIMETHOXYTETRAETHYLENE GLYCOL AS SOLVENT[a]

Solvent, %	V/V_0[b, c]	p_c	Solvent, %	V/V_0[b, c]	p_c
19.8	1.25	0.642	70.7	3.41	0.745
47.9	1.92	.675	76.0	4.16	.774
57.5	2.35	.691	79.4	4.80	.796
70.7	3.41	.743			

[a] All reactions catalyzed by *p*-toluenesulfonic acid. [b] V/V_0 = volume of polymer + solvent/volume of polymer. [c] Specific volume of equivalent quantities of tetra-(β-carboxyethyl)-cyclohexanone and diethylene glycol = 0.837 cc./g.; specific volume of dimethoxytetraethylene glycol = 1.071 cc./g.

The critical extent of reaction should be independent of temperature and values of $p_c = 0.585$ at 110.8° and p_c 0.582 at 136° bear this out.

We looked for a possible effect on the value for the gel point caused by the degree of coiling and uncoiling of the polyester molecule being formed. It might be expected that the tightly coiled molecules found in poor solvents would participate in relatively more intramolecular reaction than extended chains found in good solvents. Acetophenone was chosen as the second solvent and at 110.8° it is a poorer solvent for the polyester than is dimethoxytetraethylene glycol. Duplicate experiments at comparable dilutions gave p_c values of 0.738 and 0.740 for acetophenone and 0.743 and 0.745 for dimethoxytetraethylene glycol.

The divergence in the above values for p_c in the two solvents appears to fall within the limit of experimental error involved in determining the points. It should be noted that although acetophenone is a poorer solvent for the polyester than is dimethoxytetraethylene glycol, there is considerable doubt as to whether it can be classified as a solvent poor enough to lead to the tightly coiled molecules we were after.

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(1) The material presented was taken from the M.S. thesis of I. Miller, 1952.

(2) P. J. Flory, THIS JOURNAL, **63**, 3083 (1941).

(3) W. H. Stockmayer, "Advancing Fronts in Chemistry," Reinhold Publ. Corp., New York, N. Y., 1945, p. 61.

(4) L. L. Weil, doctoral dissertation, Columbia University, 1945.

(5) Prepared according to H. A. Bruson and T. W. Riener, THIS JOURNAL, **64**, 2850 (1942).

(6) Distilled Eastman Kodak Co. product.

(7) Supplied by Ansul Chemical Co. and distilled from sodium, b.p. 132-133° (3 mm.).