Effective Functionality and Intramolecular Reactions of Polyisocyanates and Polyols[1]

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ABSTRACT: A gel point bracketing method has been developed for the determination of the weighted average functionality ("effective functionality") of reactants involved in polycondensation reactions. Its principle lies in the coincidence of gel point and completion of reaction, where the ratio of the reactants is not stoichiometric. With this method, Stockmayer's gel equation is applicable to reactants containing arbitrary distribution of functional groups of equal or unequal reactivity. For a given polycondensation system, the effect of dilution on the gel point is in excellent agreement with a modified gel equation which accounts for intramolecular reactions. Furthermore, it is shown that the extent of intramolecular reactions depends both on dilution and on the effective functionality. Explicit relations have been obtained which allow the calculation of the extent of intramolecular reactions. It is concluded that cyclization in polyol–polyisocyanate systems is negligibly small, over a large range of concentrations, when the functionality of both reactants approaches the value of two.

The Flory–Stockmayer polycondensation theory[2] for complex, branched reactants predicts the extent of reaction at which weight average properties of the product, such as the weight average molecular weight, become infinitely large. This critical reaction extent is defined as the gel point. The so-called Stockmayer gel equation resulting from this theory is shown below for an AB-type polycondensation, a reaction where groups of type A can react only with groups of type B

$$(P_AP_B)_{gel} = (f_e - 1)^{-1}(g_e - 1)^{-1} \tag{1}$$

where P_A and P_B refer to the respective fractions of groups A and B reacted and f_e and g_e are the weighted average functionalities (referred to as effective functionalities) of reactants A and B, respectively, defined as

$$f_e = \sum_i i^2A_i / \sum_i iA_i \tag{2a}$$

and

$$g_e = \sum_j j^2B_j / \sum_j jB_j \tag{2b}$$

Here A_i is the number of moles of reactant A bearing i-functional groups and B_j is the number of moles of reactant B bearing j-functional groups.

Stockmayer's gel equation is useful for the prediction of gel point or for the determination of effective functionality, provided three basic assumptions of the gel equation are met, *viz.*, equal reactivity of like groups and absence of cyclization and of side reactions. For certain systems, such as carboxy-terminated polybutadiene–polyol reactions, these assumptions appear to be fulfilled, as has been shown recently by Strecker and French.[3] In the case of polyisocyanates, which are materials of particular interest to us, the basic requirements of Stockmayer's gel equation cannot usually be met, mainly because of the frequent occurrence of like groups of unequal reactivity and the need for relatively dilute systems to detect the gel point. It will be shown below, however, that a useful form of Stockmayer's gel equation can be retained for the calculation of the true effective functionality of such reactants by using a relatively simple gel point method based on complete reactions.

Gel Equations for Complete Reactions. Effect of Functional Groups of Unequal Reactivity. When a polycondensation reaction is allowed to proceed to completion under nonstoichiometric conditions, for example groups of type A being in excess, P_A is equal to the initial mole ratio of B to A groups, and $P_B = 1$. Thus, there will be a critical initial ratio of the reactive groups for which gelation will coincide with the completion of the reaction. Stockmayer's gel equation, eq 1, simplifies then to the following form

$$(P_A)_{gel} = (f_e - 1)^{-1}(g_e - 1)^{-1} \tag{3}$$

where $(P_A)_{gel}$ is the critical initial ratio of B to A groups. The corresponding equation for the converse case (B groups in excess) is

$$(P_B)_{gel} = (f_e - 1)^{-1}(g_e - 1)^{-1} \tag{4}$$

A particularly useful feature of these equations is their applicability to like groups of unequal reactivity, provided such groups are used in stoichiometric deficiency. The condition of equal reactivity, however, is still required for functional groups present in stoichiometric excess. The correctness of these statements is intuitively obvious but can be proved rigorously through the application of gelation theory to such systems as shown in the Appendix I. In theory, therefore, eq 3 and 4 are applicable for the determination of the effective functionality of reactants containing any distribution of functional groups and their reactivities.

Effect of Dilution. For the case of complete reaction with equally reactive B groups used in excess, eq II-9 of Appendix II becomes

$$(P_B)_{gel} = (1 - k/c)^{-1}(f_e - 1)^{-1}(g_e - 1)^{-1} \tag{5}$$

where

$$k = 1.341Bm/A \tag{5a}$$

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[1] Paper presented in part at the 156th National Meeting of the American Chemical Society, Polymer Division, Atlantic City, N. J., 1968. This is Contribution No. 195 from the Elastomers Research Laboratories.

[2] W. H. Stockmayer, *J. Polym. Sci.*, **9**, 69 (1952).

[3] R. A. H. Strecker and D. M. French, *J. Appl. Polym. Sci.*, **12**, 1697 (1968).

and

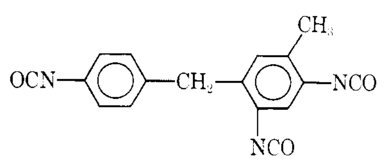
$$B = [3/(2\pi\nu)]^{3/2}/2b^3 \tag{5b}$$

c is the concentration of reactive groups of one of the reactants in moles per (m) liter, A is a parameter of the reaction conditions, ν is the number of chain atoms per unit (where a unit contains two functional groups of each type), and b is the effective bond length.

Experimental verification of the validity of eq 5 and the effect of varying functionalities of the reactants on the parameter k will be discussed later.

Experimental Section

Materials. Poly(tetramethylene ether) glycol of molecular weight of 1000 PTMEG-1000) was used as the polyol of known functionality for the determination of the effective functionality of polyisocyanates. Various developmental as well as commercially available polyisocyanates were used for this investigation. With the exception of polymethylenepoly-(phenyl isocyanate) (PAPI) and the pure triisocyanate (I),[4]



I

the polyisocyanates were special grades of Du Pont's toluene diisocyanates used in the production of foams and coatings. The isocyanate content of the polyisocyanates was determined by reacting a sample with an excess of 0.1 N dibutylamine and back-titrating with 0.1 N HCl in the presence of bromophenol blue.[5a]

Freshly distilled toluene diisocyanate (Du Pont "Hylene" TM, an 80/20 mixture of 2,4/2,6-toluene diisocyanate) and/or methylenebis(4,4′-cyclohexyl isocyanate) (Du Pont "Hylene" W) were employed for the determination of the effective functionality of several commercial polyols used for flexible polyurethan foams. The equivalent weight of polyols was determined by known esterification methods.[5b] The water content of polyols (including PTMEG) was maintained at 70–300 ppm by drying the polyols *in vacuo* at 100° for 24 hr and storing the dried materials over molecular sieve (Linde Molecular Sieve, Type 5A). The molecular weight of the polyols was determined cryoscopically in benzene.

Anhydrous tetrahydrofuran (THF) was used for the preparation of stock solutions of the reagents and for the reactions.

Gel Point Method. Stock solutions of reactants of known and unknown functionality, and of catalyst (dibutyltin dilaurate) were prepared in anhydrous THF. A series of reaction mixtures of varying ratios of the reactive groups were then prepared in 2-oz bottles. A predetermined amount of anhydrous THF was added prior to the reaction to obtain the desired concentration of reactants. The reactions were allowed to proceed to completion under agitation and the gel point was determined from visual inspection of the reactant mixtures. At moderate concentrations of polyols (0.5 mol of hydroxyl groups/1000 ml), the abrupt change from liquid to gel could be easily detected for a reactant ratio interval of 0.02 and even lower. At higher concentrations (1 mol of OH groups/1000 ml), the high viscosity of the system raised the ratio interval to 0.04, but the precision was easily improved by diluting the system after the reaction. The gel point was defined as the initial reactant ratio intermediate between the gelling and nongelling ratios. Completion of the main reaction was confirmed in preliminary studies by ir absorption at 4.4 μ. Furthermore, in order to ascertain the absence of subsequent side reactions, all critical reaction mixtures were stored for at least 1 month. No change in gel point was observed in all cases.

TABLE I

TYPICAL PREPARATION OF MATERIALS FOR THE DETERMINATION OF GEL POINT AT 0.5 *M* HYDROXYL CONCENTRATION. REACTION MIXTURE OF VARIOUS REACTANT RATIOS (P_B)[a]

P_B	Solvent, ml	Stock solutions,[b] ml a	b	c
0.98	10.5	6.12	2.0	1.0
0.96	10.8	6.25	2.0	1.0
0.94	11.1	6.38	2.0	1.0

[a] Solvent, tetrahydrofuran stored over sodium. [b] Stock solutions: (a) diol of mol wt ~ 1000 (*e.g.*, PTMEG-1000), 0.160 mol of OH/100 ml; (b) polyisocyanate (any f_e), 0.48 mol of NCO/100 ml; (c) dibutyltin dilaurate (T-12), 2–20 g/100 ml.

The concentration of the catalyst was chosen such that the slowest reaction, *viz.*, the reaction between secondary hydroxyl groups and alicyclic isocyanates, could be completed in less than 6 hr. Since no attention is required during the reaction, any convenient time span can be selected for the gelation experiments by a suitable adjustment of the catalyst concentration.

All stock solutions were stored over Linde Molecular Sieve, Type 5A. This material was used also for the gelation experiments in order to eliminate the effect of an accidental pick-up of moisture. No effect of molecular sieve on the gel point was observed in preliminary experiments.

Table I illustrates a typical preparation of reactants for the determination of polyisocyanate functionality.

In all subsequent discussions, the symbols A and B will refer to isocyanate and hydroxyl groups, respectively.

Results and Discussion

Effective Functionality of Polyisocyanates. The experimental procedure consisted of reacting a polyisocyanate of unknown functionality with a stoichiometric excess of the diol (PTMEG-1000). Since both hydroxyl groups in the diol are well separated, the plausible assumption was made that all available hydroxyl groups have identical reactivity irrespective of the extent of reaction. Therefore, eq 5 is applicable for any reactivity ratio of the isocyanate groups, which are used in deficiency. Since $g_e = 2$ for these systems, eq 5 assumes the simple form

$$(P_B)_{gel} = (1 - k/c)^{-1}(f_e - 1)^{-1} \tag{6}$$

It is convenient at this stage to introduce the term "apparent effective functionality," f_e', defined by the relation

$$(P_B)_{gel} = (f_e' - 1)^{-1} \tag{7}$$

Substitution of eq 7 into eq 6 yields the following equation after suitable rearrangement

$$f_e' = -\frac{k(f_e - 1)}{c} + f_e \equiv \frac{\phi(f_e)}{c} + f_e \tag{8}$$

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(4) Prepared by Dr. G. K. Hoeschele, Du Pont Elastomer Chemicals Department.

(5) (a) J. H. Saunders and K. C. Frisch, "Polyurethanes, Chemistry and Technology," Vol. 1, Interscience Publishers, New York, N. Y., 1962, p 29. (b) ASTM Method D 1638-61T.

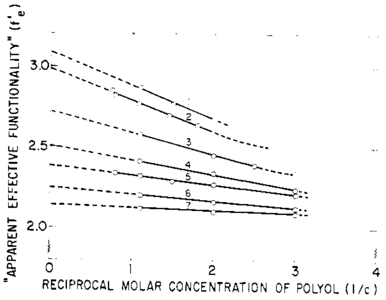

Figure 1. Effect of concentration on the gel point in the diol–polyisocyanate system: curve 1, polymethylenepoly(phenyl isocyanate) (PAPI); curve 2, 2,4,4′-triisocyanato-5-methyldiphenylmethane; curves 3–7, Du Pont's special grades of polyisocyanates.

Therefore, a plot of f_e' (calculated from gel point data according to eq 7) against reciprocal of the concentration should be linear for a given polyisocyanate–diol system, if experimental data fit the theory. This is indeed the case as illustrated in Figure 1 for seven polyisocyanate–diol systems. For values above a minimum concentration, the plots are linear, as predicted from eq 8. Assuming that the linearity is maintained up to the hypothetical infinite concentration ($1/c = 0$), the extrapolated data should, according to eq 8, yield the true effective functionality, f_e. The correctness of such extrapolation is well demonstrated by the fact that the extrapolated value for the pure triisocyanate (Figure 1) is 2.98 in excellent agreement with the predicted value of 3.00.

In order to assess the parameter k of eq 8, the slopes, $-\phi(f_e)$, of Figure 1, have been plotted against f_e. The plot shown in Figure 2 is linear and obeys the empirical relation

$$-\phi(f_e) = k_1 f_e - k_2 = 0.205 f_e - 0.424 \qquad (9)$$

Replacing $\phi(f_e)$ with $k(f_e - 1)$ gives the relation

$$k = (k_1 f_e - k_2)/(f_e - 1) = (0.205 f_e - 0.424)/(f_e - 1) \qquad (10)$$

Since the presently theoretically indeterminable parameter A is related to k through eq 5a, the dependence of A on the functionality of the polyisocyanates in the polyisocyanate–diol systems can be expressed as

$$A = 1.341 B\mathrm{m}/k = 1.341 B\mathrm{m}(f_e - 1)/(0.205 f_e - 0.424) \qquad (11)$$

The dependence of the reaction parameter A on the functionality of the polyisocyanates is possibly due to the reaction conditions (nonstoichiometric gelation). The reaction parameter A appears to be independent of functionality for selected polyester and polyalkoxysilane gel systems prepared from stoichiometrically equivalent reactants.[6] This point, however, is not firmly established, since the gel data available from literature indicate a rather serious scatter of experimental results.[6]

The molecular significance of the parameter B has been tentatively confirmed by replacing 1000 mol wt diol (PTMEG-1000) with 2000 mol wt diol (PTMEG-2000) for the pure triisocyanate system. As expected, the data extrapolate to similar f_e (Figure 3). Furthermore, the slope ϕ for PTMEG-1000 (ϕ_1) is about 2.3 times larger as compared to the slope for PTMEG-2000 (ϕ_2). It follows from eq 5a and the definitions of ϕ (eq 8) and of B (eq 5b) that

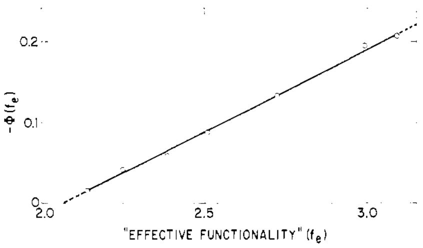

Figure 2. Dependence of $\phi(f_e)$ on effective functionality of polyisocyanates.

$$\phi_1/\phi_2 = (\nu_2 b_2^2/\nu_1 b_1^2)^{3/2} \approx (\nu_2/\nu_1)^{3/2} \qquad (12)$$

Since ν denotes the number of chain atoms per each unit, the theoretical ratio is 2.58 assigning to each unit (containing two groups of each type) ten atoms from the aromatic isocyanate and 140 and 70 atoms, respectively, from PTMEG-2000 and 1000. This is in reasonable agreement with the experimental slope ratio of 2.3.

Assuming that ϕ_2 follows a similar functional relation as ϕ (eq 9), the following is obtained for PTMEG-2000–polyisocyanate systems

$$\phi_2 = \phi_1/2.3 = (k_1 f_e - k_2)/2.3 = 0.089 f_e - 0.185 \qquad (9a)$$

The data for various polyols, to be discussed later, support the correctness of such an assumption.

An interesting aspect of the empirical relation expressed by eq 9 is that the constant k_2 is approximately twice as high as k_1. Thus, eq 9 can be expressed to a good approximation in terms of one constant only, *viz.*

$$-\phi(f_e) = k_1(f_e - 2) \qquad (13)$$

This relation implies that, at least for this diol, intramolecular reactions are absent, or negligibly small, when the functionality of the polyisocyanate approaches the value of two. It is also illuminating to obtain some numerical data on the extent of intramolecular reactions at the gel point for various diol–polyisocyanate systems from relations derived below.

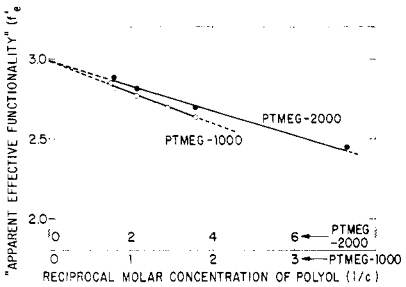

Figure 3. Effect of molecular weight of diol on $f_e' - 1/c$ relation.

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(6) (a) F. P. Price, J. H. Gibbs, and B. H. Zimm, *J. Phys. Chem.*, **62**, 972 (1958); (b) F. P. Price, *ibid.*, **62**, 977 (1958).

Table II
Extent of Cyclization in
Ptmeg-1000–Polyisocyanate Systems

Molar concentration of hydroxyl groups of PTMEG-1000	Mole % of NCO reacted intramolecularly Effective functionality 2.15	2.5	3.0
0.9	0.81	3.33	5.45
0.5	1.47	6.09	10.1
0.3	2.46	10.4	<17.4

Define ρ_c as the fraction of intramolecularly reacted species present in deficiency. It follows from gel theory that

$$(P_B)_{gel}(1 - \rho_c)^2 = (f_e - 1)^{-1} \tag{14}$$

Now substitution of eq 14 into eq 8 and 9 yields

$$\rho_c = 1 - \{1 - (0.205f_e - 0.424)/(f_e - 1)c\}^{1/2} \tag{15}$$

The extent of intramolecular reaction calculated from eq 15 is shown in Table II for selected values of functionality and concentration of PTMEG-1000–polyisocyanate systems. Equation 15 is, of course, valid only for the range of concentrations, in which f_e' is linear with respect to $1/c$ (Figure 1).

Before closing the subject of polyisocyanate functionality, it should be pointed out that the validity of the gel equation (8) for various reactivities of polyisocyanates has been confirmed in the course of this study. In one case, a poly(oxypropylene)polyol ("Voranol" CP-3000, equiv wt 1000) has been treated with symmetric ("Hylene" W) and asymmetric ("Hylene" TM) diisocyanates, respectively. As shown in Figure 4 (curve 2), the gel point data for both reactants agree very well. Furthermore, a mixture of both diisocyanates allowed to react with this polyol at $1/c$ = 1.6 gave g_e' = 2.59, in excellent agreement with the preceding data. In another case, a 1:1 equivalent mixture of "Hylene" TM (80/20 ratio of 2,4-/2,6-toluene diisocyanate) and PAPI (polymethylenepoly(phenylisocyanate)) was allowed to react with PTMEG-1000. The calculated f_e of the mixture is 2.54 as compared to 2.56 obtained by the gel method, again verifying the validity of eq 8 for unequally reactive reactants used in deficiency.

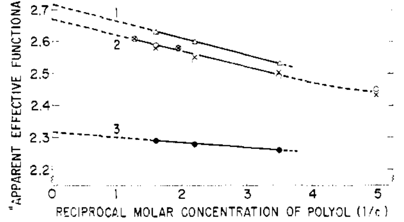

Figure 4. Effect of concentration on the gel point in polyol–diisocyanate systems: curve 1, Witco "Fomrez" 50/"Hylene" TM; curve 2, "Voranol" CP-3000 ("Hylene" TM (×); "Hylene" W (○)); curve 3, Witco "Fomrez" 52/"Hylene" TM.

Table III
Functionality of Selected
Polyols Used for Flexible Foams

Material	$\bar{M}_n$	$\bar{E}_n$	g_n (eq 16)	g_e (gel method)
Polyether "triol" ("Voranol" CP-3000)	2073	996	2.08	2.67
Polyester "triol" (Witco "Fomrez" 50)	2810	1087	2.56	2.72
Polyester (polyol) (Witco "Fomrez" 52)	2265	1120	2.02	2.31

Effective Functionality of Polyols. This investigation has been confined to three polyols used in the preparation of resilient foams. The reaction components of such foams are usually a diisocyanate, water, and a polyol of an average equivalent weight of about 1000. The polyol may be a triol or a mixture of diol and triol. The functionality of such polyols is of considerable importance as regards cell opening and many properties related to cross-link density.

In theory, the number average functionality, g_n, can be determined from the average molecular weight $\bar{M}_n$ (corrected for water) and the equivalent weight $\bar{E}_n$ according to the equation

$$g_n = \bar{M}_n/\bar{E}_n \tag{16}$$

The determination of functionality of high molecular weight polyols by the molecular weight method is rather unsatisfactory due to a relatively high experimental error (±5%), but particularly due to a very strong effect of potentially present low molecular weight inert materials. The gel point method, on the other hand, is insensitive to the presence of inert materials and it is precise to about 1%. Moreover, weight average and number average functionalities of conventional polyols used for flexible foams will differ by only 4% in the most unfavorable case (50/50 equivalent ratio of diol and triol). Therefore, our gelling method appears to be eminently suitable for the determination of number, as well as weight average functionalities of such materials.

In Table III, functionalities of the polyols are compared with respect to the method used. Even though the water content has been excluded in the calculation of the molecular weight, the functionality of these materials is appreciably lower by the molecular weight method than by the gel point method, the latter giving results closer to the expected functionalities.

The gel point data were obtained by using a stoichiometric excess of the polyols. The plots of the "apparent effective functionality," g_e', of the polyols against the reciprocal molar concentration of polyol (Figure 4) show a linear relation over a similar concentration range found previously for PTMEG-2000–polyisocyanate systems. The three values obtained for the slopes, $\phi(g_e)$, of the curves of Figure 4 indicate that, as in the case of the diol–polyisocyanate systems, $\phi(g_e)$ is linear in g_e (Figure 5), giving the following empirical relation

$$-\phi(g_e) = 0.096g_e - 0.207 \approx 0.1(g_e - 2) \quad (17)$$

The constants of eq 17 are in good agreement with those of eq 9a for PTMEG-2000. Considering that the gel equation (5) is symmetric with respect to functionalities of the reactants and that the molecular parameter B for PTMEG-2000 and the polyols (equivalent weight 1000) is of the same magnitude, the values of the constants in eq 9, 9a, and 17 lend support to the correctness of the theoretical basis resulting in the gel equation (5).

Conclusions

A gel point method based on the coincidence of gelation and completion of reaction is eminently suitable for the determination of the effective functionality of reactants having any distribution of functional groups and their reactivities. Experimental data confirm the theoretical prediction of the effect of dilution on the gel point for a given polycondensation system. The effect of functionality on the extent of cyclization is possibly due to the reaction conditions, *i.e.*, gelation under nonstoichiometric conditions. Further experimental studies, however, involving various systems and reaction conditions, are required to clarify this point and also to determine whether the empirical constants obtained for the modified gel equation are related for all systems through the molecular parameter B.

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Appendix I

Gel Equation for the Determination of Effective Functionality of Reactants of Any Distribution of Functional Groups and Their Reactivities. Consider an original mixture of reactants consisting of $A_1, A_2, \ldots A_i$ moles of one reactant bearing 1,2. . .i functional groups of type A each, and $B_1, B_2, \ldots B_j$ moles of the other reactant bearing 1, 2. . .j functional groups of type B each. Assume that type A has functional groups of equal reactivity and is employed in stoichiometric excess, whereas type B may or may not have functional groups of equal reactivity.

The fraction of functional groups carried by molecules of a given type (A_i or B_j) is as follows:

$$\rho_i = iA_i/\sum_i iA_i$$

and (I-1)

$$\rho_j = jB_j/\sum_j jB_j$$

From the definition of effective functionality, it follows that

$$f_e = \sum_i i^2A_i/\sum_i iA_i = \sum_i i\rho_i$$

and

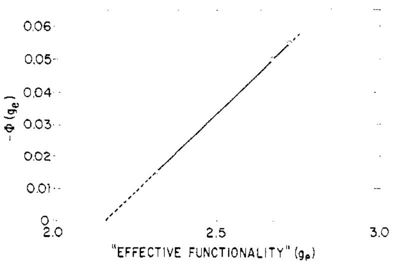


Figure 5. Dependence of $\phi(g_e)$ on effective functionality of polyols.

$$g_e = \sum_j j^2B_j/\sum_j jB_j = \sum_j j\rho_j \quad \text{(I-2)}$$

When the reaction is allowed to proceed to completion, the respective reaction probabilities can be expressed in terms of the initial number of functional groups, *viz.*

$$P_A = \sum_j jB_j/\sum_i iA_i$$

and (I-3)

$$P_B = 1$$

Gelation will coincide exactly with the completion of reaction for a unique P_A that fulfills the criterion of gelation.

A general mathematical statement of the criterion of gelation has been given by Case[7] as

$$P = \Sigma P' = 1 \text{ (for gelation)} \quad \text{(I-4)}$$

where P = propagation expectation and P' = partial propagation expectation (*i.e.*, a given path of propagation).

Propagation expectation may be defined as the mean expectation of reappearance of any given unit or structure in the chain or branches of the chain which start at such unit or structure.

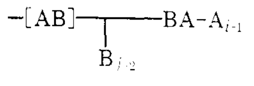
Consider a bond –[AB]– selected at random from the reacted system. Our objective is to compute the probability of recurrence of the –[AB]– bond.

1. The probability that B is a part of B_j is ρ_j. The corresponding structure is $-[AB]-B_{j-1}$.

2. The probability that any of the $(j - 1)$ groups of type B has reacted with a group A belonging to A_i is

$$\rho_j(j - 1)\rho_i \quad \text{(I-5)}$$

The corresponding structure may be illustrated as



$$-[AB]\underset{\displaystyle B_{j-2}}{\overset{}{\text{—}\!\!\top\!\!\text{—}}}BA-A_{i-1}$$

Since all B groups are assumed to have reacted, eq I-5 retains its validity irrespective whether all B groups are equally or unequally reactive.

3. The probability that any of the $(i - 1)$ groups of type A (belonging to the structure shown in 2) has reacted with any B group is

$$P'_{ij} = \rho_j(j - 1)\rho_i(i - 1)P_A \quad \text{(I-6)}$$

Equation I-6 represents the partial propagation

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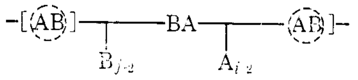
[7] L. C. Case, *J. Polym. Sci.*, **26**, 333 (1957).

expectation of the recurrence of the –[AB]– bond in the particular structure



$$-[(AB)]-\underset{B_{j-2}}{\top}-BA-\underset{A_{i-2}}{\top}-(AB)]-$$

The propagation expectation P for any structure is the sum over all species, *i.e.*

$$P = \sum_{ij} P'_{ij} = P_A \sum_{ij} \rho_i(i - 1)\rho_j(j - 1)$$

or (I-7)

$$P = P_A(f_e - 1)(g_e - 1)$$

Gelation will occur when $P = 1$. Therefore, the condition for the critical (gel) point is

$$(P_A)_{gel} = (f_e - 1)^{-1}(g_e - 1)^{-1} \tag{I-8}$$

The converse case, *i.e.*, a system containing a stoichiometric excess of B groups of equal reactivity and A groups of any reactivity can be treated in identical fashion to yield

$$(P_B)_{gel} = (f_e - 1)^{-1}(g_e - 1)^{-1} \tag{I-9}$$

Appendix II

Gel Equation in the Presence of Cyclization. The problem of ring formation in polycondensation reactions has been treated theoretically by several investigators.[8-11] Jacobson and Stockmayer[8a] derived quantitative expressions for the effect of dilution and of molecular weight on the fraction of rings formed in *linear* polycondensation systems.

Harris[8b] extended the theory of molecular weight distribution in branched-chain polymers by including possible intramolecular reactions for the case of pure f-functional monomers.

Kinetics and equilibria of polycondensation reactions accompanied by cyclization have been treated by Whittle[9] and by Gordon and Scantlebury[10] using stochastic and branching theories, respectively. From the differential equations derived in these papers, the degree of cyclization can be estimated by using appropriate methods of calculation. Kilb[11] derived an approximate gel equation to include intramolecular reactions in a system consisting of difunctional monomers of type A (A_2 monomers) and a mixture of difunctional and pure f-functional monomers of type B (B_2 and B_f monomers), were $f \geq 3$. In spite of several approximations, Kilb's theory was found in reasonable agreement with experimental gel point data on selected polyesters[6a] and polyalkoxysilanes.[6b]

In connection with the gel point studies discussed in this paper, it was of interest to obtain an expression for the dependence of gel point on dilution for polycondensation systems consisting of monomers of arbitrary distribution of their functional groups. This can be achieved by considering ring formation in the context of a generalized method of calculating the extent of reaction at gelation.[12]

Modified Gel Equation. Consider an original mixture of reactants consisting of $A_1, A_2, \ldots A_i$ moles of reactants of type A bearing, respectively, 1, 2. . .i functional groups and $B_1, B_2, \ldots B_j$ moles of reactant of type B bearing, respectively, 1, 2. . .j functional groups. All unreacted groups of the same kind are assumed to be equally reactive.

Let r_n be the probability of forming n-unit ring, where a single unit is defined to contain two groups of each type along the backbone forming the ring.

Consider a bond –[AB]– picked at random from the reacted system. The objective is to compute the probability for the recurrence of the bond without cyclization (partial propagation expectation P'_{ij}). After summing up over all monomers and ring sizes (total propagation expectation P), gelation will occur when $P = 1$.

The probability that B of the –[AB]– bond belongs to B_j monomer is ρ_j; the probability that any of the $(j - 1)$ groups of type B has reacted with a group A belonging to A_i, which is not a part of the molecule chosen at random, is

$$\rho_j P_B(j - 1)\rho_i\left(1 - \sum_{n=1}^{n'} r_n\right) \tag{II-1}$$

where n' is the number of units present in the chain selected at random.

The probability of any of the $(i - 1)$ groups reacting with any B group other than those derived from the same molecule is the partial propagation expectation, $P'_{i,j}$, viz.

$$P'_{i,j} = \rho_j P_B(j - 1)\rho_i\left(1 - \sum_{n=1}^{n'} r_n\right)^2 P_A(i - 1) \tag{II-2}$$

Summing $P'_{i,j}$ over all species and ring sizes and equating the sum to unity yields the gel point

$$1 = (P_A P_B)_{gel}\left(1 - \sum_{n=1}^{\infty} r_n\right)^2 \sum_i \sum_j \rho_i(i - 1)\rho_j(j - 1)$$

or

$$(P_A P_B)_{gel} = \left(1 - \sum_{n=1}^{\infty} r_n\right)^{-2}(f_e - 1)^{-1}(g_e - 1)^{-1} \tag{II-3}$$

For a small extent of cyclization, the gel equation can be approximated to

$$(P_A P_B)_{gel} = \left(1 - 2\sum_{n=1}^{\infty} r_n\right)^{-1}(f_e - 1)^{-1}(g_e - 1)^{-1} \tag{II-4}$$

The problem remains to compute

$$\sum_{n=1}^{\infty} r_n$$

In analogy to Kilb's treatment and considering that the gel point theory confines itself to chain propagation, Jacobson and Stockmayer's results for linear systems

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(8) (a) H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.*, **18**, 1600 (1950); (b) F. E. Harris, *ibid.*, **23**, 1518 (1955).

(9) P. Whittle, *Proc. Roy. Soc.* (London), **A285**, 501 (1965).

(10) M. Gordon and G. R. Scantlebury, *J. Chem. Soc.*, *B*, 1 (1967).

(11) R. W. Kilb, *J. Phys. Chem.*, **62**, 969 (1958).

(12) A. W. Fogiel and C. W. Stewart, *J. Polym. Sci.*, *Part A-2*, 7, 1116 (1969).

will be applied to obtain an approximation for r_n. According to Jacobson and Stockmayer,[8a] the ratio of the number of rings of n units (R_n) to the number of chains of n units (C_n) is

$$R_n/C_n = BVn^{-5/2}/A \qquad \text{(II-5)}$$

where

$$B = [3/(2\pi\nu)]^{3/2}/2b^3 \qquad \text{(II-6)}$$

A is a parameter of the reaction conditions, V denotes the total volume of the system, ν is the number of chain atoms per unit, and b is the effective bond length.

Assuming a small extent of cyclization

$$r_n \sim R_n/C_n = BVn^{-5/2}/A = (B\text{m}/A)(1/c)n^{-5/2} \qquad \text{(II-7)}$$

where c is the concentration of reactive groups of one of the reactants in moles per liter. Summation of r_n over all ring sizes yields

$$\sum_{n=1}^{\infty} r_n = (B\text{m}/A)(1/c) \sum_{n=1}^{\infty} n^{-5/2} \qquad \text{(II-8)}$$

The infinite series

$$\sum_{n=1}^{\infty} n^{-5/2}$$

is a well-known Riemann ζ function which has the value of 1.341. For a given polycondensation system, all parameters may be combined to give

$$2\sum_{n=1}^{\infty} r_n = k/c$$

Substituting this value into eq II-4 yields Stockmayer's gel equation[2] modified to account for ring formation, *viz.*

$$(P_\text{A}P_\text{B})_\text{gel} = (1 - k/c)^{-1}(f_\text{e} - 1)^{-1}(g_\text{e} - 1)^{-1} \qquad \text{(II-9)}$$

The Photodegradation of Polypropylene Films. II. Photolysis of Ketonic Oxidation Products[1,2]

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ABSTRACT: Oxidation products can be expected to be inadvertently produced during the processing of polypropylene. In order to study the nature and photolytic mechanisms of these products, polypropylene films were prepared from resin which had been extensively air oxidized at 225° for various times. These films were then degraded under vacuum by irradiating at various wavelengths in the region 2200–3800 Å. Photolytic changes in the oxidized film samples were followed by glpc and ir analysis, and by film weight loss. The ir spectra of the air-oxidized films were compared with the ir spectra of model compounds related to polypropylene. From this comparison, and a consideration of the changes detected in the oxidized films during irradiation, the main oxidation products were believed to be the polymeric ketones $\sim CH(CH_3)CH_2C(=O)CH_2CH(CH_3)\sim$ (A) and $CH(CH_3)CH_2C(=O)CH_3$ (B). A study of the ir changes and the composition of the volatile products produced during irradiation indicated that ketone A is photolyzed primarily by a Norrish type I scission to give carbon monoxide and two macroradicals, whereas ketone B is photolyzed by a Norrish type II scission to give acetone and an unsaturated polymer chain end. The quantum yield for each photolytic reaction was determined from measurements of ir change and weight loss at various irradiation times. Both quantum yields were found to be approximately 0.08. The Norrish type I cleavage of ketones A and B is believed to be a possible source of initiation in the very early stages of the photooxidative deterioration of polypropylene. In later stages of deterioration, however, the photooxidation is probably dominated by other initiation steps, such as hydroperoxide photolysis.

Polypropylene has found wide commercial application in the form of fibers and films, despite the problems of thermal and photooxidative instability associated with this polymer. A partial solution of these problems has been achieved by the development of many ultraviolet (uv) stabilizers and antioxidant systems for use with polypropylene.[3] However, relatively little basic research has been published on the complex interplay of competing chemical reactions and physical effects involved in the photooxidative deterioration of the solid polymer. "Pure" saturated polyolefins are not expected to show a uv absorption beyond 2000 Å[4] and consequently should be indefinitely stable to the sunlight transmitted by the atmosphere (wavelengths greater than 2900 Å). However, any impurity in polypropylene which has a uv absorption extending to greater than 2900 Å will be a potential cause of photodegradation on exposure of the polymer to sunlight. Uv stabilizers protect polypropylene by screening the incident radiation from the chromophoric impurities as well as by energy transfer from the chromophores to the stabilizer.[5] It is essential that the nature, electronic absorption spectrum, and primary photolytic process of potential chromophoric impurities

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(1) N.R.C.C. No. 11,009.

(2) Previous paper in this series: Y. Kato, D. J. Carlsson, and D. M. Wiles, *J. Appl. Polym. Sci.*, in press.

(3) See, for example, J. E. Bonkowski, *Textile Res. J.*, **39**, 243 (1969).

(4) R. H. Partridge, *J. Chem. Phys.*, **45**, 1679 (1966).

(5) (a) P. J. Briggs and J. F. McKellar, *J. Appl. Polym. Sci.*, **12**, 1825 (1968); (b) A. P. Pivovarov and A. F. Lukovnikov, *Khim. Vysokikh Energii*, **2**, 220 (1968).