

Gel Point for Multifunctional Polycondensation Systems

1. Stoichiometric Case

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Abstract

The Probabilistic Theory of Crosslinked Systems (PTCS) proposed originally by the author to treat crosslinking of preexisting linear macromolecules (KLONOWSKI 1979) is applied to the calculation of the critical gel point for multifunctional polycondensation systems. The results seem to be in better agreement with experiments than those given by other existing theories.

Introduction

The size distribution of aggregates in multifunctional polycondensation has been extensively explored by many authors, based on a variety of mathematical approaches (cf. STAFFORD 1981). The different theories give different values of the critical conversion (critical extent of reaction), p_{crit} , at which gelation of the system occurs. For some authors (FLORY 1941; STOCKMAYER 1943, 1944) the critical gel point is reached when the weight-average degree of polymerization, \bar{M}_w , becomes infinite, i.e. when the conversion, p , is equal to

$$p_{crit} = 1/(f-1) \quad (1)$$

Other authors (BRUNEAU 1967; WHITEWAY 1970) say that at the critical gel point the number-average degree of polymerization, \bar{M}_n , becomes infinite, i.e. when p is equal to

$$p_{crit} = 2/f \quad (2)$$

where f denotes the functionality of monomers undergoing polycondensation (ought not to be confused with the functionality of a crosslink).

For a mixture of A- and B-kind monomers, $R_r A_r$ and $Q_r B_r$, one introduces functional group fractions

$$y_{Ir} = f_{Ir} x_{Ir} / \sum_{r=1} f_{Ir} x_{Ir} \quad (I=A,B) \quad (3)$$

where x_{Ir} are mole fractions of given monomers of each kind

$$\sum_{r=1} x_{Ar} = 1; \quad \sum_{r=1} x_{Br} = 1 \quad (4)$$

The summations over r denote summations over all monomers of

A- and B-kind respectively, present in the system. The effective mean functionalities are defined as number-average functionalities with respect to functional group fractions, i.e. as weight-average functionalities with respect to mole fractions

$$\bar{f}_I = \sum_{r=1}^{\infty} v_{Ir} f_{Ir} = \sum_{r=1}^{\infty} f_{Ir}^2 x_{Ir} / \sum_{r=1}^{\infty} f_{Ir} x_{Ir} \quad (I=A, B) \quad (5)$$

and

$$\bar{f} = \frac{1}{2}(\bar{f}_A + \bar{f}_B) \quad (6)$$

With such defined effective functionalities \bar{f}_A and \bar{f}_B , Eqs. (1) and (2) are generalized respectively to STAFFORD (1981)

$$p_{crit} = [(p_A p_B)_{crit}]^{1/2} = (\bar{f}_A - 1)^{-1/2} (\bar{f}_B - 1)^{-1/2} \quad (7)$$

$$p_{crit} = \left[\frac{1}{4}(\bar{f}_A + \bar{f}_B) \right]^{-1} = 2/\bar{f} \quad (8)$$

Equ.(7) gives the same results as equations derived originally by FLORY (1941). For polycondensation of one kind of f-functional monomers one has $\bar{f}_A = \bar{f}_B = f$ and (7) reduces to (1), (8) reduces to (2). There is a misprint or an obscurity in STAFFORD's (1981) Equ.(29) - the right-hand side ought to be taken to the power (-1).

In our opinion the problem of finding p_{crit} for different gelation mechanisms ought to be based on serious probabilistic arguments. Recent works by YAN (1983) seem to show that Equ.(2) gives rather maximal possible value for tree-like systems than the critical one.

Probabilistic calculation of critical gel point

The Probabilistic Theory of Crosslinked Systems (PTCS) (KLONOWSKI 1979), firstly applied to the crosslinking of long primary macromolecules may easily be applied for multifunctional polycondensation systems. Based on the statistics of network defects, PTCS concludes that in the critical gel point (if closed cycles are not taken into account as in papers by other authors cited above) one has

$$(2n_0 + n_1 - n_3) \Big|_{\alpha=\alpha_{cr}} = 0 \quad (9)$$

where n_k are contributions of crosslinks (junctions) with k free chain ends respectively (Fig.1) and PTCS shows how these contributions may be easily calculated for any crosslinking density index, l . Here and after, to be in accordance with notions used in our other papers, we use α and α_{cr} to denote the degree of conversion, instead of p and p_{crit} ; we use also X^A and X^B instead of \bar{f}_A and \bar{f}_B .

In the case under consideration where A can only react with B and vice versa, in all formulae for n_k (Fig.1) in any term the first factor must refer to groups of type A (p_r^A , $r=0,1,2$) and the second to groups of type B (p_r^B , $r=0,1,2$); p_r^A and p_r^B are probabilities of a group of type A or B respectively which contributes to the junction r free chain ends when forming a crosslink with a group of the "opposite" type. The

deduction of Equ.(9) is based on purely topological considerations and so it is not important how long a "free chain" is - it may be a methyl group or even a single hydrogen or oxygen atom attached to the crosslinked unit (group). Thus in the model under consideration in all discussed cases the crosslink functionality may remain equal to 4.

Also the expression of p_r^I (I=A,B) through distribution functions, $f_q^I(\alpha)$, of reacted groups between primary molecules (here monomers) remains unchanged (cf. KLONOWSKI 1979):

$$p_2^I = f_1^I / l^I \quad (10)$$

$$p_1^I = 2(1 - f_0^I - f_1^I) / l^I \quad (11)$$

$$p_0^I = 1 - p_1^I - p_2^I \quad (I=A,B) \quad (12)$$

The only difference is that one must take all characteristics for any type of groups separately (i.e. α^I , $p_r^I(\alpha^I)$, $f_q^I(\alpha^I)$ etc. for I=A,B) and instead of Poissonian f_q one ought to take (if the crosslinking process may be assumed to occur at random) binomial ones:

$$f_0^I = (1 - \alpha^I)^{X^I} \quad (13)$$

$$f_1^I = l^I(1 - \alpha^I)^{(X^I-1)} \quad (14)$$

where

$$l^I = X^I \alpha^I \quad (15)$$

For the stoichiometric case

$$\alpha^A = \alpha^B = \alpha \quad (16)$$

Introducing (13) - (16) into (10) - (12) and then into the formulae for n_k (cf. Fig.1), and using the critical condition in the form (9), one obtains after some rearrangements an equation for the critical extent of reaction, α_{cr} , in the multifunctional polycondensation (X^A, X^B)-system, i.e. the reaction of X^A -functional monomers of kind A with X^B -functional monomers of kind B:

$$\left\{ \frac{2(1 - \alpha)^{X^A} + X^A \alpha - 2}{X^A \alpha} + \frac{2(1 - \alpha)^{X^B} + X^B \alpha - 2}{X^B \alpha} + 2(1 - \alpha) [(X^A - 1) + (X^B - 1)] \right\} \Big|_{\alpha = \alpha_{cr}} = 0 \quad (17)$$

Numerical results

Equ.(17) may be numerically solved for α_{cr} for any pair (X^A, X^B). The results are shown in TABLE 1 in comparison with results based on Eqs. (7) and (8) and with experimental results for different stoichiometric systems (partially after STAFFORD 1981).

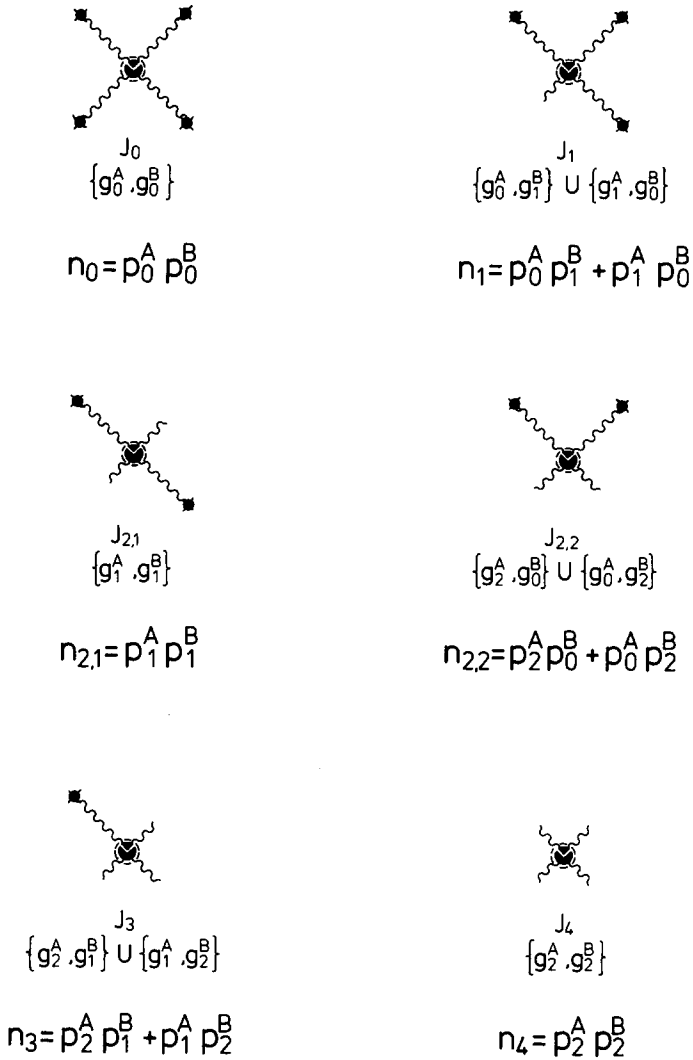








Fig.1. Different classes of crosslinks present in the system. Under each class its composition of different classes of active groups (i.e. of groups with different number, $r=0,1,2$, of free "chain ends") and appropriate contributions, n_k ($k=0, \dots, 4$ = number of free chain ends emanating from a crosslink of the k -th class) is indicated.

-  - group of type A;
-  - group of type B;
-  - crosslink under consideration;
-  - another crosslink;
-  - chain leading to a next crosslink;
-  - "free chain end".

Free ends are drawn short to underline that such a "chain" maybe a small group of atoms or even one atom.

TABLE 1
Critical gel point for multifunctional condensation systems

No.	System (X ^A , X ^B)	\bar{f}	α_{cr}^{Exp}	Theories, α_{cr}^{Th}					
				Equ.(7) ($\bar{M}_w \rightarrow \infty$)	Δ [%]	Equ.(8) ($\bar{M}_n \rightarrow \infty$)	Δ [%]	PTCS	Δ [%]
1.	(4,3)	3.5	0.490	0.400	-18.4	0.571	+16.5	0.520	+ 6.1
2.	(3,3)	3.0	0.580	0.500	-13.8	0.667	+15.0	0.616	+ 6.2
3.	(4,2)	3.0	0.623	0.577	- 7.4	0.667	+ 7.1	0.696	+11.8
4.	(3,2)	2.5	0.770	0.707	- 8.2	0.800	+ 3.8	0.806	+ 4.7
5.	"-	"-	0.719	"-	- 2.0	"-	+11.3	"-	+12.0
6.	"-	"-	0.795	"-	-11.0	"-	+ 0.4	"-	+ 1.0

Note: Error Δ has been calculated as follows:

$$\Delta = [(\alpha_{cr}^{Th} - \alpha_{cr}^{Exp}) / \alpha_{cr}^{Exp}] \cdot 100 \%$$

The systems investigated experimentally were respectively:

1. 3M pentaerythritol + 4M tricarballylic acid
(DURAND, BRUNEAU 1978)
2. 1M glycerine (or 1M trimethylol propane)
+ 1M tricarballylic acid
(DURAND, BRUNEAU 1978)
3. 1M pentaerythritol + 2M adipic acid
(GORDON, SCANTLEBURY 1967)
4. 2M glycerine + 3M adipic acid
(DURAND, BRUNEAU 1978)
5. 2M 1,1,1 trimethylol ethane + 3M adipic acid
(GORDON, SCANTLEBURY 1967)
6. 3M phthalic anhydride + 2M glycerine
(KIENLE, van der MEULEN, PETKE 1939, 1940)

Discussion

As one may see in TABLE 1 the calculations for the systems (4,3) and (3,3) based on the PTCS are in better agreement with experimental results than calculations based on Equ. (7) ($\alpha_{cr} = \alpha(\bar{M}_w \rightarrow \infty)$) and on Equ.(8) ($\alpha_{cr} = \alpha(\bar{M}_n \rightarrow \infty)$). For systems (4,2) PTCS seems to be in slightly less agreement with experiments than the other theories, however, Equ.(8) gives for this case exactly the same result as for the case (3,3), which seems to support objections concerning the validity of this approach. For systems (3,2) experiments show a great dispersion of the order of 15%, i.e. often greater than the errors in theoretical predictions and so the appreciation of validity of different theories is in this case very difficult.

Treating all multifunctional polycondensation systems as having tetrafunctional crosslinks may seem to be not justified. This is equivalent to the assumption that active groups which form crosslinks are arranged along linear chains of primary molecules (here monomers) but not on their very ends.

However PTCS may be easily modified, i.e. another set of crosslink classes than those shown in Fig.1 may be imagined (and their contributions may be easily evaluated) to take into account that the active groups are on the very ends of the primary monomers (end-to-end binding). Non-linear arrangements of reactive groups in monomers can also be represented. Then e.g. in the system (3,2) the crosslink functionality is equal 3 and not 4.

But after making the necessary calculations, the numerical results obtained, at least as far as α_{cr} is concerned, have been exactly the same as those given in TABLE 1 for the model shown in Fig.1 and so we will not give further considerations to these calculations here. From a topological point of view even a single atom may be treated as a free "chain end". The general scheme of tetrafunctional crosslinks (Fig.1) may therefore be applied both to crosslinking of pre-existing long linear macromolecules as well as to different cases of multifunctional polycondensation.

Applications of PTCS to non-stoichiometric multifunctional polycondensation systems as well as to systems with greater number of primary monomers are now in progress.

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References

1. C.-M. Bruneau, C.R. Acad. Sci. C264, 1168 (1967).
2. D. Durand and C.-M. Bruneau, Makromol. Chem. 179, 147 (1978).
3. P.J. Flory, J. Am. Chem. Soc. 63, 3083, 3091, 3096 (1941).
4. M. Gordon and G.R. Scantlebury, J. Chem. Soc. B, 1 (1967).
5. R.H. Kienle, P.A. van der Meulen, and F.E. Petke, J. Am. Chem. Soc. 61, 2258, 2268 (1939); 62, 1053 (1940).
6. W. Klonowski, Rheol. Acta 18, 442, 667, 673 (1979).
7. W. Klonowski, Polymer Bulletin 7, 255 (1982) +)
8. J.W. Stafford, J. Polym. Sci. Pol. Ch. Ed. 19, 3219 (1981).
9. W.M. Stockmayer, J. Chem. Phys. 11, 45 (1943); 12, 125 (1944).
10. S.G. Whiteway, I.B. Smith, and C.R. Masson, Can. J. Chem. 48, 33, 201, 1456 (1970).
11. J.F. Yan, J. Chem. Phys. 78, 6893 (1983).

+) ERRATA: In this article the correct Equation (7) should read:

$$f_1 = [1(1 - \beta)w_d]^{1/2} \quad (7)$$

On the pages 259 - 261:
value of b, equation for b, our b, values of b
- everywhere b should read β .