NOTE

Extension of Simple Polycondensation Gelation Theories to Simple Radical and Mixed Polycondensation/Radical Gelation

A. PIZZI

ENSTIB, University of Nancy 1, Epinal, France

INTRODUCTION

The existing theories of polycondensation concentrate on the determination, by different mathematical approaches and different physicochemical approximations, of the degree of conversion and, hence, of the advancement of polymerization at the point of gel, and on the calculation of basic polymer parameters derived from the determination of the gel point.[1–3] Among these, in the field of polycondensation, must be remembered (1) the gel theory of Carothers[4] in which the critical degree of conversion at the gel point (p_{gel}) is defined as $p_{gel} = 2/f$, with f being the average functionality of the monomers in the system; (2) the probabilistic gel theory of Flory[5]–Stockmayer[6,7] in which p_{gel} is defined through the coefficient of branching $\alpha = 1/(f - 1)$, f being the functionality of the monomer of greater functionality, through the expression $\alpha = rp^2\rho/[1 - rp^2 2) - \rho)]$—where p is both the degree of conversion and the probability that a certain reactive group has in fact reacted, ρ is the proportion of such a reactive group belonging to branching units, and r is the ratio of the types of reactive groups of the two monomers participating in the polycondensation; (3) the cascade process theory of Gordon[8,9] based on more complex functions than the two preceding ones, but also offering some further advantages on them; (4) the Miller–Macosko[10] recursive method; and (5) the stochastic graph theory of Bruneau,[11] more complete but very complex and very complicated to use, as well as even more complex theories that can be found in the review literature.[2,3] Although the more complex theories define to a much greater extent the reality of gelation, the simpler ones are much more used to solve applied, everyday problems. Thus, among these theories, the first two are of such a simplicity as to be constantly used in applied practice, whereas the third and fourth theories are also sometimes used in more complex research applications.

Recently, in the quest of simple systems to solve everyday applied networking problems, an equation, and simpler regressions also, correlating the relative deflections obtained by thermomechanical analysis with the sum of the interfacial energy of interaction of a synthetic polymer with wood plus the internal cohesive strength of the hardened synthetic polymer has been obtained,[10,11] namely

$$E = -km/(\alpha f) \quad (1)$$

where k is a constant, depending on the testing conditions used; m is the average number of degrees of freedom between cross-linking nodes of a hardened network; E is the sum of the energy of interaction at the interface synthetic polymer/substrate and of the internal cohesive energy of the synthetic polymer (the internal energy of the substrate is not considered because the deflection measured are relative to the substrate alone); and α is Flory's coefficient of branching for polycondensates. From this were derived, by adaptation of already existing gel theories, simple equations forecasting with greater precision the degree of conversion p at the gel point for polycondensation,[10] such as

$$p_{gel} = 1/f + (1/2)\sqrt{\alpha/r} \quad (2)$$

where **f** is Carothers' average functionality of the system and $\boldsymbol{\alpha}$ is Flory's coefficient of branching calculated from Flory's functionality of the reagent of higher functionality, and in its most general form in the case of a system with any number of monomers

$$p_{gel} = \Sigma n_X/\Sigma(f_X n_X) + (1/2)\sqrt{\alpha/(\Sigma r_X + \Sigma r_X r_Y)} \quad (3)$$

Table I Experimental[16] and Calculated Values for the Degree of Conversion of Radical Crosslinking for Tripropylene Glycol Diacrylate (TPGDA)

	Experimental $p_{rad,gel}$	Calculated $p_{rad,gel}$ [Flory's eq. (5)]	Calculated ($p_{rad,gel}$ Carothers)	Calculated $p_{rad,gel}$ [Carothers + Flory eq. (2)]
TPGDA	0.438	0.33	0.5	0.42

that simplifies the case of three monomers in which one can react with the other two, but where these last two cannot react with each other (i.e., resorcinol + formaldehyde + acetaldehyde) to the equation

$$p_{gel} = \Sigma n_X/\Sigma(f_X n_X) + (1/2)\sqrt{\alpha/(\Sigma r_X)} \qquad (4)$$

where the $\sqrt{\ }$ is eliminated in the case of difunctional monomers not being present in the system.

The equation $E = -km/(\alpha f)$ has been shown to work also for radical hardening polymers, with the provisio that the coefficient α is not anymore Flory's coefficient of branching, but a similar coefficient calculated in the same manner[10,11] by substituting the number of reactive carbon atoms to the functionality (i.e., for each C═C bond present this gives two reactive carbons, and thus $\alpha = 1/(f - 1)$, where f is 2 rather than 1 as it would be in polycondensates). As a consequence, it would be of interest to adapt, or to modify if necessary, simpler polycondensation gel theories, both Flory's as well as the above equations, to the case of gelation of radical addition polymers and to the case of mixed polycondensation/radical addition polymers, such as the case of unsaturated polyesters where the polymer is built up by polycondensation but is networked and hardened by radical addition reactions. This is needed to present a simple method for the approximate resolution of applied problems.

EXPERIMENTAL

The experimental values of the degrees of conversion at the point of gel have been taken from the literature for both the case of unsaturated polyesters,[12–15] with and without styrene obtained by gel times and Fourier transform infrared-derived degrees of conversion, as well as for the case of polyfunctional acrylic monomers,[16] such as linear tripropylene glycol diacrylate obtained by turbidimetry and Fourier transform infrared.

DISCUSSION

The case of networking by radical addition polymerization is the only one that is most easily checked. In this

case, in a normal monomer presenting a single C═C double bond $\alpha = 1/(2 - 1) = 1$ and thus according to Flory's theory $p_{gel} = 1$, hence only linear polymers are formed and no covalent tridimensional crosslinking can occur. In this case, only entanglement networking can occur. In the case in which more than one C═C double bond exists on the monomer, then $\alpha < 1$ and crosslinking by radical addition will only occur. In the case of radical addition homopolymerizations, only even integer values of monomer functionality can exist with this system. Thus, for 1, 2, and 3, respectively, C═C double bond monomer functionality f can only be equal to 2, 4, and 6, respectively, and the values of α will be 1, 0.33, 0.2, respectively. Using the formula, at 100% degree of conversion for $DP_w = (1 + r)/1 - r)$, because r can only be equal to 1 in the case of the homopolymerization of a single type of monomer, then $DP_w = \infty$, which correctly describes both the formation of a infinitely long linear polymer (homopolymerization of a monomer presenting only one C═C double bond), as well as the formation of a crosslinked network (homopolymerization of a monomer presenting two or more C═C double bonds). In this case, it is not necessary to use any of eqs. (2)–(4) for p_{gel} determination because Carothers' average functionality of the system and Flory's functionality coincide. Thus, for homopolymerization, Flory's formulas with a different meaning for α, namely

$$p_{gel} = \sqrt{\alpha/r} \quad \text{and} \quad p_{gel} = \alpha/r \qquad (5)$$

as well as Carothers'[4,10] formula and the mixed Carothers–Flory formula[10] [eq. (2)] are equally valid for the homopolymerization of a monomer presenting only one C═C double bond, giving exactly the same result of $p_{gel} = 1$, thus the lack of crosslinking. For the homopolymerization of a monomer presenting two or more C═C double bonds instead the three formulas calculate different values for p_{gel}. An example of the correspondence between experimental values and calculated values of p_{gel} for an acrylic monomer presenting two C═C double bonds is shown in Table I. It is clear that eq. (2) forecasts a value of p_{gel} much closer to the experimental value, also indicating in the case of simple, single monomer-type radical crosslinking its higher correlation with experimental results. It must be clearly pointed out that such an approach is only valid for radical reactions involving a single type of monomer. It

cannot be used in the case of the radical copolymerization of two different monomers because, in this case, a purely statistical approach without considering the relative rates of homo- and heteropolymerization cannot explain what occurs.

The second problem of interest is that of a linear polymer formed by polycondensation and hardened by radical addition. To explain this case better, the particular case of the coreaction of maleic anhydride with ethylene glycol to form an unsaturated polyester, which is then hardened by radical addition through the residual unsaturation carried by the maleic acid structure, will be considered. The methodology for such a system is as follows:

1. First, determine the numerical value of the degree of polymerization for the polycondensation portion of the reaction. The normal formula for DP_n at parity of reactive groups for the two reagents is $DP_n = 1/(1 - p)$ should apply. This is true if one uses the formula for p_{polyc} of the polycondensation part of the reaction, but if it is considered that the polycondensation constitutes only part of the total reaction, the remaining portion being the radical crosslinking reaction used to network the system tridimensionally, then as a first approximation, $p_{polyc} = 0.5\ p_{tot}$, where p_{tot} is the total degree of conversion for the sum of the two reactions (polycondensation and radical), and $DP_n = 0.5/(0.5 - p_{tot})$. It is necessary to determine DP_n, or without knowing it, it is not possible to determine the functionality of the average oligomer formed by polycondensation, functionality that is necessary to determine the coefficient of branching α for the second step: that of radical crosslinking.

2. The second step entails the determination of the α_{rad} for the radical reaction step. As $\alpha_{rad} = 1/(f_{rad} - 1)$ were $f_{rad} = DP_{n\,polyc} \times$ (number of C=C bonds in repeating unit) $\times$ 2, the factor 2 takes into account the definition of the modified α defined in the introduction, then

$$\alpha_{rad} = 1/[(DP_{n\ polyc} \times \text{(number of C=C bonds)} \times 2) - 1] \quad (6)$$

3. A general formula to define the total system would then be

$$p_{tot,\,gel} = (1/2)[\ \sqrt{(\alpha_{polyc}/r_{polyc}) + (\alpha_{rad}/r_{rad})}] \quad (7)$$

and under a more general form

$$p_{tot,\,gel} = (1/2)\ [(\alpha_{polyc}/r_{polyc})^{\mathbf{n}} + (\alpha_{rad}/r_{rad})^{\mathbf{m}}], \quad (8)$$

where n is $\frac{1}{2}$ or 1, depending on the presence or not of difunctional monomers in the polycondensation and m is $\frac{1}{2}$ or 1, depending on the presence or not of difunctional monomers in the radical step of the reaction. However, eqs. (7) and (8) are based on the gross approximation $p_{polyc} = 0.5\ p_{tot}$, which is an approximation because the contribution of the polycondensation to the gelling of the whole system is of 50% only when $p_{polyc} = 1$, the only case for which eq. (8) would be valid. In other cases, $p_{polyc} \neq 1$; hence, $p_{polyc} \neq 0.5\ p_{tot}$ and the polycondensation contribution to p_{tot} might not be 50%, as implied by this expression. A more adequate formula should then be

$$p_{tot,\,gel} = (1/2)[p_{tot,\,from\,polyc} = (\alpha_{rad}/r_{rad})^{\mathbf{m}}]. \quad (9)$$

This expression is valid, and the problem then shifts to determining the value of $p_{tot,\,from\,polyc}$; hence, the value of p_{tot} contributed by the first step: polycondensation. In the case of a linear unsaturated polyester as the one from maleic anhydride and ethylene glycol, the system does not gel due to the impossibility of forming tridimensional cross-linking, and thus the first term of eq. (8) always has a value of 1 when the reagents are in equimolar quantities. The correction that is needed from eqs. (8) and (9) is then

$$p_{tot,\,gel} = (1/2)[p_{polyc}(\alpha_{polyc}/r_{polyc})^{\mathbf{n}} + (\alpha_{rad}/r_{rad})^{\mathbf{m}}]. \quad (10)$$

It is now necessary to check this expression with experimental data of the determination of p_{gel}. For example, in the equimolar maleic anhydride + ethylene glycol case at $p_{polyc} = 0.9$, $DP_{n,tot} = 0.5/(0.5 - 0.45) = 10$ and hence $\alpha_{rad} = 1/(10 \times 2 \times 1) - 1) = 0.0526$, and eq. (10) then yields at the given $p_{polyc} = 0.9$, a value of $p_{tot,gel} = (1/2)(0.9 \times 1 + 0.0526) = 0.476$. This is valid in the case no reactive diluting monomer, such as styrene, is added after polycondensation and before radical cross-linking. In unsaturated polyesters, styrene monomer is generally added, and its presence must also be taken into account. Thus, if for instance an equimolar amount of C=C is present in the system from the maleic acid residue on the polyester oligomers and from the styrene monomer α_{rad} still has the same value at 0.0526, but as of now a real difunctional species is present, namely the styrene monomer, on top of the oligomer of average degree of polymerization of 10 (see above), m in eq. (10) will be $\frac{1}{2}$ and $p_{tot,gel} = (1/2)(0.9 \times 1 + \sqrt{0.0526}) = 0.565$. With the introduction of styrene, and also in the case of high-viscosity polyesters, as again $p_{rad} \neq 0.5$, p_{tot}, a corrective factor for the second term of eq. (10) is also needed. Thus,

$$p_{tot,\,gel} = (1/2)\ [p_{polyc}(\alpha_{polyc}/r_{polyc})^{\mathbf{n}} + p_{rad}(\alpha_{rad}/r_{rad})^{\mathbf{m}}], \quad (11)$$

Table II   Experimental[12,13] and Calculated Values for a Maleic Anhydride + Ethylene Glycol without Styrene and for a Maleic/Phthalic/Ethylene Glycol + Styrene Polyesters

	Experimental $p_{polycond.}$	Experimental p_{rad}	Experimental $p_{gel, tot}$	Calculated		
				$p_{gel, tot}$ [eqs. (9) & (10)]	$p_{gel, tot}$ [eq. (12)]	$p_{gel, tot}$ [eq. (13)]
Without styrene	0.942	0.011	0.476	0.486	0.500	0.493
With styrene	0.942	0.015	0.513	0.558	0.528	0.543

which, considering that maximum conversion in the radical reaction is generally 92–95%, changes the values calculated above to 0.475 and 0.559. Equation (10) is the easier one to use; but, if Carothers' equation or eq. (2) is used, eq. (9) then becomes

$$p_{tot, gel} = (1/2)[p_{polyc} + (2/f)_{rad}] \qquad (12)$$

$$p_{tot, gel} = (1/2) \, [p_{polyc} + (1/f$$
$$+ (1/2)(\alpha_{rad}/r_{rad})^{\mathbf{m}})_{rad}] \quad (13)$$

in both of which f is Carothers' average functionality of the system.

For simpler systems then, eq. (9), and hence eqs. (10) and (11) are the best to use. For more complex systems, eqs. 12 and 13 are best, especially eq. (12). It is now necessary to check this expression with experimental data of the determination of p_{gel} (see Table II). The initial polycondensation system is not just comprised of difunctional monomers, but comprises instead monomers of functionality >2; the most apt equations [from eqs. (2), (3), and (4)] would be: 2)) for simpler radical systems [in which oligomers have all the same functionality (i.e., the case of a polyester without styrene) Table II]

$$p_{tot, gel} = (1/2) \, [p_{polyc}(1/f + (1/2)(\alpha_{polyc}/r_{polyc})^{\mathbf{n}})$$
$$+ p_{rad}(\alpha_{rad}/r_{rad})^{\mathbf{m}}]; \quad (14)$$

and (2) for more complex radical systems [in which species of different average functionality are present (i.e., the case of an unsaturated polyester with styrene monomer) Table II]

$$p_{tot, gel} = (1/2) \, [p_{polyc}(1/f$$
$$+ (1/2)(\alpha_{polyc}/r_{polyc})^{\mathbf{n}}) + p_{rad}(2/f)_{rad}] \quad (15)$$

and expanding eqs. 2)4) and 2)5) by the use of eq. (3) to all possible cases of polycondensation, taking $\mathbf{f_X}$ as Flory's functionality for each monomer present[10]

$$p_{tot, gel} = (1/2) \, [p_{polyc}(\Sigma \mathbf{n_X}/\Sigma(\mathbf{f_X n_X}) + (1/2)(\alpha/(\Sigma r_X$$
$$+ \Sigma r_X r_Y))^{\mathbf{n}}) + p_{rad}(\alpha_{rad}/r_{rad})^{\mathbf{m}}] \quad (16)$$

for simpler radical systems, whereas for more complex radical systems

$$p_{tot, gel} = (1/2)[p_{polyc}(\Sigma \mathbf{n_X}/\Sigma(\mathbf{f_X n_X})$$
$$+ (1/2)(\alpha/(\Sigma r_X + \Sigma r_X r_Y))^{\mathbf{n}}) + p_{rad}(2/f)_{rad}] \quad (17)$$

From the results obtained, it can be seen that the total degree of conversion at the gel point varies according to the extent of advancement of the first reaction step, namely the polycondensation, to lower p_{polyc} corresponding to a higher p_{rad} to reach gelation, as indeed it should be.

The equations presented indicate clearly the predominance of the contribution of the polycondensation to reach $p_{tot, gel}$, as indeed shown experimentally. It is well known[17] that p_{gel} in a polycondensation occurs at degrees of conversion much higher that in radical addition polymerizations (p_{rad} in the order of 0.05 or lower being quite common) and the contributions of the two terms in eqs. (10) and (11) is in line with the experimental evidence for this point of view. The correspondence between experimental and calculated results is shown in Table II: the approach seems to work in the simpler cases, but the calculated results slowly and progressively diverge from the experimental reality with increasing complexity of the system.

The above system has been discussed in DP_n, as befit the use for the polycondensation portion of Flory's theory of gelation in which the concept of gel point is that of an infinitely long linear polymer just before tridimensional cross-linking starts. However, well-established knowledge[17] shows that it is the value of DP_w that goes to ∞ at p_{gel} and not the value of DP_n. If discussed purely in light of Flory's theory, the equations above are than valid in DP_n; but, if discussed in light of the reality of the existence of a gel and a sol at p_{gel}, then what is shown above is valid for DP_w rather than DP_n.

CONCLUSIONS

Simple polycondensation statistical gel theory equations can be adapted, without recurring to kinetic

terms in the equations, to the case of gelation in the simpler cases of radical addition polymers; but, more important to the case of gelation of mixed polycondensation/radical addition polymers, such as the case of unsaturated polyesters where the polymer is built up by polycondensation, but is networked and hardened by radical addition reactions. The equations and approach presented are free of kinetic terms and are useful as a method simpler than existing ones for the approximate resolution of applied problems in mixed polycondensation/radical addition gelation. The method and equations outlined are apt to describe well the simpler polycondensation/radical addition systems, but progressively diverge from the experimental reality with increasing complexity of the system. The results and equations obtained also indicate the predominance of polycondensation in reaching the gel point of the system in mixed polycondensation/radical systems.

REFERENCES

1. Dusek, K. in Polymer Networks '91, Dusek, K.; Kuchanov, S. I., Eds.; VSP, Utrecht: The Netherlands, 1992; Chapter 2.
2. Kuchanov, S. I.; Panyukov, S. V. in Polymer Networks '91, Dusek, K.; Kuchanov, S. I., Eds.; VSP, Utrecht: The Netherlands, 1992; Chapter 3.
3. Rozenberg, B. A.; Irzhak, V. I. in Polymer Networks '91, Dusek, K.; Kuchanov, S. I., Eds.; VSP, Utrecht: The Netherlands, 1992; Chapter 2.
4. Carothers, W. H. Collected Papers, Interscience, New York, 1940.
5. Flory, P. J. J Am Chem Soc 1939, 61, 3334; 1940, 62, 2261; 1941, 63, 3083.
6. Stockmayer, W. H.; Weil, L. L. in Advancing Fronts in Chemistry, Reinhold: New York, 1945; Chapter 6.
7. Jacobson, H.; Beckmann, C. O.; Stockmayer, W. H. J Phys Chem 1956, 18, 1607.
8. Gordon, M. Proc Roy Soc (Lond) 1962, A268, 240.
9. Gordon, M.; Scantlebury, G. R. Trans Faraday Soc 1964, 60, 604.
10. Pizzi, A. J Appl Polym Sci 1997, 63, 603.
11. Pizzi, A.; Probst, F.; Deglise, X. J Adhesion Sci Technol 1997, 11, 573.
12. Paauw, M. M.Sc. Thesis, University of the Witwatersrand, Johannesburg, South Africa, 1992.
13. Paauw, M.; Pizzi, A. J Appl Polym Sci 1993, 50, 1287.
14. Paauw, M.; Pizzi, A. J Appl Polym Sci 1991, 42, 1377.
15. Paauw, M.; Pizzi, A. J Appl Polym Sci 1993, 48, 931.
16. Godard, V. Ph.D. Thesis, University of Nancy, Nancy, France, 1998.
17. Macosko, C. W. Br Polym J 1985, 17, 239.